Ph.D. THESIS - C.M.DIAZ

"EMF STUDIES OF OXYGEN IN MOLTEN METALS"

Errata

1. Title page - for EMF'S STUDIES read EMF STUDIES.

2. Page 103, line 6, for 'althoigh' read 'although'.

3. Page 142, Fig.III.21, ordinate should read:

$$\log {}^{p_{CO_2}} /(p_{CO} \times \text{atom \% [O]})$$

instead of:

$$\log {}^{p_{CO_2}} / \; p_{CO}$$

EMF'S STUDIES OF OXYGEN IN MOLTEN METALS

A THESIS

Submitted For The Degree of

DOCTOR OF PHILOSOPHY

in the

University of London

by

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December, 1966.

ABSTRACT

Solid electrolyte galvanic cells with potential value as devices for measuring oxygen contents in molten metals (silver and copper) have been studied. The compatibility of the different materials used in these cells with the conditions which could be found in industrial practice were examined. A controlled oxygen partial pressure was always kept over the molten metal to compare observed with calculated emf's.

Cells of the type:

$$\text{Stainless Steel, Ag(l), } O_2\text{(g)(P}'\text{)/ZrO}_2\text{.CaO/ Ag(l), } O_2\text{(g) (Patm), Stainless Steel}$$

were used in the case of silver. A close agreement between experimental and calculated emf's was found in the temperature range 980-1160°C. It was confirmed that oxygen solubility in liquid silver obeys Sievert's law up to 1 atm.

Two types of cell were used for measurements in molten copper:

$$\text{Pt, Ni-NiO/solid electrolyte/Cu(l), } (CO_2+CO)\text{, cermet, Pt,} \quad \text{(I)}$$

and:

$$\text{Pt, cermet, } (CO_2+CO)\text{, Cu(l)/solid electrolyte/} O_2\text{(Patm), Pt} \quad \text{(II)}$$

Polarisation of the Ni-NiO reference electrode occurred in cells of type I, its magnitude being dependant upon the difference of oxygen chemical potential between the electrodes. Attempts to establish the cause of polarisation were only partially successful and indicate that electronic conduction of the solid electrolyte would be mainly responsible for the polarisation process.

Observed and calculated emf's for cells of type II were in close agreement. The potential value of this cell for mass transfer studies was established.

Oxygen solubility data have been compared with previous results.

CONTENTS

INTRODUCTION 1

CHAPTER I - THE ELECTROCHEMICAL METHOD FOR MEASURING OXYGEN CHEMICAL POTENTIALS

I.1 Introduction 3

I.2 Electrochemistry of Galvanic Cells with Solid Electrolytes . . . .

I.2.1 General Considerations . . 4

I.2.2.Emf of Cells with Solid Electrolytes 6

I.3 The Properties of Solid Electrolytes . 10

I.3.1 Zirconia Based Electrolytes . 11

a) Structure of Zirconia Based Solid Solutions 11

b) Electrical Conductivity . . . 15

c) Nature of the Electrical Conductivity of Zirconia Based Solid Solutions . 18

d) Commercial Zirconia Solid Oxide Electrolyte Material . . . 25

I.3.2. Other Solid Electrolytes . . 27

I.4 Polarisation Phenomena . . . 28

I.5 Research Programme 32

CHAPTER II - MEASUREMENTS IN MOLTEN SILVER

II.1 Review of the Literature . . . 34

II.2 Experimental 35

a) Materials 35

b) Apparatus 37

c) Procedure 45

II.3 Results and Discussion

a) Experiments at 980°C . . . 51

b) Experiments at higher temperatures 59

II.4 Conclusions 61

CHAPTER III - MEASUREMENTS IN MOLTEN COPPER

III.1 The Copper-Oxygen System . . . 64

III.2 Experimental

III.2.1 General Considerations . . 71

III.2.2.Compatibility Tests. Materials Used 74

III.2.3 Apparatus and Analytical Techniques 78

a) Gas Train 78

b) The Cell 82

c) Gas Analysis 89

d) Oxygen Determination in Copper . 93

III.2.4 Experimental Procedure . . 94

III.3 Results and Discussion

III.3.1 Cells with Ni-NiO as Reference Electrode

a) Calculated emf's 97

b) Experiments at 1100°C . . . 98

c) Coulometric Titrations at 1100°C . 102

d) Experiments with Cells of the Type Pt, Ni-NiO/Solid Elect./(CO_2 + CO), Pt. 110

e) Nature of the Polarisation Phenomena 114

f) Experiments at 1200°C . . . 126

III.3.2 Cells with Pt. O_2 as Reference Electrode . . . .

a) Results at 1100°C and 1200°C . 128

b) Kinetics of Oxygen Transfer from the CO_2/CO Mixture to the Metal . 132

III.3.3 Oxygen Solubility in Molten Copper 140

III.4 Previous Measurements of Oxygen in Molten Copper with Solid Electrolyte Galvanic Cells. 140

III.5 General Discussion and Conclusions . 145

ACKNOWLEDGEMENTS 147

REFERENCES 148

APPENDIX i

INTRODUCTION

The refining of many metals by pyrometallurgical processess generally consists of a series of selective oxidation and deoxidation stages with the object of controlling the level of additions and impurities in the finished product. Deoxidation is usually the last controllable chemical operation before the composition of the metal is fixed by solidification. The oxygen content has generally a big effect on the properties of metals. Unfortunately most of the present methods of sampling and oxygen analysis of liquid metals are inaccurate or slow. Consequently there is a big interest in the development of a quick and reliable method. High temperature galvanic cells using solid electrolytes look the most promising devices for this purpose and a substantial research effort is being dedicated to the study of their behaviour. Galvanic cells of this type could be plunged directly into the molten metals giving a rapid measurement of its oxygen content and the possibility of precise control of the refining operation.

Galvanic cells for measuring oxygen contents in molten metals can also be valuable tools in scientific and technical research work. Provided

that fully reversible cells are used, they replace advantageously the complex equilibration techniques for the study of oxygen-molten metals and alloys equilibria. The rapid response of galvanic cells to any change in the oxygen potential of the electrodes makes them an ideal device for the investigation of mass-trasfer phenomena.

Many problems, however, may arise during the operation of solid electrolyte cells for measuring oxygen contents in molten metals. The main object of the present work has been to identify these difficulties, understand their nature and to suggest possible solutions.

CHAPTER I

THE ELECTROCHEMICAL METHOD FOR MEASURING OXYGEN CHEMICAL POTENTIALS

I.1 INTRODUCTION

Galvanic cells using solid electrolytes for measuring oxygen chemical potentials in metal systems have been known for a long time. Treadwell[1] in 1916 successfully studied several metal-metal oxide equilibria by means of cells incorporating an auxiliary porcelain solid electrolyte. Later on, he determined the free energy of formation of Al_2O_3 and MgO using the same technique[2],[3]. However, the method was not fully exploited until Kiukkola and Wagner[4] published their critical survey of high temperature galvanic cells used for the determination of the free energy of formation of a number of compounds, and established the advantages of employing solid electrolytes. The same authors[5] carried out a successful research on the free energy of formation of several oxides, using zirconia calcia solutions as solid electrolytes. The work of Kiukkola and Wagner was the starting point of the present extensive use of the electrochemical method for measuring oxygen activities in high temperature systems.

Molten metals equilibrated with a gaseous

phase were already present in the cells used by Treadwell[1]. He employed silver saturated with oxygen as a reference electrode in the cell

$Cu(S)/Cu_2O(S)$, borate melt/porcelain/O_2,Ag(l)

But only in the last three years has the technique been widely used for determination of oxygen activities in molten metals. Measurements in lead and tin have been made by Alcock and Belford[6,7] in copper by several authors[8-12], in cobalt and nickel by Fischer and Ackermann[11] and in iron and steel by these same investigators[13,14]. Some of this work, relevant to the present investiation, will be reviewed in more detail later.

I.2 ELECTROCHEMISTRY OF GALVANIC CELLS WITH SOLID ELECTROLYTES

I.2.1 General Considerations

The free energy change ΔG of a reaction is obtained from the emf E of a reversible galvanic cell by means of the relationship

$$\Delta G = -nEF \qquad (I.1)$$

The cells which have been investigated in the present work may be regarded as oxygen concentration cells. One of the electrodes was the molten metal M being studied, equilibrated with a gaseous phase of given oxygen potential. When silver was being

studied the reference electrode was the same metal equilibrated with oxygen at atmospheric pressures, in the case of copper, the reference electrode was either nickel-nickel oxide, whose oxygen chemical potential is determined by temperature or Pt, pure oxygen at atmospheric pressure.

The chemical potential of oxygen is defined by the relationship:

$$\mu_{O_2} = \mu^{\circ}_{O_2} + RT\ln P_{O_2} \qquad (1.2)$$

The free energy change associated with a cell of the type:

$$^{-}Pt,\ O_2(p')/\text{solid electrolyte}/O_2(p''),\ Pt^{+}$$

is:

$$\Delta G = \mu'_{O_2} - \mu''_{O_2} = RT\ln \frac{P'_{O_2}}{P''_{O_2}} \qquad (I.3)$$

and consequently:

$$E = \frac{RT}{4F} \ln \frac{P''_{O_2}}{P'_{O_2}} \qquad (I.4)$$

If the left electrode of the cell is actually the metal M equilibrated with P'_{O_2}, the oxygen dissolution reaction may be written:

$$\tfrac{1}{2}O_2(g) = [O]_M \qquad (I.5)$$

with an equilibrium constant:

$$K = \frac{a[O]}{(P'_{O_2})^{\frac{1}{2}}} \qquad (I.6)$$

In very dilute solutions of oxygen in molten metals Henry's law is generally obeyed. Then:

$$a[O] = k[O] \text{ wt\%} \qquad (I.7)$$

and

$$[O] \text{ wt\%} = k' (P'_{O_2})^{\frac{1}{2}} \qquad (I.8)$$

These relationships show that reversible galvanic cells may be useful devices for oxygen determination in molten metals.

I.2.2 Emf of Cells with Solid Electrolytes

The introduction of auxiliary solid electrolytes in galvanic cells leads to several advantages. The most important advantage in the present research was the possibility of providing two separate compartments for the electrodes preventing the transport of oxygen from one to the other.

In a cell like the one described previously

$$^{-}Pt, O_2(p') / \text{solid electrolyte} / O_2(p''), Pt^{+}$$

there are chemical potential gradients across the solid. Diffusion takes place producing a charge separation due to the different mobilities of the various ions. The diffusion or junction potential established affects the flow of ions in such a way as to restore electrical neutrality and a steady-state condition is reached. The magnitude of the

diffusion potential is given by the following expression:*

$$E_{dif} = -\frac{1}{F}\int_1^2 \sum_i \frac{t_i}{z_i} d\mu_i \qquad (I.9)$$

The problem faced now is the evaluation of E_{dif} because it is going to be an integral part of the measured emf. Direct integration of expression I.9 is not possible, because the chemical potentials of individual ions are not separately determinable and no information is available about the ionic transference number dependance on composition. However, we can often determine the conditions under which the error introduced by the diffusion potential

---

* A full derivation of this expression is given in B.C.H. Steele(15) thesis based upon the method used by Wagner(16) in his theoretical treatment of the parabolic growth rate of a metal oxide film during oxidation. The rate of migration of the constituent i is determined by both the chemical and the electrical potential gradients, so the flux J_i of i in moles per unit time in the x-direction is given by:

$$J_i = -B_i C_i \left\{ \frac{1}{N} \cdot \frac{\partial \mu_i}{\partial X} + Z_i e \frac{\partial \phi}{\partial X} \right\}$$

where B_i is the mobility of particles of constituent i. The partial current density $I_i = Z_i e N J_i = Z_i F J_i$ is then:

$$I_i = -B_i C_i Z_i F \left\{ \frac{1}{N} \frac{\partial \mu_i}{\partial X} + Z_i e \frac{\partial \phi}{\partial X} \right\}$$

If the total conductivity is represented by σ and the transference number of the species i is defined by $t_i = \sigma_i / \sigma$

***

is negligible:*

In the cell

$$^{-}Pt,\ O_2(^{P'}O_2)/\text{solid electrolyte}/O_2(^{P''}O_2),\ Pt^{+}$$

$$\begin{array}{cccc} \phi' & \phi^{\alpha} & \phi^{\beta} & \phi'' \\ \bar{\mu}_e' & \mu_e^{\alpha} & \mu_e^{\beta} & \bar{\mu}_e'' \end{array}$$

ϕ' and ϕ'' are the electrical potentials of the metal electrodes and ϕ^{α} and ϕ^{β} the corresponding potentials within the electrolyte phase. $\bar{\mu}_e'$ and $\bar{\mu}_e''$ are the electrochemical potentials of the electrons in the metal electrodes and μ_e^{α} and μ_e^{β} their chemical potentials within the electrolyte. The emf of this cell is given by:

$$E = \phi'' - \phi' = \frac{1}{F}(\bar{\mu}_e' - \bar{\mu}_e'') \qquad (I.10)$$

Assuming local equilibrium at both metal/

*** $$I_i = -\sigma\left\{\frac{1}{F}\ \frac{t_i}{Z_i}\ \frac{\partial \mu_i}{\partial X} + ti\ \frac{\partial \phi}{\partial X}\right\}$$

In the absence of any external electrical circuit $\Sigma I_i = 0$ and consequently:

$$\Delta\phi = E_{dif} = -\frac{1}{F}\int_1^2 \Sigma_i\ \frac{t_i}{Z_i}\ d\mu_i$$

---

* The following considerations are based on a thorough discussion of this problem by B.C.H. Steele(15).

electrolyte interfaces and considering that the metal electrodes have the same chemical composition it follows that:

$$E = \frac{1}{F}\left(\mu_e^{\alpha} - \mu_e^{\beta}\right) + \left(\phi^{\beta} - \phi^{\alpha}\right) \qquad (I.11)$$

where $\phi^{\beta} - \phi^{\alpha} = \Delta\phi$ is the diffusion potential.

If both electrodes are reversible to oxygen ions the local equilibrium at the metal/electrolyte interfaces can be expressed by:

Left: $2O^{-2} = O_2 + 4e$ and $4\mu_e^{\alpha} = -\mu_{O_2}^{\alpha} + 2\mu_{O^{2-}}^{\alpha}$

Right: $O_2 + 4e = 2O^{2-}$ and $4\mu_e^{\beta} = -\mu_{O_2}^{\beta} + 2\mu_{O^{2-}}^{\beta}$

$$\therefore \frac{1}{F}\left(\mu_e^{\alpha} - \mu_e^{\beta}\right) = \frac{1}{4F}\left\{\int_{\alpha}^{\beta} d\mu_{O_2} - 2\int_{\alpha}^{\beta} d\mu_{O^{2-}}\right\} \qquad (I.12)$$

According to relation (I.9)

$$\Delta\phi = -\frac{1}{F}\int_{\alpha}^{\beta} \sum_i \frac{t_i}{Z_i}\, d\mu_i$$

Experimental data indicate that for the solid oxide electrolytes used in this investigation the transference numbers of the cations are much lower than $t_{O^{2-}}$ (See section I. 3.1,C). The same is true for t_e, within certain limits of temperature and P_{O_2} It follows then that:

$$\Delta\phi = \frac{1}{2F}\int_{\alpha}^{\beta} d\mu_{O^{2-}}$$

$$\therefore E = \frac{1}{4F}\int_{\mu_{O_2}^{\alpha}}^{\mu_{O_2}^{\beta}} d\mu_{O_2} = \frac{1}{4F}\left(\mu_{O_2}^{\beta} - \mu_{O_2}^{\alpha}\right) = \frac{RT}{4F}\ln\frac{P''_{O_2}}{P'_{O_2}} \qquad (I.13)$$

which is the same as expression I.4.

The conditions where it is possible to apply the relationship $\Delta G = -nEF$ to a cell may be summarised as follows:

a) Reversibility of the electrodes and absence of secondary reactions;

b) The oxygen transference number of the electrolyte must greatly exceed the transference number of any other charged species.

c) The electronic contribution to the electrolyte conductivity must be negligible.

Conditions b and c are satisfied by some ceramic materials. Little is known about reversibility of electrodes normally used in high temperature cells and polarisation problems may arise. These points will be discussed more extensively in the following sections.

I.3 THE PROPERTIES OF SOLID ELECTROLYTES

Many oxides and oxide solid solutions are known to behave as either mixed or almost pure ionic conductors. Simple binary oxides generally belong to the first group. Some oxide solid solutions based on zirconia, thoria or hafnia possess predominantly ionic conduction and they are consequently ideal materials to be employed as solid electrolytes

in galvanic cells. For reasons which are given later, zirconia oxide solutions containing calcia or yttria were employed in this investigation. Their structure and properties, together with the properties of some other solid electrolytes, will be briefly reviewed.

I.3.1 Zirconia Based Electrolytes

Although the electrolytic properties of zirconia based oxide solutions were first observed by Nernst[17] in 1900, they have been more extensively studied, and related to the structure of these materials, only very recently.

a) Structure of Zirconia Based Solid Solutions

Ruff and Ebert[18] and later Geller and Yavorsky[19] established that if a sufficient amount of Y_2O_3 is combined with ZrO_2, a stable cubic form of ZrO_2 solid solution with the fluorite structure (Fig. I.1) is obtained. Zirconia calcia solid solutions, and some other zirconia based solutions, have the same structure.

In a perfect ideal lattice with an atom on every lattice site there would be no ionic mobility. Electrolytic conductivity in ionic solids is due to lattice disorder, or defects, of either Schottky, Frenkel or a combined type. Wagner[20] extended

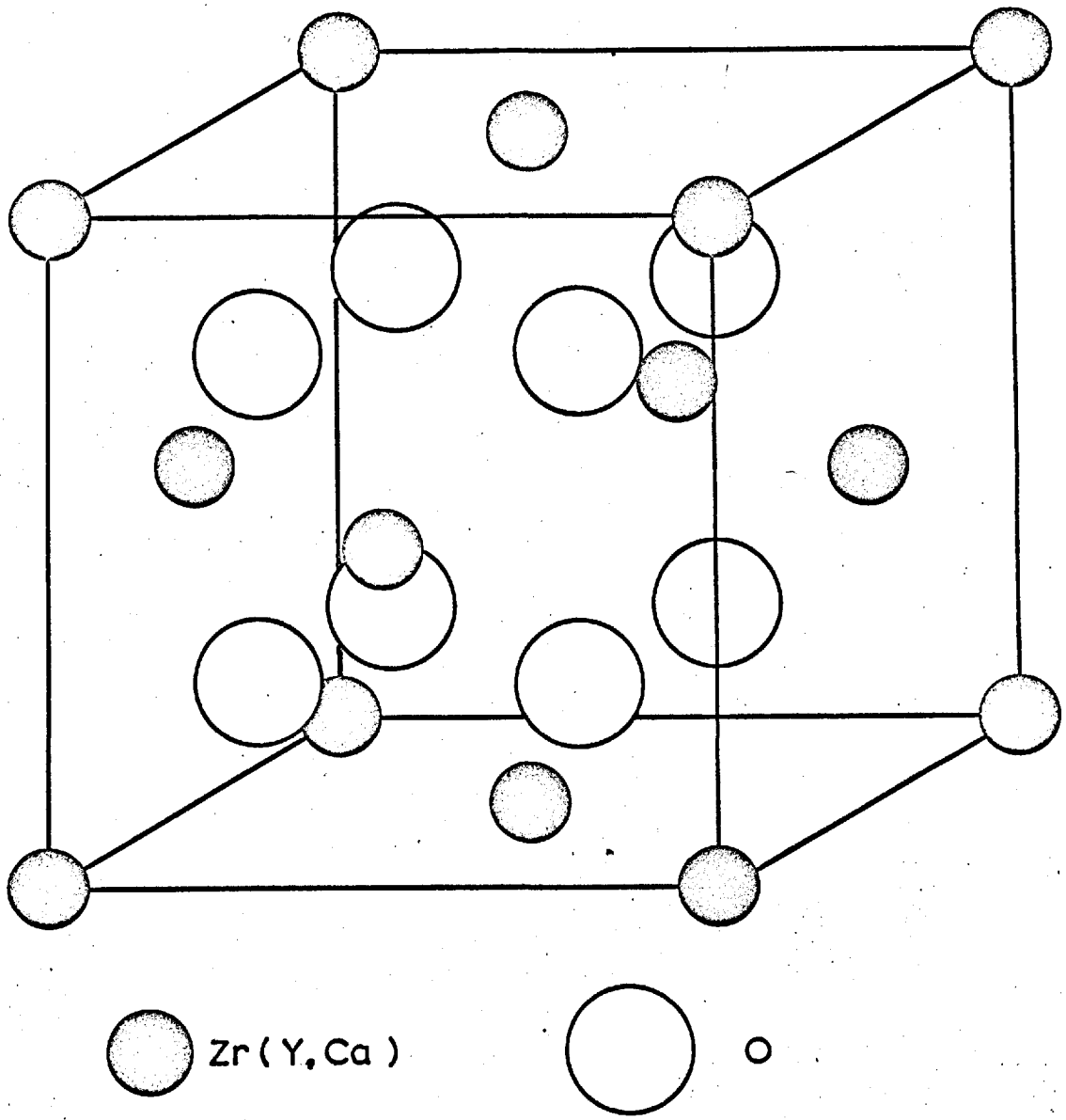


FIG. I.1 THE FLUORITE STRUCTURE

these ideas to zirconia based solid solutions in order to explain their ionic conductivity. He suggested that when either Ca^{2+} or Y^{3+} ions are substituted for Zr^{4+} ions in the fluorite-type structure of these materials, anion vacancies are created to preserve the electrical neutrality of the lattice. These vacancies are responsible for the high oxygen mobilities. Hund[21] compared experimental densities for the system ZrO_2-CaO with those calculated from lattice parameters to test Wagner's model against one in which all the anion sites are occupied and the excess cations are in interstitial positions. His results favoured the anion vacancy model. Hund suggested that Ca^{2+} and Zr^{4+} were randomly distributed on the completely filled cation lattice with randomly distributed anion vacancies, whose large concentration was fixed by composition and independent of oxygen pressure and temperature. Direct evidence confirming this model has been given by Tien and Subbarao[22] and Carter and Roth[23] who studied the structure of zirconia calcia solutions by means of neutron, x-ray and electron diffraction. The only challenge to this model so far has been by Dines and Roy[28] who concluded from their com-

parison of observed and calculated densities of ZrO_2.CaO solutions, that the pure anion vacancy model would be valid only at low temperatures. They presented evidence proving that about 1800° and 10 mole% CaO, the interstitial cation model is in better agreement with the observed densities of the ZrO_2-CaO solutions. This suggestion needs further confirmation.

Some modifications to the original Wagner's and Hund's ideas have been recently proposed. As these modifications are partially based on the observed electrical conductivity of zirconia based solutions they will be discussed after presenting the relevant data.

There is still some discrepancy about the field of stability of the zirconia based solid solutions in the phase diagrams of the respective systems, in spite of extensive research using x-ray and petrographic techniques. Some authors[21,23,24,29] place the solid solutions limits for calcia stabilized zirconia at 10 and 20 mole% CaO, while others[22,25,27] give 12 and 22 mole% CaO as the phase boundaries for the fluorite-type structure. The lower phase boundary for yttria stabilized zirconia has been reported as 7 mole% Y_2O_3 by Duwez et al[26] while

recent determinations by Strickler and Carlson[25,31] put it at 9 mole % Y_2O_3. There is agreement concerning the upper phase boundary which is placed at about 50 mole% Y_2O_3.

b) Electrical Conductivity

The high oxygen mobility showed by zirconia based solid solutions is due to their defect structure as already stated. The electrical conductivity of these materials, as a function of composition and temperature, has been determined by several investigators[22,23,25,29,30,31,32]. Fig. I.2 reproduces the results of Strickler and Carlson[25] which check reasonably well with other recent work. Although the values obtained by the different authors are somewhat discordant there is agreement with respect to the influence of Y_2O_3 or CaO content on conductivity. In fact, it has been shown that conductivity exhibits a maximum for solid solutions with compositions about the lower phase boundaries for the fluorite-type structure (8-9% for yttria stabilized zirconia and 12-13% for calcia stabilized zirconia). Increasing Y_2O_3 or CaO contents mean a decrease of conductivity for any given temperature.

Anion vacancies dominate the conduction mechanism (see Section III.1.3) and their concentration

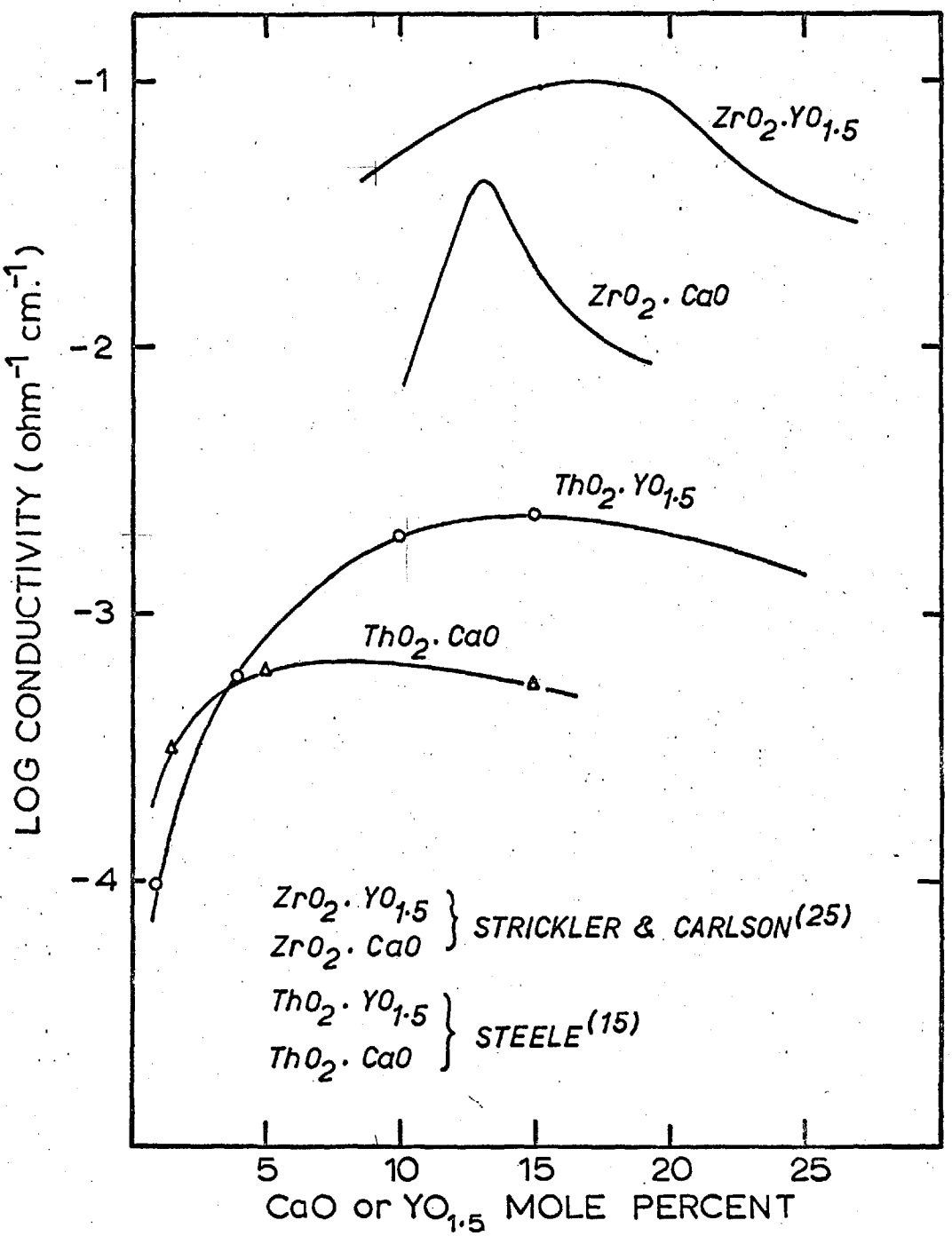


FIG. I.2 CONDUCTIVITY OF SOME SELECTED FLUORITE SOLID SOLUTIONS AT 1000°C

is fixed by composition. It may be expected then a linear dependance of conductivity upon defect concentration (Y_2O_3 or CaO content). Several explanations have been offered to account for the failure of these materials to behave according to this pattern. These explanations may be summarised as follows:

i) Ordering of vacancies and calcium or yttrium ions in the stabilized zirconia fluorite structure[22,23,25,27]. There is x-ray evidence of the formation of a superstructure with increasing CaO content. Due to the tendency of complementary defects to associate, the Ca^{2+} ordering would be accompanied by an ordering of the anion vacancies;

ii) Periodic fluctuations in composition and structure in a continuous matrix[23]. This phenomenon has been observed in $Fe_{1-x}O$, UO_{2+x} and other non-stoichiometric compounds with a large concentration of defects. As this concentration exceeds a certain value, the defects tend to segregate in-to defect-poor and defect-rich regions, which can co-exist[33].

iii) Precipitation of a second phase[23]. No experimental evidence has been reported in this respect.

These interpretations are not necessarily exclusive and may be alternate descriptions for a precipitation process.

The evidence suggests that the fluorite structure of some of these zirconia based solutions could correspond to a metastable phase. This would be especially true at low temperatures and for solid solutions with high CaO or Y_2O_3 contents. The very low diffusion coefficients of the cations (see Section I.3.1,C) would hinder the reactions towards some more stable state. This phenomenon would limit the useful range of solid solutions with a large number of random anion defects

c) Nature of the electrical conductivity of zirconia based solid solutions.

The mean O^{2-} transference number of zirconia based solid solutions is virtually unity, provided the oxygen partial pressures are not below a certain limit. There is enough evidence to justify this statement.

Kingery et al[34] determined the oxygen ion diffusion coefficient in $Zr_{0.85}\ Ca_{0.15}O_{1.85}$ and the electrical conductivity of this material over the temperature range 700-1100°C. Comparing the

experimental values with the calculated conductivity obtained from the diffusion coefficient by means of the Nernst-Einstein relation, he concluded that the entire conductivity can be attributed to oxygen ion mobility. Some doubt about Kingery's results, due to the fact that he used a correlation factor of 1 in his calculations, has been removed by Simpson and Carter[35] who obtained excellent agreement between observed oxygen ion diffusion coefficients in the temperature range 800-1100°C, and calculated values using Carter and Roth[23] conductivity data.

Weissbart and Ruka[36] observed that Faraday's laws were obeyed for reversible transfer of oxygen from cathode to anode in the cell

$$O_2(p_1),\ Pt/\ Zr_{0.85}Ca_{0.15}O_{1.85}/Pt,O_2(p_2)$$

The electronic contribution to the total conductivity was found to be less than 0.5% at about 1000°C in an oxygen atmosphere.

The problem of the electronic contribution to the total conductivity of solid electrolytes is of particular importance. If this contribution has a significative value the relation $\Delta G = -nEF$ is no longer applicable. Furthermore, in the case of electrolytes with low resistance, even a small

electronic conductivity may cause a considerable flow of oxygen from the positive to the negative electrode, especially when the difference in oxygen potentials between both electrodes is high. This oxygen flow may produce polarisation phenomena which will mean an even larger discrepancy between the theoretical and the observed emf's. Considerable attention has been then dedicated to this problem.

The total conductivity may be presented by the following expression:

$$\sigma_{Tot} = \sigma_{Ionic} + \sigma_{\oplus} + \sigma_{\ominus} \qquad (I.14)$$

where $\sigma_{\oplus}$ is the conductivity due to positive hole conduction (p-type) and $\sigma_{\ominus}$ is the conductivity due to electrons (n-type). The concentrations of excess electrons and holes in the solid electrolyte are likely to be determined by the oxygen partial pressure according to the reactions:

$$O_2(g) + 4 \text{ excess electrons} + 2 \text{ anion vacancies} = 2O^{2-} \qquad (I.15)$$

$$O_2(g) + 2 \text{ anion vacancies} = 2O^{2-} + 4 \text{ electron holes} \qquad (I.16)$$

As the concentrations of vacancies and valence electrons are fixed by composition, it follows that:

$$C_{\ominus} = K_1 (P_{O_2})^{-\frac{1}{4}} \qquad (I.17)$$

$$C_{\oplus} = K_2 (P_{O_2})^{\frac{1}{4}} \qquad (I.18)$$

In the more general case:

$$C_{\ominus} = K_1 (P_{O_2})^{-1/n} \qquad (I.19)$$

$$C_{\oplus} = K_2 (P_{O_2})^{1/m} \qquad (I.20)$$

The positive hole conduction will increase with increasing oxygen pressure and the electron conduction will increase with decreasing oxygen partial pressure. Independence of conductivity upon oxygen partial pressure has been then an indication of absence of electronic contribution.

Kiukkola and Wagner[5] found that the electrical conductivity of $Zr_{0.85}Ca_{0.15}O_{1.85}$ was virtually constant when the oxygen partial pressure was varied from 1 atm down to about 4×10^{-22} at 870°C. Kingery et al[34] obtained similar results for the same solid electrolyte at 1427° and 1627°C in the oxygen pressure range $1\text{-}10^{-10}$ atm. Steele[15] has reported independence on conductivity upon oxygen partial pressure for zirconia 10 mole% yttria from 1 to 10^{-15} atm. at 1000°C. Recent measurements[38] on zirconia 20 mole% $YO_{1.5}$ indicate that the conductivity of this material is independent of the oxygen pressure between 1 and 10^{-16} atm. up to 1600°C.

A useful extension of this approach to the problem of electronic contribution to conductivity in these materials has been proposed by Schmalzried[39,40]. He introduced two parameters $P_{\oplus}$ and $P_{\ominus}$ as the oxygen partial pressures at which σ ionic equals $\sigma_{\oplus}$ and $\sigma_{\ominus}$ respectively. It is possible then to derive expressions for the ionic transference number as a function of oxygen partial pressure and calculate the emf of a concentration cell by means of the relationship:

$$E = \frac{1}{4F}\int_{\mu'_{O_2}}^{\mu''_{O_2}} t_{ion}\, d\mu_{O_2}$$

On the other hand, emf data can be combined with conductivity results to estimate the oxygen partial pressure above which the electronic transference number exceeds 1%. Below this oxygen partial pressure the ionic transference number will be higher than 0.99. Steele[15] has done such a calculation on the basis of his experimental results for cells with ZrO_2 CaO solid electrolytes and found that the corresponding lower limit for $t_{ion} > 0.99$ is $P_{O_2} = 10^{-15}$ atm. For commercial zirconia electrolytes of similar composition, Schmalzried[40] has reported a lower limit for

$t_{ion} > 0.99$ of 10^{-16} atm. at 1000°C. Similar observations have been made by Bray and Merten[37] with cells containing $ZrO_2.YO_{1.5}$ solid solutions. They gave a lower limit for $t_{ion} > 0.99$ of 10^{-15} atm. All these calculations and observations are in good agreement with Aronson[41] experimental work on the composition of pure ZrO_2 upon oxygen partial pressure, which indicated that some reduction of the oxide takes place about this level of oxygen potential. However, most of these calculations are based on observed emf's which were only slightly different from the expected emf's assuming $t_{ion}=1$. The experimental errors in some cases might have been higher than the difference between observed and calculated emf's. But even if the discrepancies had been bigger it would be difficult to distinguish between the effect of electronic conduction and any electrode effect due to polarisation. The results for the lower P_{O_2} limit for $t_{ion} > 0.99$ in zirconia based solutions according to Schmalzried relationships should be considered then only as useful approximations.

Measurements of the cation (Zr^{4+}, Ca^{2+}, Y^{3+}) diffusion coefficients [37,42,43] show that these are several orders of magnitude lower than the

oxygen ion diffusion coefficient. Table I.1 gives the values of the cation diffusion coefficients of stabilized zirconia at 1000°C compared with the oxygen ion diffusion coefficient.

TABLE I.1

Cation and anion diffusion coefficients in stabilized zirconia at 1000°C

$D_{O2-} = 9.4 \times 10^{-8}$ cm^{2}sec^{-1} (in $Zr_{0.858}Ca_{0.142}O_{1.858}$)	(35)
$D_{Zr4+} = 3.7 \times 10^{-19}$ cm^{2}sec^{-1} (in $Zr_{0.84}Ca_{0.16}O_{1.84}$)	(42)
$D_{Ca2+} = 7.0 \times 10^{-19}$ cm^{2}sec^{-1} (in $Zr_{0.84}Ca_{0.16}O_{1.84}$)	(42)
$D_{Y3+} \leq 7 \times 10^{-15}$ cm^{2}sec^{-1} (in $Zr_{0.90}Y_{0.10}O_{1.95}$)	(37)

It may be concluded, therefore, that stabilized zirconia solid solutions satisfy the requirements specified in section I. 2.2., provided they are not used in cells with too low oxygen partial pressures.

So far this discussion has been restricted to calcia and yttria stabilized zirconia. Several other zirconia based oxide solutions have similar properties. The electrical conductivity and phase relations in some of these systems have been recently studied by Strickler and Carlson[31].

Most of the conclusions concerning the structure and nature of the electrical conductivity for calcia and yttria stabilised zirconia are also valid for them.

d) Commercial zirconia solid oxide electrolyte material

Most of the previous discussion is on the properties of solid electrolytes prepared from espectroscopic pure chemicals. Some information is, however, available on commercial solid electrolytes. Several investigators[15,36,40] have used stabilised zirconia tubes, supplied by different manufacturers and have found that the anionic conductivity of these materials is as good as that of the laboratory produced electrolytes.

Thorough studies on the structure and permeability of commercial stabilised zirconia tubes have been conducted at the Department of Ceramics, Leeds University [44,45]. Zirconia magnesia, zirconia calcia and zirconia yttria tubes were investigated. The main findings are summarised in the following paragraphs.

A considerable amount of impurities were present in these materials. The zirconia magnesia tubes contained for example over 3% of Al_2O_3 and

substantial percentages of other oxides (Fe_2O_3, SiO_2, TiO_2 etc). The level of impurities was so high in the case of calcia stabilised zirconia that all the zirconia grains were surrounded by an impurity phase. None of the sections observed with the microscope showed zirconia grains in contact with each other. The yttria zirconia tubes contained a smaller amount of impurities.

Commercial materials are not always fully stabilised. Only zirconia calcia proved to be fully stabilised in the fluorite structure.

Magnesia stabilised zirconia tubes became permeable at room temperature after being heated above 1000°C. This was explained on the basis of structural changes due to incomplete stabilisation. Permeation above 1000°C indicated an activated diffusion process. The activation energy calculated from the leak rate measurements was 25 Kcal $mole^{-1}$ which compares with about 30 Kcal $mole^{-1}$ obtained for oxygen diffusion in $Zr_{0.85}Ca_{0.15}O_{1.85}$ [34]. It was concluded that permeation arose from oxygen vacancy diffusion.

Similar conclusions were reached for the yttria zirconia materials. No permeability measurements were made on calcia stabilised zirconia due

to its high impurity content.

The behaviour of yttria stabilised zirconia suggested that impurities may play a role in permeation increasing the electronic conductivity of the material.

I.3.2 Other solid electrolytes

Among several other solid oxide solutions thoria based solutions have been shown to have suitable properties to be used in high temperature galvanic cells. The following is a summary of Alcock's and Steele's[46,47] study of these materials.

Pure thoria and thoria solid solutions employed as electrolytes (ThO_2.CaO, ThO_2.$YO_{1.5}$, ThO_2.$LaO_{1.5}$) possess the fluorite structure. The comparison of observed with calculated densities supports the anion vacancy model for these materials.

The conductivities of ThO_2.$YO_{1.5}$ and ThO_2-CaO solid solutions at 1000°C as a function of $YO_{1.5}$ and CaO contents were shown in Fig.I.2. It may be observed that, for similar percentages of anion vacancies, thoria based solutions have a much higher resistivity than zirconia based solutions. The results for thoria solutions suggest a maximum value for the conductivity as a function

of composition, but this is far from being as significative as in the case of the zirconia solutions. Moreover, aging experiments with ThO_2 25 mole% $YO_{1.5}$, did not reveal any structural changes of the type discussed for the zirconia stabilised solutions.

Conductivity studies as a function of P_{O_2} indicated that thoria solid oxide solutions exhibit p-type conduction at high oxygen partial pressures, but this becomes negligible below 10^{-6} atm. Alcock and Steele estimated the lower oxygen limit for $t_{ion} > 0.99$ as $P_{O_2} \sim 10^{-25}$ atm at 1000°C on the basis of the emf results obtained in cells where the thoria electrolytes were in contact with Nb-NbO and Mn-MnO respectively.

Fig. I.3 is a summary of Alcock's and Steele's conclusions on the electrolytic properties of some of these oxide solid solutions. This figure is of great value in the selection of a suitable solid electrolyte to be used in a certain galvanic cell in spite of the limitations already discussed. Unfortunately the relevant information is only available up to 1000°C.

I.4 POLARISATION PHENOMENA

During its operation, a solid electrolyte galvanic cell is subjected to the action of current

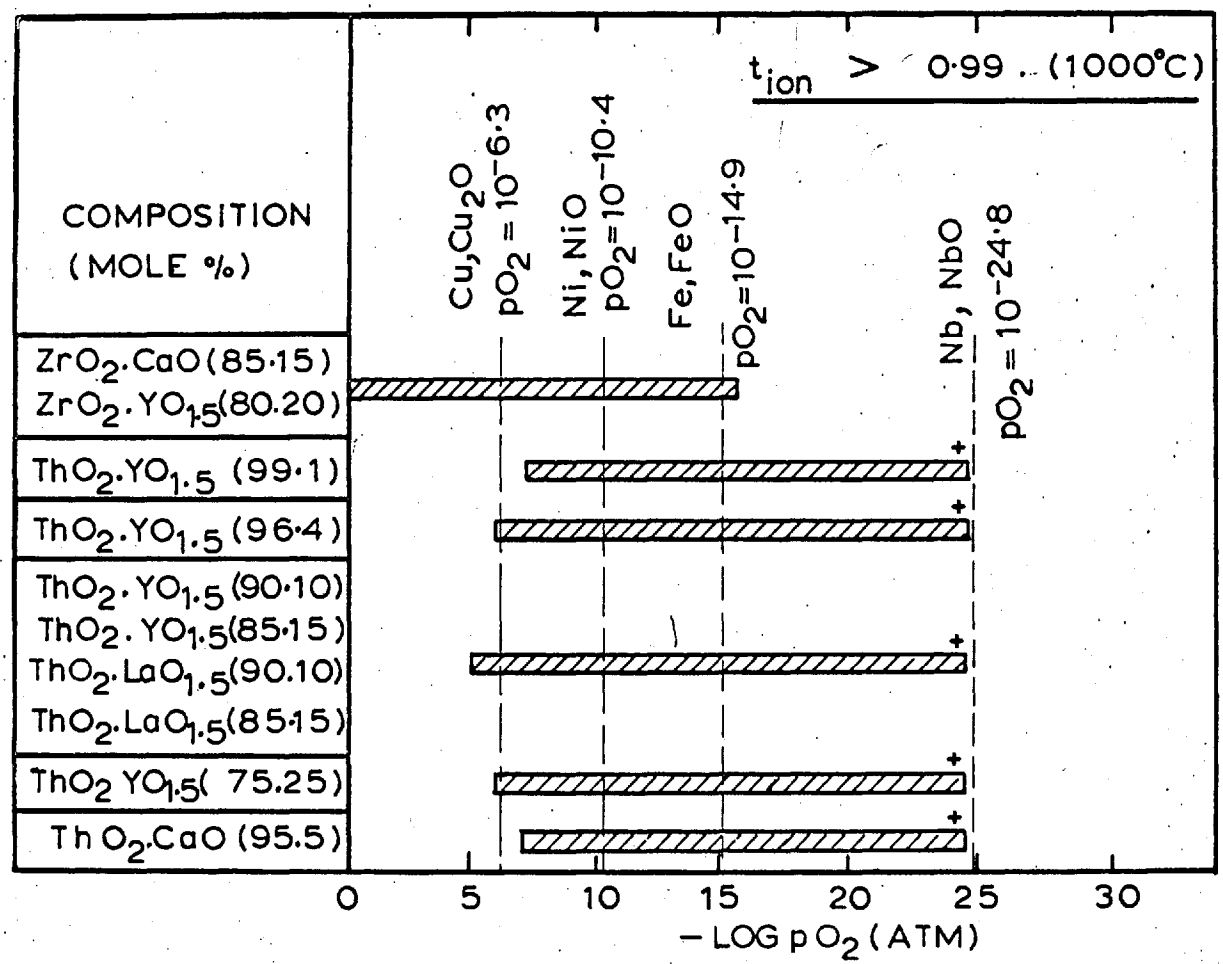


FIG. I.3 IONIC TRANSPORT NUMBER AS A FUNCTION OF COMPOSITION AND OXYGEN PRESSURE.

+ Estimated real values possibly lower

produced by two different sources: the measurement of emf and the solid electrolyte electronic contribution to conductivity. This current will lower the emf below the open-circuit value due to the resistance of the cell and polarisation phenomena at irreversible electrodes. The emf measurement effect is normally minimised by using a high impedance measuring instrument. However, the electronic contribution to conductivity is a property of the solid electrolyte material and its effect cannot be easily controlled.

A simple calculation on the basis of Ohm's law can demonstrate that the magnitude of the short-circuiting currents which may be present in a solid electrolyte galvanic cell exhibiting electronic conduction can reach substantial values, even if the electronic transference number of the electrolyte is not higher than 0.005 (See Section III.3.1,e).These currents are likely to produce electrode polarisation depending on the electrode kinetics.

Very little is know about electrode kinetics and polarisation phenomena in solid electrolyte galvanic cells. Activation polarisation depends on the particular rate-determining chemical and

electrochemical reactions at the electrode. Concentration polarisation involves mass transfer of reactants and products. Measurements on electrodes in molten salts indicate that, in general, concentration polarisation exceeds activation polarisation. This is probably the case in high temperature solid electrolyte galvanic cells.

Activation polarisation may be present in gas electrodes. Pal'guev and co-workers[48,49] have studied the polarisation of Pt, gas electrodes. For the cell

$$Pt,O_2/0.85\ ZrO_2\ 0.15\ CaO/Pt,O_2$$

no polarisation was observed in the temperature range 900-1100°C even with currents of $100mA/cm^2$ Anodic polarisation was detected in the cell

$$Pt,\ (CO + CO_2)/0.85\ ZrO_2\ 0.15\ CaO/Pt,O_2$$

Pal'guev et al. suggested that this was partially due to slow interaction between CO and O_2 (activation polarisation) but mainly to the slow transport of CO to the reaction surface (concentration polarisation). Weissbart and Ruka[36] found, in agreement with Pal'guev and co-workers, that polarisation at a Pt,O_2 electrode remained insignificant at current densities as high as $10mA/cm^2$.

Much less is known about solid electrolytes. Steele[15] reported full reversibility for Ni-NiO at currents of 1μA/cm^2 at 900°C, but with a current of 10μA/cm^2 passed during 5 minutes the Ni-NiO electrode became polarised. Alcock and Belford[6] also reported polarisation of Ni-NiO electrodes in their coulometric titration experiments. However, the currents they used were very high (400μA/cm^2) and the experimental temperature low (700°C). These are the only references found in connection with polarisation of solid oxide electrodes, although several authors mention the possibility of this phenomenon occurring in the operation of high temperature galvanic cells.

I.5 RESEARCH PROGRAMME

The operation of galvanic cells for measuring oxygen contents in molten metals may be subjected to the problems previously discussed. The uncertainty about the behaviour of the cells increases with temperature. It was decided then to start this research programme with metals whose melting points are about or little above 1000°C. Silver and copper were obvious choices.

The most important aspect in the design of the cells was the provision of an experimental method which allowed a comparison of the observed emf with the emf which should have been obtained on the basis of the oxygen potentials in both electrodes. The equilibration of the metals

being studied with gas phases of known oxygen partial pressure made possible the calculation of theoretical emf's in all the experiments.

Another important aspect was the choice of suitable materials for the contact electrodes dipping in the molten metals. These materials should have an acceptable electronic conductivity, a negligible solubility in the liquid metal and withstand highly oxidising conditions for long periods.

The selection of solid electrolytes and reference electrodes were other points to be considered. This problem appeared fairly simple in the case of silver where either ZrO_2.CaO or ZrO_2.Y_2O_3 should be used, considering the range of oxygen pressures envolved (see Fig. I.3) and Ag(l) equilibrated with oxygen at a fixed pressure was an obvious reference electrode. However, in the case of copper the problem could be more complex, especially with reference to the choice of a reference electrode.

CHAPTER II

MEASUREMENTS IN MOLTEN SILVER.

II.1 REVIEW OF THE LITERATURE

The solubility of oxygen in liquid silver has been studied as a function of pressure and temperature by Sieverts and Hagenacker[50], Donnan and Shaw[51] and Parlee and Sacris[52]. Their results (Fig. II.7) are reasonably concordant. All these investigators used a gas volumetric technique. Sieverts and Hagenacker made determinations at 973° - 1125°C mainly at 1 atm. Donnan and Shaw worked only at 1075°C. Finally Parlee and Sacris covered the temperature range 1011° - 1202°C. Mizikar, Grace and Parlee[53] have proposed the following equation to represent the solubility of oxygen in molten silver at P_{O_2} = 1 atm.

$$\log \%\underline{O} = \frac{723.7}{T} - 1.0949 \qquad \text{(II.1)}$$

based on the work of Sieverts and Hagenacker and Donnan and Shaw.

Sieverts and Hagenacker demonstrated that the solubility of oxygen in liquid silver is proportional to the square root of the pressure up to a little above 1 atm. This is proved by their measurements at 1075°C which are plottted in

Fig.II.1. Parlee and Sacris obtained identical results at 1020°C. This means that the activity coefficient of the oxygen remains constant over this range of temperatures and pressures; Henry's law behaviour, and, therefore, the activity of silver is equal to its atomic fraction.

II.2 EXPERIMENTAL

The technique employed was to measure the volume of oxygen absorbed by a known weight of silver which had been previously degassed in a Sieverts apparatus. Alloys of known oxygen content prepared in this way formed oneelectrode of the galvanic cell. The other electrode was silver saturated with oxygen at barometric pressure. The emf was thus determined as a function of the oxygen concentration at various temperatures and pressures, as well as the various times during the course of some of the equilibration experiments.

a) Materials

The oxygen for the solubility measurements was prepared by thermal decomposition of potassium, permanganate. The initial products of decomposition, which contained desorbed air, were discarded; the remainder was dried by condensing with liquid nitrogen and transferring a portion of the condensate to a storage reservoir. Dry cylinder oxygen was used in the reference electrode. The

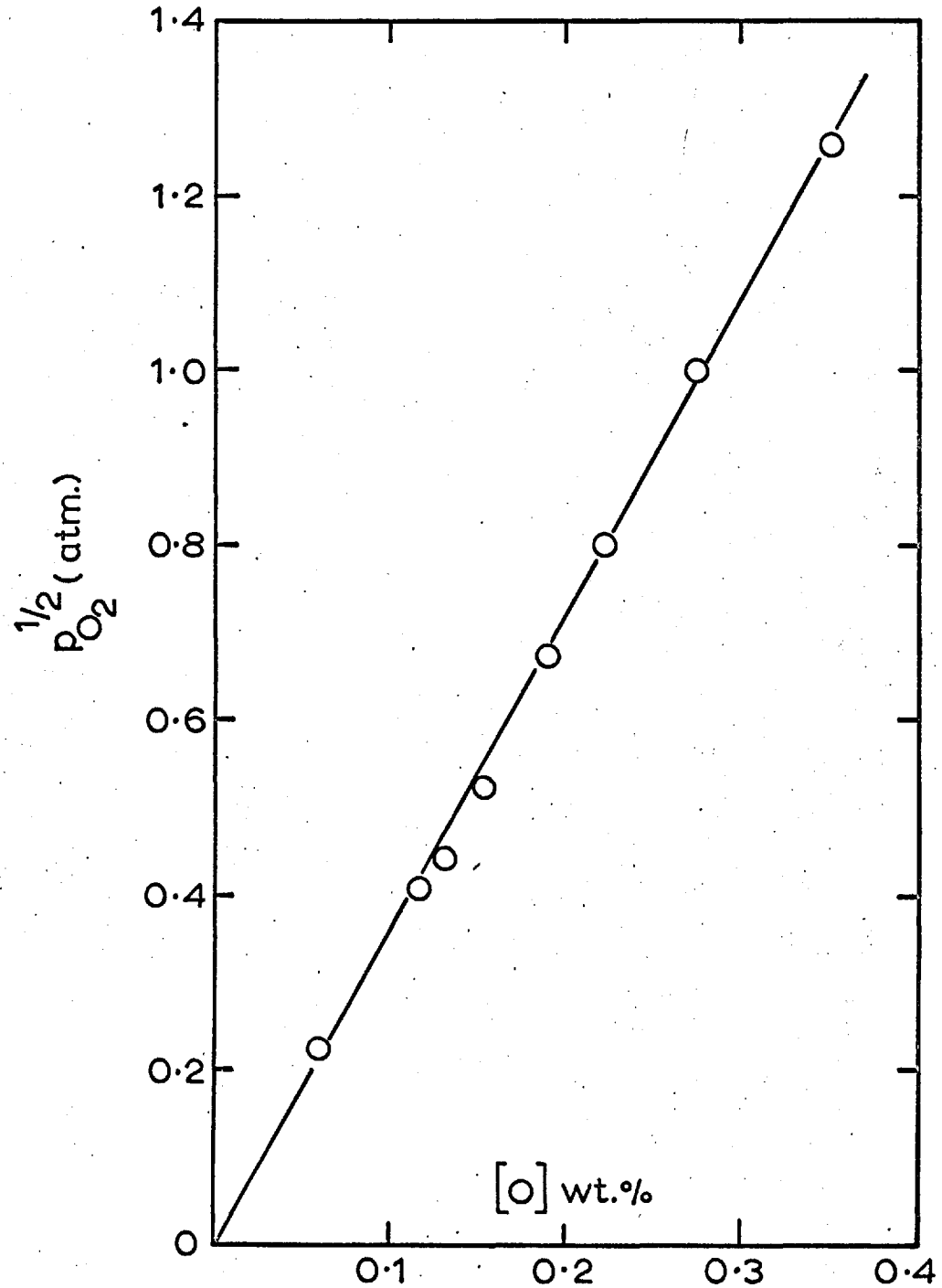


FIG.II.1 THE SOLUBILITY OF OXYGEN IN SILVER AT 1075°C AFTER SIEVERTS AND HAGENACKER

silver was of "spectroscopic" purity, containing less than 0.001 per cent total impurities, the most important being iron, 5 ppm, and Cu, 2 ppm. "Immaculate Five" stainless steel wire, 0.018 in diameter, containing 21% Ni and 23% Cr, which previous investigations in the Department had proved to be the most suitable material, was used for the electrodes.

The lime-zirconia tubes used as solid electrolyte were made commercially and contained 15 mole per cent lime. They were 15" long and ¼" outside diameter and the wall thickness was about 1.0 mm. The tubes cracked because of thermal shock if brought from room temperature to 1000°C in much less than 10 min.

b) Apparatus

The Sieverts' apparatus used in this work is illustrated in Fig. II.2. The limbs of manometer A and gas burette B were of precision bore tubing 4.00 ± 0.01 and 20.00 ± 0.02 mm in diameter respectively. The useful length of the gas burette limbs was 40 cm. All measurements were made with the right limb evacuated and this side was maintained under vacuum except when gas was being introduced to the cell in some cases. With this

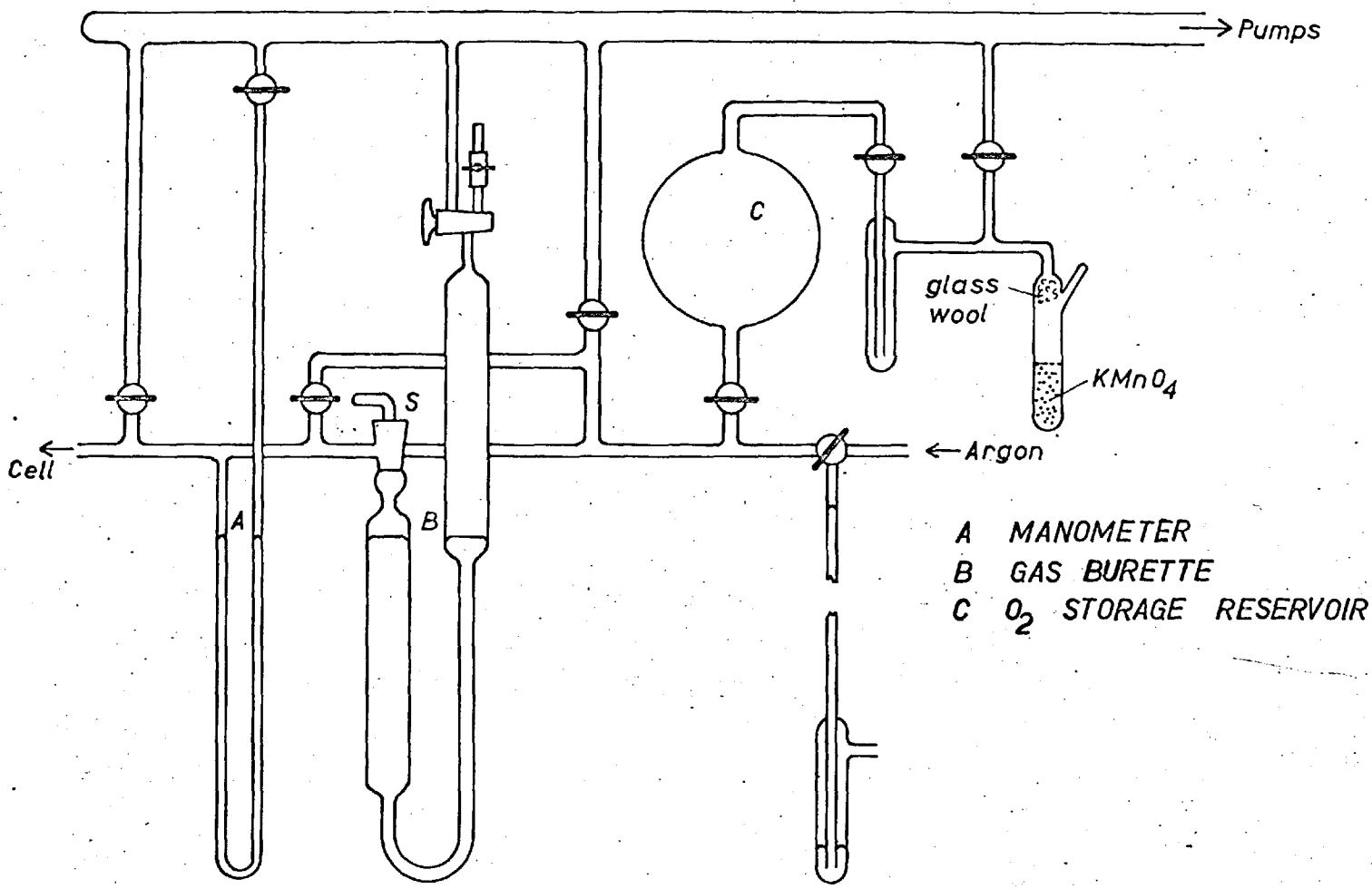


FIG. II 2 SIEVERTS APPARATUS

design, the measurements were independent of barometric pressure. The volume between stopcock S and the mercury in the left limb, when the levels in both sides were identical (zero level) was carefully calibrated. Air at barometric pressure was introduced in both limbs of the gas burette and then the right limb was evacuated. The levels in both limbs were recorded and the pressure of the gas in the left limb calculated. With these data the calculation of the volume between the stopcock and the zero level in the left limb was straightforward.

Argon, for the determination of the "hot volumes" was dried over silica gel and magnesium perchlorate and further purified by passage through titanium chips at 900°C.

The system was evacuated by a rotary pump in conjunction with an oil diffusion pump. With silver in the cell at 980° - 1160°C a vacuum of 10^{-4} to 10^{-5} mm mercury could be attained with constant pumping for all the successful cells used in this research. The vacuum was measured by means of a Pirani and Penning gauges.

The oxygen prepared by thermal decomposition of potassium permanganate was stored in the reservoir C. The tube holding the potassium permanganate, the trap and the reservoir were

evacuated prior to the preparation of a fresh quantity of oxygen. As already said, the initial products of decomposition, containing desorbed air, were discarded. The oxygen produced in a subsequent decomposition was condensed in the liquid nitrogen trap and some of it was transferred to the reservoir until it reached atmospheric pressure.

The cell is shown diagramatically in Fig.II.3. A known weight of silver, about 55 g, was held in the mullite tube F, which was 30 cm. long and had an inside diameter of 15.5 mm. for the cells without stirring and 22 mm. for those with stirring. The solid electrolyte was an impervious tube E of lime-zirconia as already described. This tube contained a small quantity of silver as the reference electrode, usually about 1.2 g. The end of this tube was located approximately 1 cm. below the level of the silver in tube F, so the silver level in both electrodes was nearly the same.

All ceramic to metal seals in the upper part of the assembly were made gas-tight with araldite. The brass head of the cell C was water cooled and had an 'O' ring between its lower and upper parts.

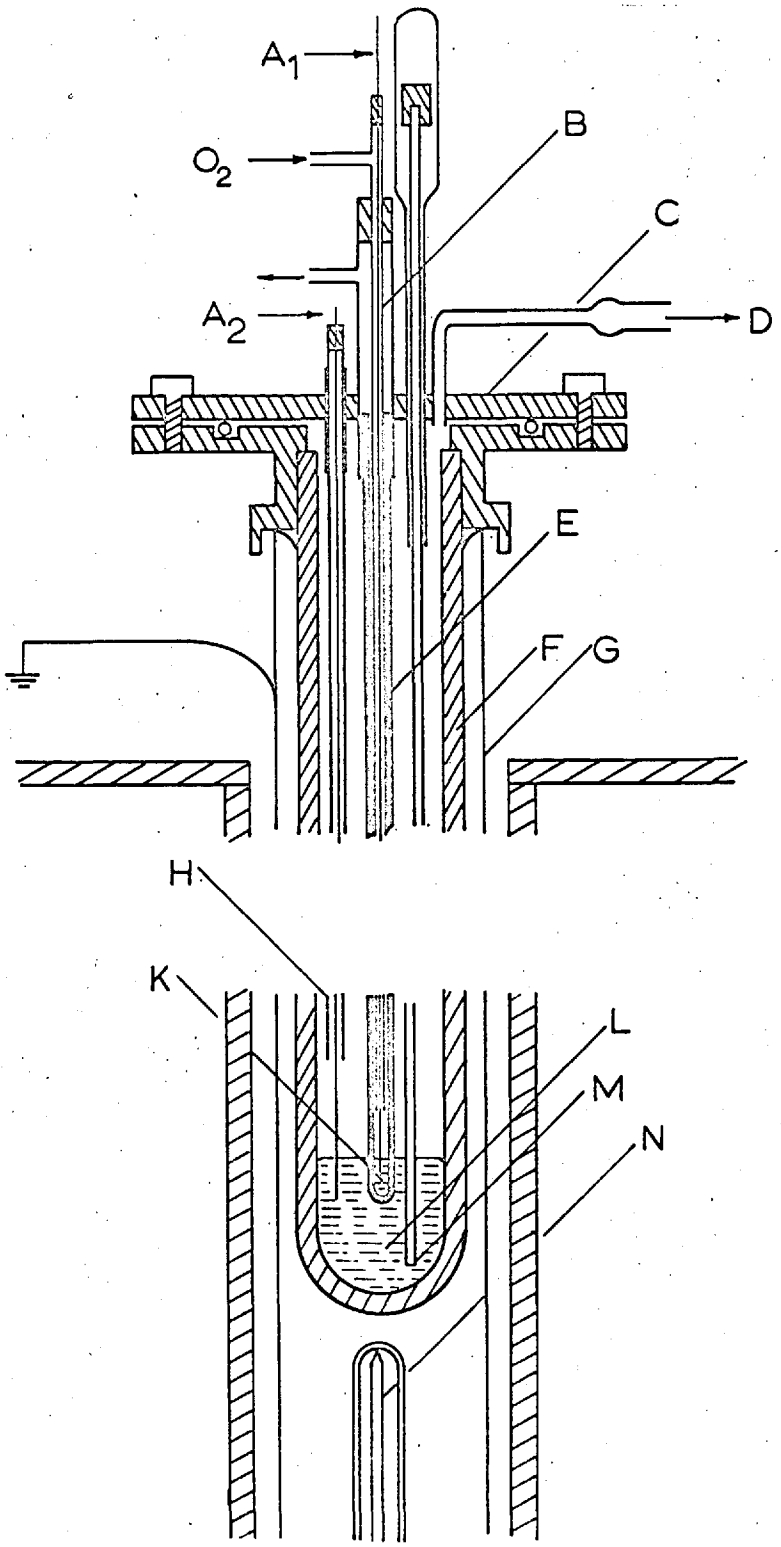


FIG. II 3 CELL USED FOR MEASURING E.M.F's IN MOLTEN SILVER

Fig.II.3 - Cell used for measuring emf's in molten silver

A_1, A_2 Stainless steel contact electrodes.

B, H Alumina sleeves.

C Brass head.

D Connection to manometer, gas burette and vacuum pumps.

E Lime-zirconia tube.

F Mullite reaction tube.

G Nimonic 75 shield.

K Reference electrode.

L Silver.

M Alumina stirrer.

N Control thermocouple.

The reference electrode K was flushed continuously with cylinder oxygen which was dried with magnesium perchlorate. The oxygen was introduced via the inner alumina tube B, 3 mm. outside diameter, and vented via dibutyl phtalate. The stainless steel electrodes A_1 and A_2 were held in position with alumina sleeves B, H. The upper ends of these tubes, 3 mm. in diameter, were sealed with small glass beads and ordinary wax.

Stirring was provided in some of the experiments in order to accelerate the slow dissolution of oxygen in silver. The stirring mechanism consisted of an alumina rod M, 3 mm. diam, with an iron upper end which was moved up and down with a magnet.

The cell was suspended in a vertical Kanthal wound furnace, the temperature of which was controlled to better than $\pm$ 1°C by a Kelvin-Hughes controller. The control Pt.-Pt.13% Rh. thermocouple N was inserted from the lower end of the furnace tube just below the bottom of the cell. A resistance was placed across the terminals of the mercury switch so that when this was opened the furnace winding was not completely disconnected

from the power supply, but it was connected to it in series with this resistance. The overall effect was that the power supply to the furnace in the OFF position of the control system was approximately 80% of that in the ON position.

The temperature of the system was measured by a Pt.-Pt.13% Rh. thermocouple (not shown in Fig.II.3) located in the silver at the same depth as the reference electrode and protected by an alumina sheath.

Electrical shielding was effected by means of a Nimonic 75 tube G which was maintained at ground potential. The brass head of the cell and the exterior casing of the furnace were also electrically grounded.

The emf's were measured with a Vibron electrometer* of input resistance 10^{17} ohms. The accuracy was 1% or better depending on the range employed.

The electrode A_1 was connected to the high terminal on the instrument with screened non-microphonic co-axial cable. A_2 was connected to earth together with the furnace screen, the brass head of the cell and the metal case of the electrometer.

* E.I.L. Vibron Electrometer Model 33B-2

c) Procedure

After assembling, the cells were tested for gas-tightness, first at room temperature and then at the particular experimental temperature which was going to be tried. This was thought a necessary precaution, because some of the ceramic tubes used showed at high temperature a porosity which was incompatible with the nature of the solubility experiments. The cells were considered satisfactory if a vacuum better than 10^{-4} was obtained and the pressure did not increase beyond 10^{-3} cm in one hour after the system had been outgassed and isolated from the pumps.

The silver was cut off from 7 mm. diam. rods with a clean high speed hacksaw blade. The surface layer of the rods was removed with a clean file. The silver piece used in the reference electrode had to be machined to fit the diameter of the lime-zirconia tube. Afterwards the surface of the little piece of silver was carefully cleaned from any trace of grease.

Due to the narrowness of the small cells the silver had to be melted before inserting the reference electrode, thermocouple sheath and contact electrode. This was done in air. With the silver just over the melting point the assembly of the

cell was completed. This technique, which was not very convenient, was improved with the cells with stirring, where the extra space available allowed the complete assembly of the cell at room temperature. The melting operation was done in these cases under argon.

Prior to each series of measurements, and independently of the method of assembly of the cell, silver was degassed by pumping down the system for about twelve hours while the metal was kept just below its melting point. This was generally done overnight. In the experiments at 980°C, after reaching the experimental temperature the system was still pumped down for a short while (10 to 15 minutes). Degassing was controlled by measurement of the pressure with the Pirani and Penning gauges and following the variation of the emf in the electrometer. With the technique described, emf's of the order of 350 to 400 mv were reached at 980°C. The latter value corresponds to a residual partial pressure of oxygen of 3×10^{-4} mm. and an oxygen content in the metal of approximately 2 ppm. Further evacuation did not yield initial emf's substantially higher than this and increased the danger of silver losses by evaporation and condensation in the cold walls of the

cell. Further elimination of oxygen from the metal phase could be effected by passing a reverse current through the cell for a short period. Higher values of the emf wereobtained, but these gradually decreased on allowing the system to stand with the pumps in operation and generally reverted to about 400 mv in a short period of time. On the other hand, the starting level of oxygen already mentioned was satisfactory considering the high solubility of oxygen in silver. In the experiments at temperatures higher than 980°C this technique of degassing was slightly modified to avoid excessive evaporation of the metal. After pumping down the system with the silver just below the melting point, the metal was melted and taken to the experimental temperature under argon. With the short period of pumping preceding the introduction of oxygen to the system similar levels of emf's were reached.

The "hot volumes" of the cell as a function of pressure had to be measured before each series of experiments. Argon was used for this purpose. The "hot volumes" were of the order of 40 cc. for the cells without stirring and 75cc. for those with stirring at N.T.P. They were independent of pressure, if reduced to N.T.P., when

allowance was made for changes in the level of mercury in the manometer.

The procedure for determination of the "hot volumes" was as follows. The left limb of the gas burette was filled with argon and the system evacuated. After reading the mercury levels in both limbs of the gas burette, the left limb was connected to the system through tap S (Fig.II.2). When the pressure in the manometer of the system became steady, the mercury levels in the gas burette were read again and the room temperature recorded. Tap S was closed, the system evacuated and a fresh quantity of argon admitted. With the data so obtained the volumes of argon ("hot volumes" of the cell) which had been introduced into the system were calculated. Table II.1 gives a typical set of values. The "hot volumes" have been reduced to N.T.P. and allowance has been made for changes in the level of mercury in the manometer.

TABLE II.1

P(mmHg)	Hot Volume (N.T.P.) c.c.
80.52	37.60
59.15	37.52
41.17	37.71
31.00	37.62
27.94	37.63
17.20	37.53
8.90	37.40

Althoug "hot volumes" were measured with liquid silver in the cell, a check was made initally with no silver present to compare the "hot volumes" obtained with oxygen and argon. The difference was negligible at very low pressures but became of the order of $1\pm0.5\%$ at around 1 atm. (oxygen "hot volumes" being larger than argon) in the experimental temperature range. Due to the high solubility of oxygen in liquid silver, this difference was so small as to have no discernable effect on the results at equilibrium. The slight correction was, however, applied when necessary to the measurements in the early stages of equilibration to allow for this effect in calculating the oxygen content of the metal.

After ending the "hot volumes" determina-

tion the system and the gas burette were evacuated and oxygen from the storage reservoir C was admitted into the left limb of the burette. The system was ready to start a series of solubility measurements.

A series of experiments consisted in successive equilibrations of the silver contained in the cell with oxygen whose pressure was gradually increased. At the experimental temperature, oxygen was progressively added to the cell to go from the low to the high pressures. At each particular pressure enough time was allowed for the system to reach equilibrium.

A characteristic feature of the first experiments done at 980°C was the slowness with which equilibrium was established for both the pressure and emf after oxygen was admitted to the system. Times required for equilibration varied from several hours at the lowest oxygen pressures employed to over 48 hours for equilibrium pressures in excess of 0.5 atm. Stirring was then provided in some of the experiments and equilibrium between gas and metal could be attained within 45 minutes of making a sudden change in the gas pressure.

II.3 RESULTS AND DISCUSSION

a) Experiments at 980°C

The results of the solubility measurements at 980°C are shown in Fig.II.4 where the observed oxygen content is plotted against the square root of the oxygen pressure in atmospheres. The solubility obbeys Sieverts law in confirmation of previous information available. The results are also summarized in Table II.2. They correspond to two different emf cells and a Sieverts cell (without electrodes) which was operated to determine the possible effect of the stainless steel or the solid electrolyte on the solubility measurements. No difference was observed. Table II.2 also contains the emf's found. They are compared with the emf's calculated from the equilibrium oxygen pressure and the barometric pressure, which is the oxygen pressure in the reference electrode.

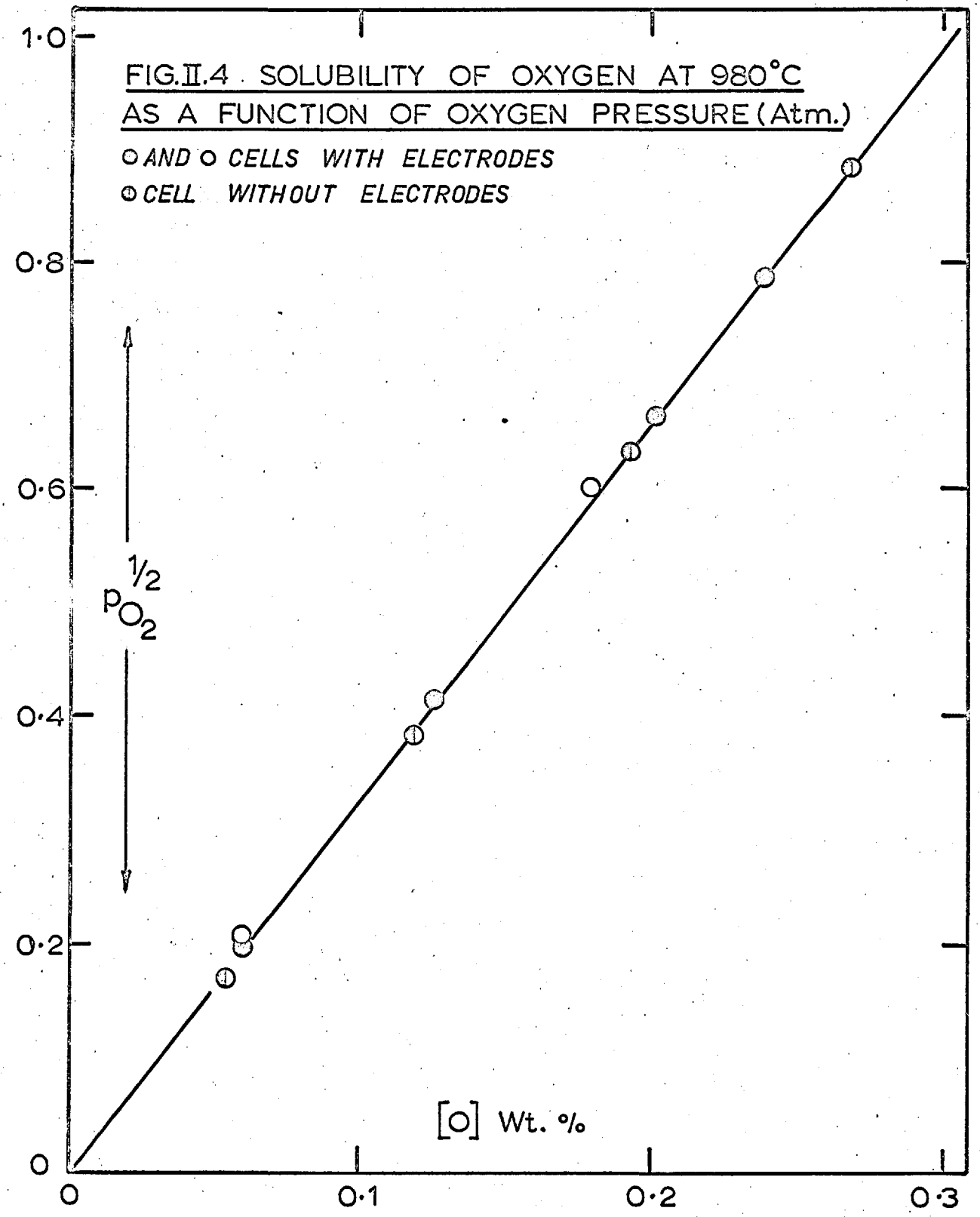

FIG.II.4 SOLUBILITY OF OXYGEN AT 980°C
AS A FUNCTION OF OXYGEN PRESSURE (Atm.)
○ AND ○ CELLS WITH ELECTRODES
◎ CELL WITHOUT ELECTRODES
1·0
0·8
0·6
0·4
0·2
0
$P_{O_2}^{1/2}$
[O] Wt. %
0
0·1
0·2
0·3

TABLE II.2

Results at 980°C

Cell	$P_{O_2}^{\frac{1}{2}}$ (atm)	[O] wt.%	emf obs. (mv)	emf calc. (mv)
emf 1	0.2075	0.061	85.3	84.7
	0.600	0.1795	27.3	27.4
emf 2	0.199	0.060	88.2	87.2
	0.415	0.1255	46.8	47.4
	0.663	0.2025	21.6	22.5
	0.782	0.241	12.7	13.6
Sieverts	0.169	0.053		
	0.384	0.119		
	0.632	0.193		
	0.882	0.2674		

The results show that for solutions of oxygen in liquid silver Henry's law is obeyed up to the pressures employed. Concentrations may, therefore, be used in place of activities in the expression of the emf of the cell. In a reversible cell, the emf is given by:

$$E = \frac{RT}{nF} \ln \frac{[O]\,atm}{[O]_{P_{eq}}} \qquad (II.2)$$

Where $[O]_{P_{eq}}$ is the equilibrium oxygen content of the silver in one half of the cell and [O] atm is the oxygen content in the reference electrode.

As Sieverts law is obeyed, [O] atm in equation II.2 may be replaced by $k_{P_{at}^{\frac{1}{2}}}$, where k is

the Sieverts coefficient for the solubility at temperature T and P_{at} is the barometric pressure at the time of measurement. Equation II.2 may, therefore, be written:

$$E - \frac{RT}{nF} \ln P_{at}^{\frac{1}{2}} = \frac{RT}{nF} \ln \frac{k}{[O]_{P_{eq}}} = \frac{RT}{nF} \ln \frac{[O]_{1atm}}{[O]_{P_{eq}}} \qquad (II.3)$$

where $[O]_{1atm}$ is the oxygen content in equilibrium with oxygen at 1 atmosphere.

The term $\frac{RT}{nF} \ln P_{at}^{\frac{1}{2}}$, which is small and may be either positive or negative, thus normalizes the emf measurements to a standard pressure of 1 atm for the reference electrode.

Equation II.2 predicts that, at constant temperature, a plot of $E - \frac{RT}{nF} \ln P_{at}^{\frac{1}{2}}$ against $\log [O]_{P_{eq}}$ will be linear. This plot is shown in Fig.II.5 for the results at 980°C. The line is theoretical and corresponds to the value of $k = 0.304$ found independently in the solubility measurement.

The observed emf's were quite steady over long periods of time.

The manner in which the emf varied with time during approach to equilibrium in the experiments without stirring is of particular interest in the analysis of the results. Fig.II.6a

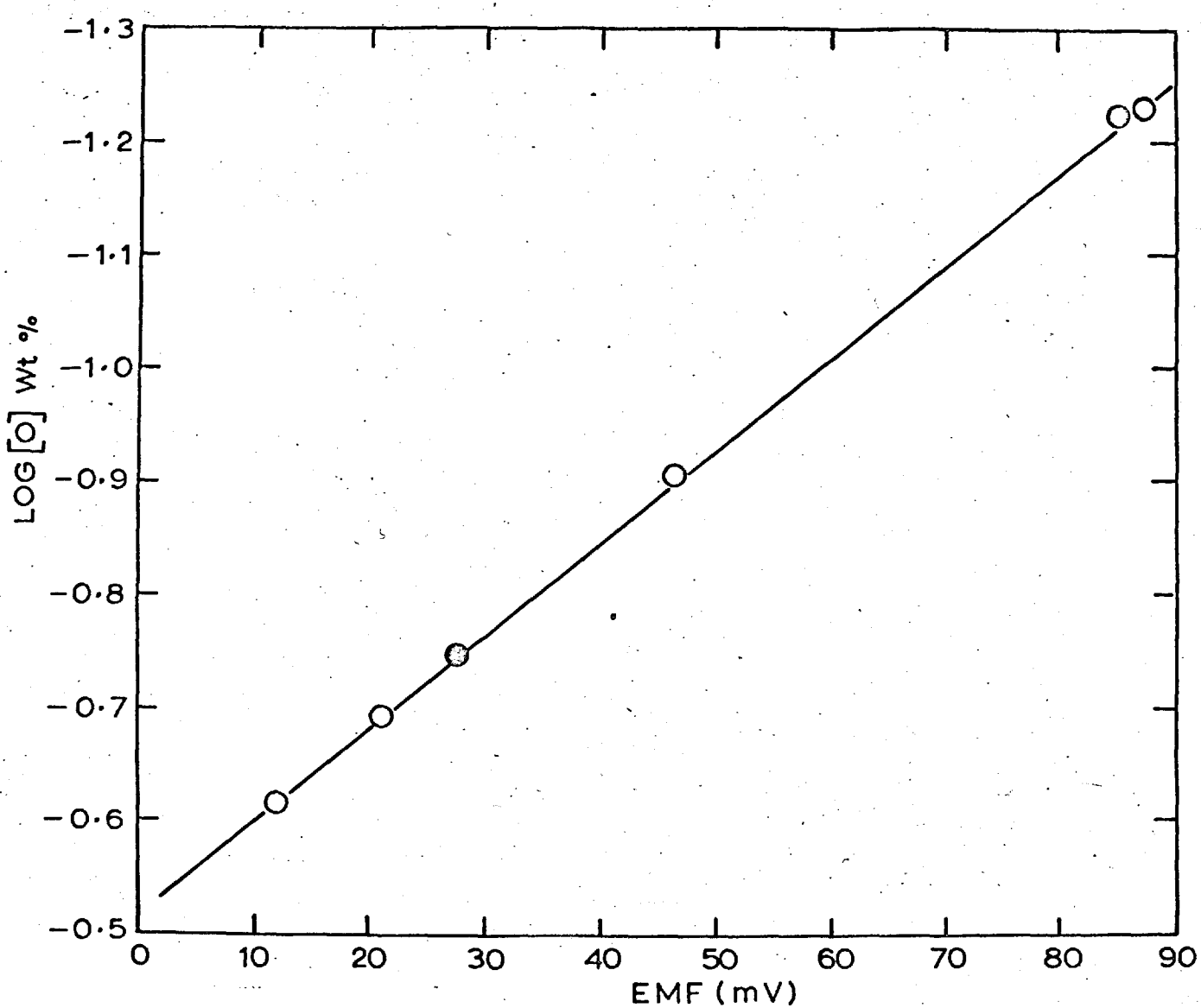


FIG. II.5 E.M.F's MEASURED AT 980°C WITH TWO DIFFERENT LIME-ZIRCONIA TUBES. THE STRAIGHT LINE SHOWS THE THEORETICAL RELATIONSHIPS CALCULATED FROM SOLUBILITY VALUES

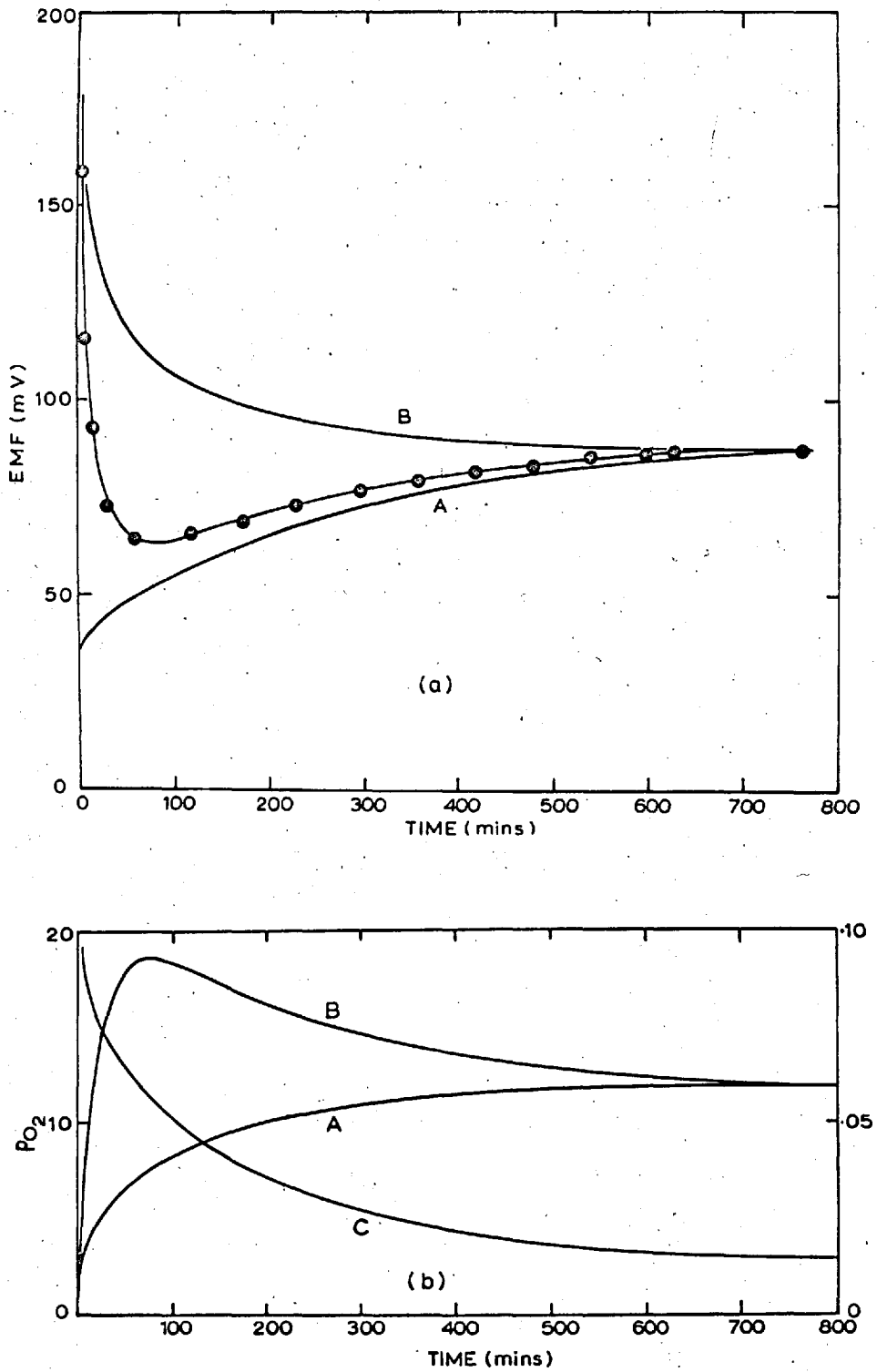


FIG. II.6 (See caption in page 57)

Fig.II.6 Results of an experiment at 980°C with no stirring in which the oxygen pressure over the metal was suddenly raised from 0 to 20 cms. Hg. (a) • measured emf's; Curve A, emf's calculated from oxygen pressures measured over the metal; Curve B, emf's calculated from absorbed oxygen assuming uniform distribution in the metal. (b) Corresponding gas pressures (cm Hg) and concentrations for (a) above. Curve A, mean concentration of oxygen in the silver; Curve B, oxygen concentration calculated from observed emf's, with right hand vertical scale; Curve C, oxygen pressure over the metal, with left hand vertical scale.

illustrates one of these experiments. The points in this figure show the emf observed as oxygen was absorbed by the molten silver. Curve A shows the emf which would have been observed if the outer electrode (Fig.II.3) had been functioning as an oxygen gas electrode, and responding solely to the decreasing oxygen pressure over the metal. Curve B shows the emf which would have been recorded if the oxygen absorbed had been at all times uniformly distributed in the metal and the electrode had been responding to it.

It is evident that the observed emf's were initially far removed from those corresponding to the gas above the metal, and that the outer electrode was responding to the oxygen in the upper part of the silver. In this region, with no stirring, it is reasonable to expect that the concentration of dissolved oxygen would first exceed its final equilibrium value and then fall as the oxygen became uniformly distributed through the metal, and the gas pressure fell correspondingly to its final value, as shown in Fig.II.6b. With stirring, the observed emf's were much closer to those calculated from the mean oxygen concentration than those shown in Fig.II.6.

On completion of measurements of the type illustrated by Fig.II.6, the cell was evacuated by connecting the system directly to the pumps. Although the pressure in the cell dropped immediately to a value less than 1 mm. Hg the emf did not change abruptly, but persisted for a short period at the equilibrium value before commencing to increase slowly as oxygen moved out of the liquid.

b) Experiments at Higher Temperatures

Two series of experiments were done at 1080°C using a Sieverts type cell (without electrodes) with stirring. The solubility results obtained were considerably lower than those previously reported by other investigators. On disassembling the cell it was realised that a substantial amount of silver had been vapourised during the experiments and condensed on the cold part of the cell. This phenomenon had been negligible at 980°C. The solubility of oxygen in the solid phase which has been studied by Sieverts and Hagenacker[50] and by Steacie and Johnson[54], is markedly lower than in the liquid, it reaches a maximum of 0.01% at 939°C, and this explains the discrepancies already mentioned.

Silver vaporisation was particularly important in experiments carried out at low oxygen pressures. Similar difficulties were found by Sacrisand Farlee[52] during their measurements. It was decided then to do the experiments at temperatures over 980°C only at 1 atm pressure.

The emf cell used was operated at 1055°, 1105° and 1160°C. The experiments were conducted in such a way that the silver was always under a gas pressure of about 1 atm. This was done by introducing O_2 into the cell in successive stages. Pressuresof O_2 higher than 1 atm were obtained by admitting air into the right limb of the gas burette. Very little evaporation of silver was observed during these experiments.

The solubility results and the emf's observed are summarised in Table II.3.

TABLE II.3

Results at 1055°, 1105° and 1160°C and P_{O_2} = 1 atm.

t°C	[O] wt.%	emf obs (mv)	emf calc. (mv)
1055	0.279	-1.2	-0.2
1105	0.270	-1.0	0.0
1160	0.262	-0.9	+0.2

The solubility values together with those of Sieverts and Hagenacker, Donnan and Shaw and

Sacris and Parlee at 1 atm pressure are plotted in Fig.II.7. There is a close agreement between the new results and those published previously. At about 1160°C the stainless steel electrodes begin to oxidize slowly but visibly; this may be the cause of the slightly high value obtained for the solubility under 1 atm at this pressure.

The observed emf's are in good agreement with the calculated emf's.

The line drawn in Fig.II.7, which is the best line through all the data, excluding that one at 1160°C, leads to the equation:

$$\log [O] \text{ wt.\%} = \frac{737.6}{T} - 1.107 \qquad \text{(II.4)}$$

$$\text{or} \quad \log [O] \text{ atm \%} = \frac{737.6}{T} - 0.281 \qquad \text{(II.5)}$$

The equation was calculated by the least squares method and differs only slightly from that proposed by Mizikar, Grace and Parlee[53]. The following values are found for $\Delta\bar{H}$ and $\Delta\bar{S}$:

$$\Delta\bar{H} = -3380 \text{ cal per } \tfrac{1}{2} O_2$$

$$\Delta\bar{S} = -1.3 \text{ cal deg}^{-1} \text{ at 1g atom\%}$$

II.4. CONCLUSIONS

The main feature of the experimental technique used in this study was the possibility of testing the behaviour of the cell by comparing a theoretical emf value, calculated on the basis

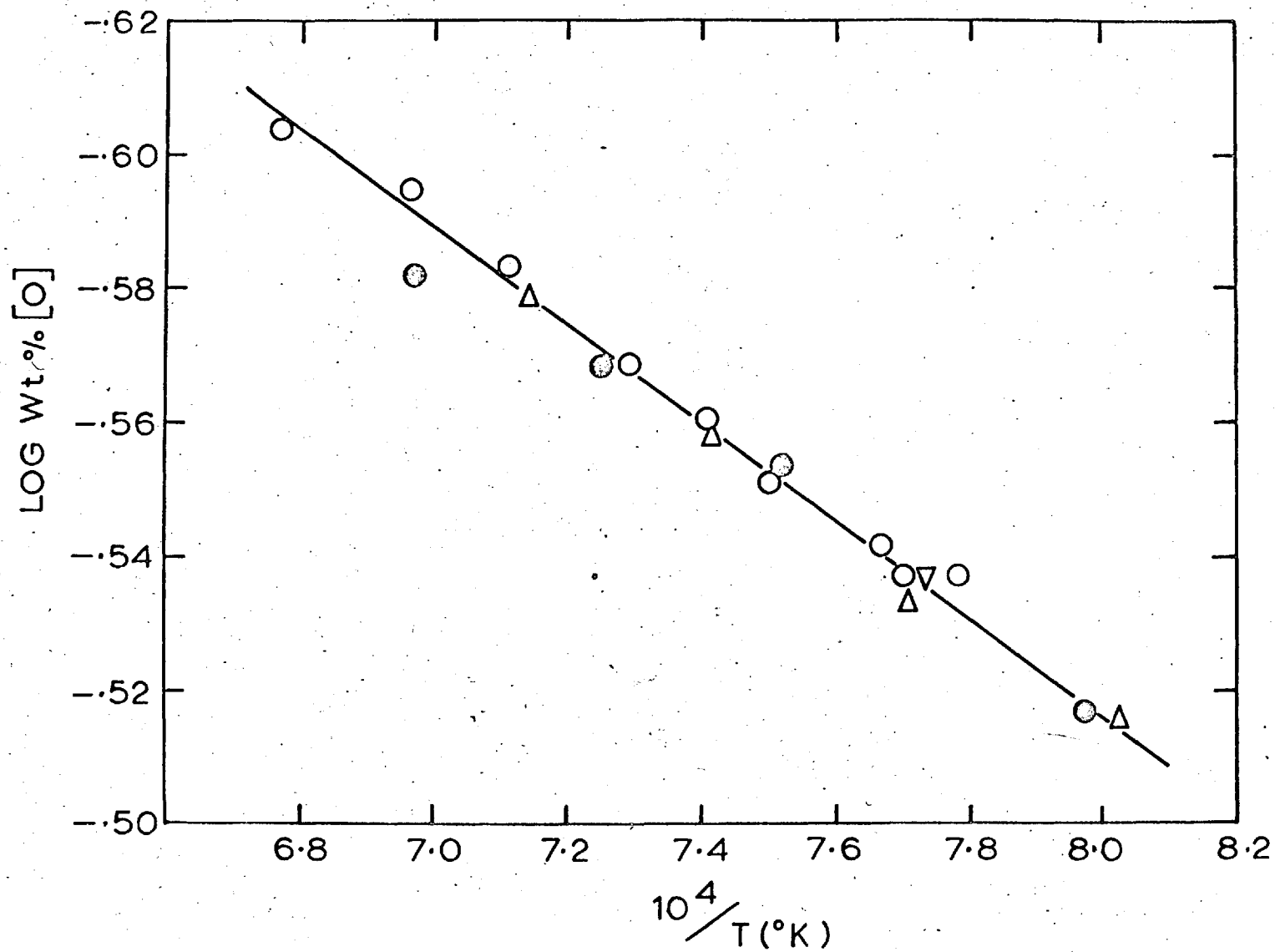


FIG. II.7 SOLUBILITY OF OXYGEN AT ONE ATMOSPHERE PRESSURE SHOWN AS A FUNCTION OF THE ABSOLUTE TEMPERATURE O THIS WORK O PARLEE & SACRIS[52] Δ SIEVERTS & HAGENACKER[50] ∇ DONNAN & SHAW[51]

of the Sieverts type of measurements, with the observed one. Secondly, the experiments without stirring and the constancy of the emf value on evacuation of the system after equilibrium are good evidences that the cell was reacting towards the oxygen content of the silver and not the gas phase. Thirdly, the experiments with stirring showed that the reaction of the cell was almost instantaneous after producing a change in the oxygen content of the metal. It is then possible to say that a cell of this kind is a reliable device for the determination of oxygen contents in silver in the concentration and temperature ranges studied. It has been actually used[55] in the investigation of the rate of oxygen transfer from a gas jet into molten silver.

Previous results of oxygen solubility in liquid silver have been confirmed.

CHAPTER III

MEASUREMENTS IN MOLTEN COPPER

III.1 The Copper-Oxygen System

Hansen[56] prepared the phase diagram for the system Copper-Oxygen from various sources (Fig. III.1). Only the value for the melting point of Cu_2O has been changed to the temperature reported by Rossini et al[57].

The system has been extensively studied only up to 1200°C, which is the most interesting region for extractive metallurgy. There is some uncertainty concerning the values of the monotectic temperature and the composition of the oxygen saturated copper melts in equilibrium with $Cu_2O(s)$. Tomlinson and Young[58] have studied the equilibrium $Cu_2O(s)$ - Cu(l) saturated with oxygen and CO_2/CO gas mixtures. Values for the composition of the Cu(l) saturated with oxygen have been calculated by extrapolating their oxygen solubility results to the P_{O_2} corresponding to that equilibrium. These values are shown in Fig. III.2 and they are in a reasonably good agreement with Hansen's phase boundary. Rickert and Wagner[10] using a 'coulometric titration' technique, have also confirmed Hansen's Cu-Cu_2O phase boundary

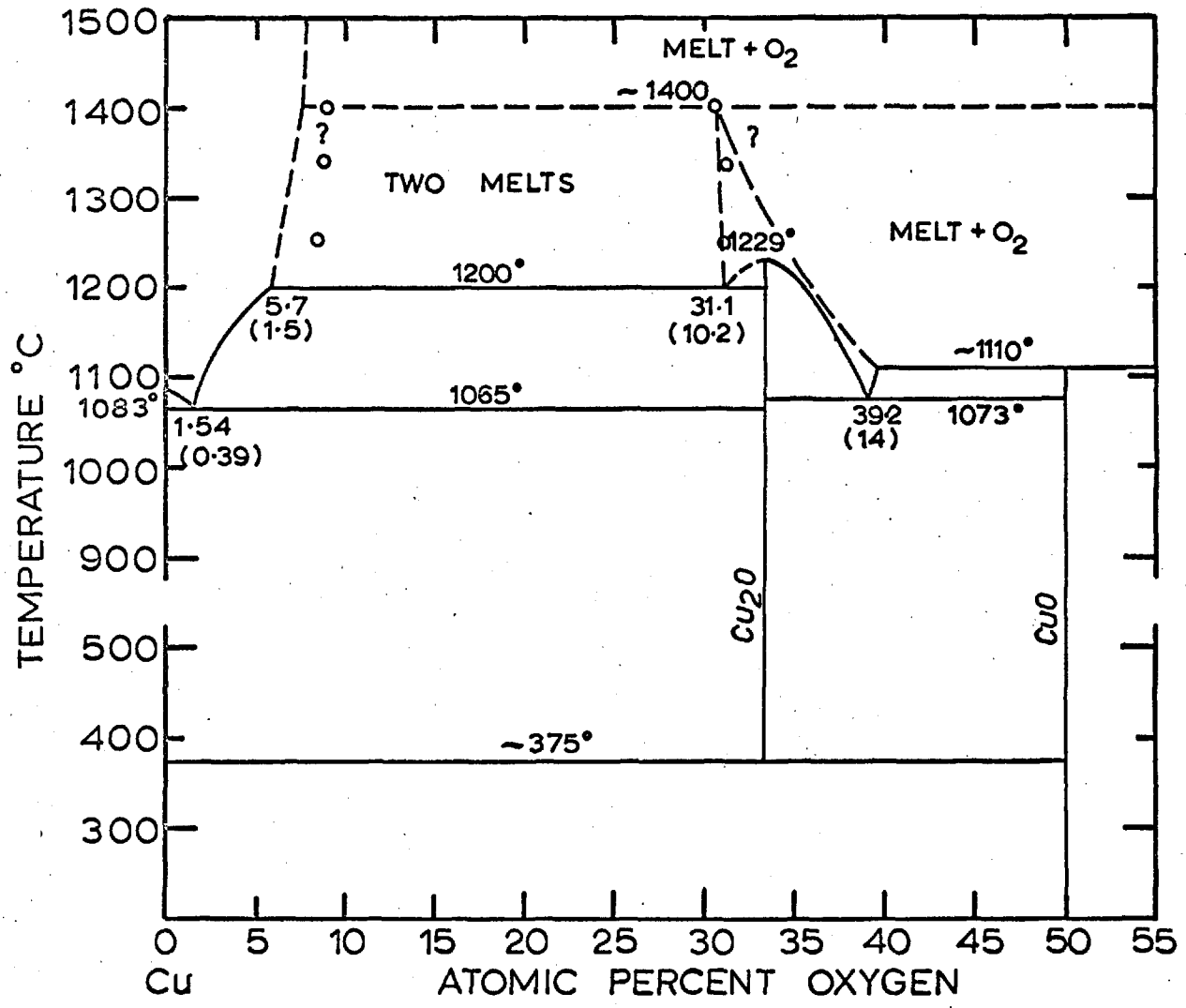


FIG. III.1 THE Cu-O PHASE DIAGRAM AFTER HANSEN[56]
o SLADE & FARROW[59] PHASE BOUNDARIES
FOR THE MISCIBILITY GAP

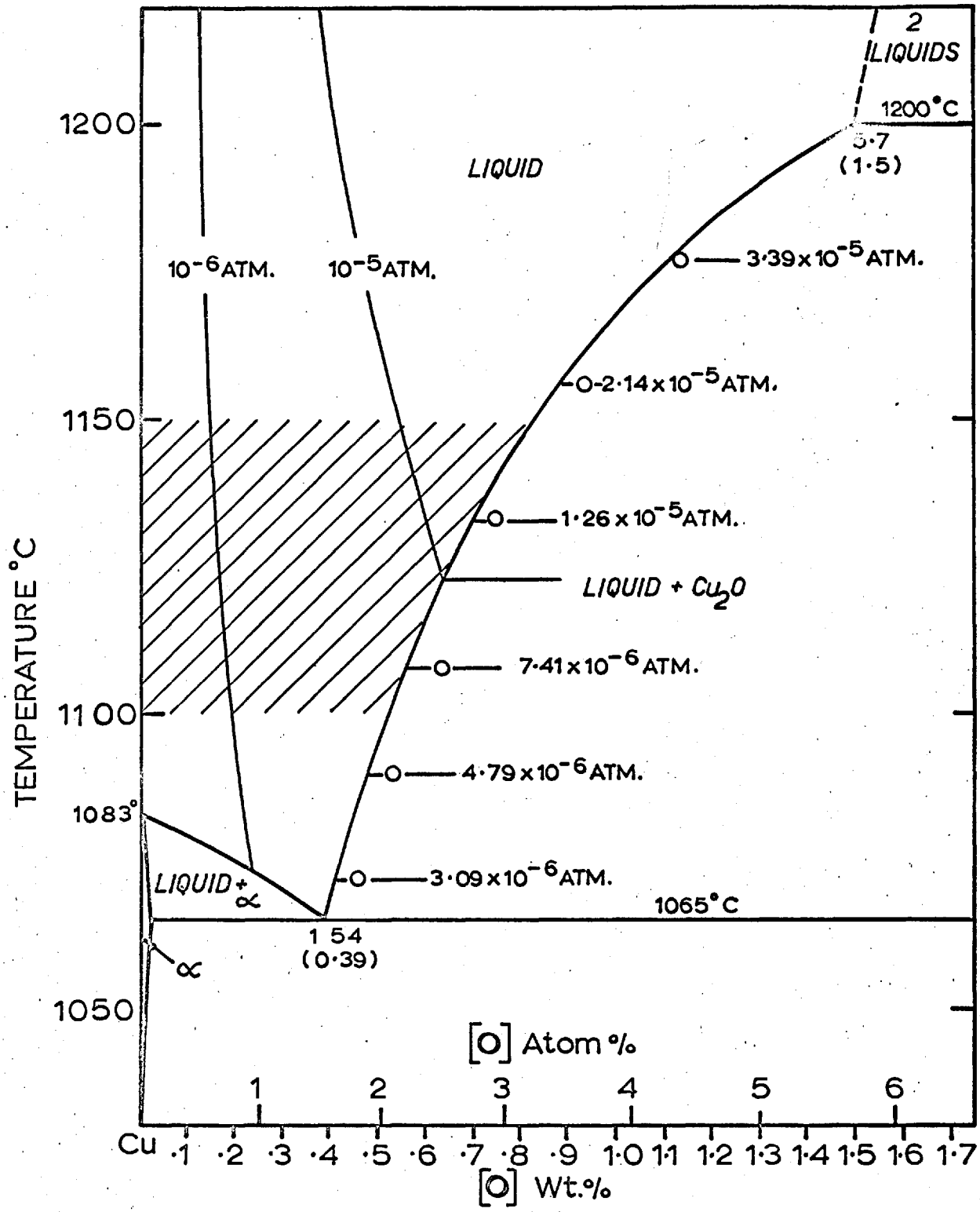


FIG. III.2 OXYGEN PRESSURES IN EQUILIBRIUM WITH THE Cu,[O] MELTS AT DIFFERENT TEMPERATURES CALCULATED FROM YOUNG & TOMLINSONS[58] RESULTS.

o Cu(l), Cu_2O (s) PHASE BOUNDARY AS EXTRAPOLATED FROM THE SAME AUTHOR'S RESULTS

between the eutectic and the monotectic temperatures. The only discrepant results in this respect are those obtained by Osterwald[8] who did a thorough investigation of the Copper-Oxygen phase diagram by an electrochemical method. He reported a monotectic temperature of 1216±5°C and an oxygen content of 9 atom % for the Cu melt in equilibrium with Cu_2O(s) at this temperature. It is not possible to explain such a discrepancy from the experimental details given by the different authors.

The phase boundaries of the two liquids miscibility gap have been estimated by Hansen (dashed lines). There are two sets of experimental values available which are, however, inconsistent with the composition of the monotectic melt as given by Hansen. Slade and Farrow[59] did equilibrium studies at 1254, 1340 and 1400°C using a quenching technique. Their results are indicated by circles in Fig. II.1. Osterwald[8] found, in line with his phase boundary below the monotectic temperature, that the copper melts in equilibrium with the Cu_2O rich phase had a much higher oxygen content than the one suggested by Hansen, even higher than that reported by Slade and Farrow. This part of the phase diagram needs further

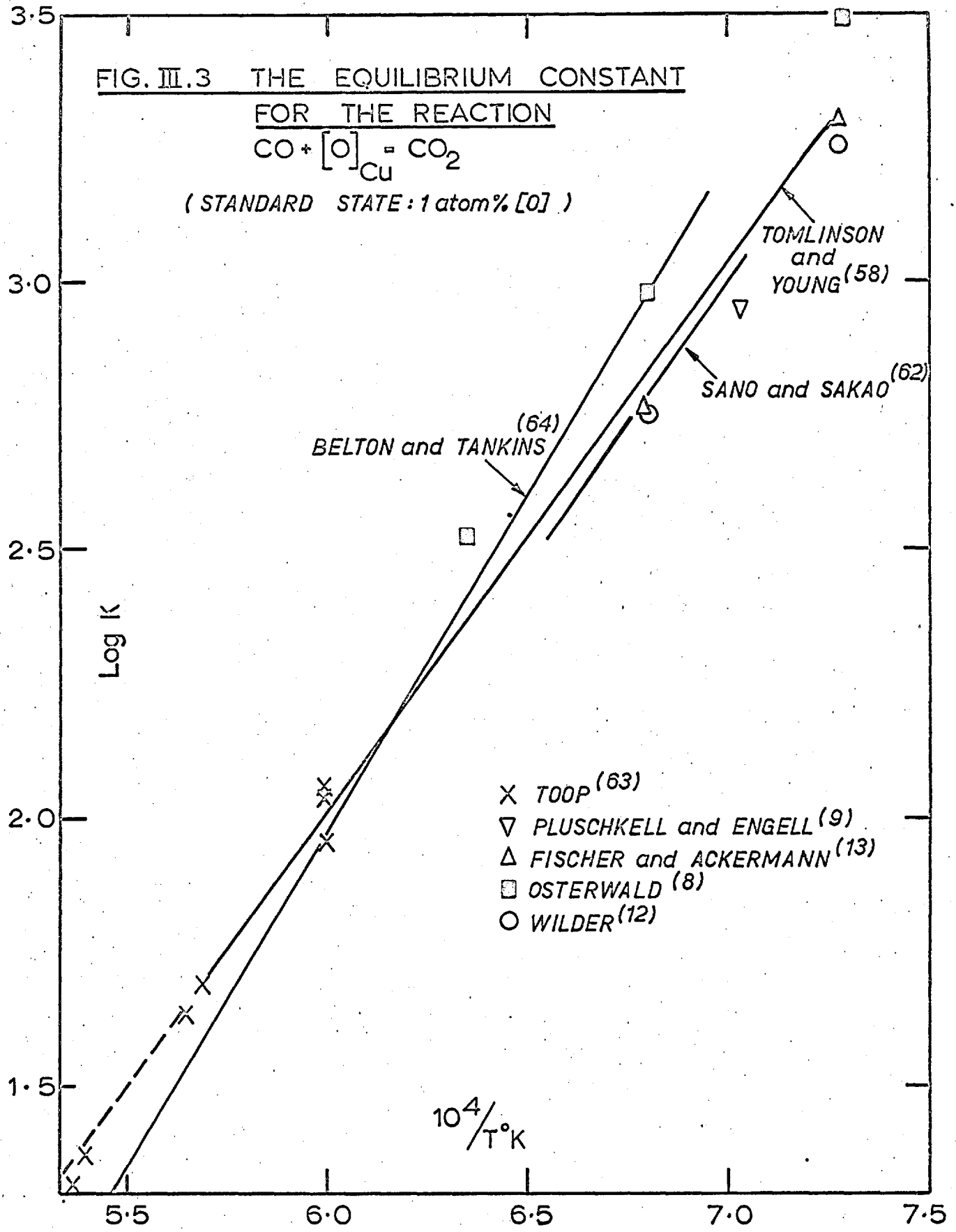
clarification.

The solubility of oxygen in molten copper, in the low oxygen concentration range, has been studied up to 1600°C. Girardi and Siebert[60] (1090°-1300°C), Sano and Sakao[61][62] (1115-1256°C) and Tomlinson and Young[58] (1085-1500°C) have equilibrated liquid copper, contained in Al_2O_3, with CO/CO_2 gas mixtures. Toop[63] (1300-1600°C) levitated small copper beads in streams of CO/CO_2 gas mixtures and Belton and Tankins[64] (1150-1605°C) used H_2/H_2O gas mixtures in their equilibrium experiments. The results of all these authors are in reasonably good agreement, with the exception of those of Girardi and Siebert which are lower, but it seems that their equilibrated copper samples lost a significant amount of oxygen, before being analised, due to the quenching technique used.

The work of Sano and Sakao, Tomlinson and Young, Toop and Belton and Tankins are compared in Fig. III.3. All the lines and points correspond to the reaction,

$$CO + [O] = CO_2 \qquad \text{(III.1)}$$

and the log K values have been calculated with 1 atom % O as standard state. Toop's points actually


FIG. III.3 THE EQUILIBRIUM CONSTANT FOR THE REACTION
CO + [O]Cu = CO2
(STANDARD STATE : 1 atom% [O])
TOMLINSON and YOUNG (58)
SANO and SAKAO (62)
BELTON and TANKINS (64)
TOOP (63)
PLUSCHKELL and ENGELL (9)
FISCHER and ACKERMANN (13)
OSTERWALD (8)
WILDER (12)
Log K
10^4/T°K
3·5
3·0
2·5
2·0
1·5
5·5
6·0
6·5
7·0
7·5

correspond to log P_{CO_2}/P_{CO} x at % O, but his experiments were done with very low oxygen concentrations and therefore they can be considered as true log K values without significant error. These results, which were obtained approaching equilibrium from both the high and low sides, are certainly in better agreement with those of Tomlinson and Young which are probably the most reliable.

These authors[58] studied the reaction III.1 for which:

$$K = \frac{P_{CO_2}}{P_{CO}x \text{ at\%}[O]x \ f'_O} \qquad \text{(III.2)}$$

The activity coefficient of oxygen, f'_O, is based on the reference state of the infinitely dilute solution of oxygen in liquid pure copper and the concentration in atom percent.

From the experimental results between 1100° and 1300°C, it was found that oxygen solubility in copper deviates positively from Sievert's law and log f'_O is independent of temperature and can be represented by the following relationship:

$$\log f'_O = -0.041 \text{ atom \% [O]} \qquad \text{(III.3)}$$

the standard deviation being $\pm$ 0.005 atom % [O] at 1100°C and $\pm$ 0.007 atom % [O] at 1300°C.

The value of K is given by:

$$\log K = \frac{10,150}{T} - 4.07 \pm 0.015 \qquad \text{(III.4)}$$

and hence

$$\Delta G^\circ = -46,440 + 18.6T \pm 150 \text{ cal} \qquad \text{(III.5)}$$

Due to the rather few experiments done at 1400 and 1500°C, these results should be considered as reliable only up to 1300°C.

The oxygen pressures in equilibrium with the Cu,[O], melts at different temperatures, calculated from Young and Tomlinson's results have been indicated in Fig. III.2.

Several investigators[8,9,11,12] have recently made determinations of oxygen solubility in molten copper by the electrochemical technique. All of them have added oxygen to the liquid metal in the form of a copper oxide. The oxygen pressure in equilibrium with the oxygen dissolved in the copper was calculated from the emf's. Their results are also shown in Fig. III.3. They will be discussed more extensively in section III.4.

III.2 EXPERIMENTAL

III.2.1 General Considerations

Fire refining temperatures in copper metallurgy are usually around 1150°C and the metal is

cast between 1105°C and 1120°C. The oxygen content of the molten metal during refining may vary between near saturation down to different limits depending on the product being obtained. Anodes are generally cast with 0.1% oxygen. Tough pitch copper contains 0.025% to 0.08% oxygen, although this may sometimes exceed 0.10%. Oxygen free, high conductivity copper ('OFHC' copper) has a very low oxygen content measured in a few p.p.m. The fire refining temperature and oxygen content ranges of copper are indicated in Fig. III.2 as a shaded area. The control of the oxygen content of copper before casting is of great importance. It was decided, therefore, to concentrate the effort in the investigation of the behaviour of galvanic cells in the dilute solution region of the shaded area indicated in the phase diagram, with a slightly more extended temperature range, 1100° - 1200°C.

The oxygen partial pressures of the gas phase in equilibrium with molten copper at these temperatures (see Fig. III.2) are easily obtained with CO_2/CO gas mixtures which can be prepared in the laboratory in a wide range of proportions. The molten metal equilibrated with a CO_2/CO mixture, bubbled through it, was going to constitute one

electrode of the galvanic cell under investigation. The order of magnitude of the oxygen pressures envolved indicated that $ZrO_2.CaO$ or $ZrO_2.YO_{1.5}$ were the most convenient solid electrolytes. Two more general aspects concerning the experimental technique were unresolved: the choice of an appropriate reference electrode and a convenient material for the contact electrode dipping in the molten copper.

The aim of this part of the present work, as already stated, was the study of cells which could be eventually used as convenient devices for the determination of oxygen in molten copper. One requirement, therefore, which the reference electrode should fulfill was that of simplicity. Gas electrodes (Pt,O_2 or Pt, air) were extremely convenient from this point of view. However, the emf's which develop between the reference and copper, $[O]_{Cu}$ electrodes in this case would be big (several hundreds of milivolts) and there was the risk of polarisation of the copper electrode. The alternative was the use of a metal-metal oxide solid electrode in inert atmosphere with an equilibrium oxygen pressure of the order of magnitude of that existing in the copper elec-

trode. Nickel-nickel oxide satisfied this requirement. Furthermore the free energy of formation of nickel oxide in the temperature range of interest has been fairly well established[15]. The oxygen pressures in equilibrium with nickel-nickel oxide are about 10^{-9} and 10^{-8} atm. at 1100° and 1200°C respectively. These oxygen pressures correspond approximately to oxygen contents in molten copper of about 0.01% and 0.015% at the temperatures previously indicated. Therefore, in the case of dilute oxygen-copper solutions the magnitude of the emf's which should be obtained was small, thus diminishing the danger of polarisation phenomena. Nickel-nickel oxide was the first reference electrode to be tried. Gas electrodes were left as alternatives, depending on the results of the experiments with nickel-nickel oxide as a reference.

The selection of the material for the contact electrode dipping in the molten copper was made by means of compatibility tests which will be described in the next section.

III.2.2 Compatibility Tests. Materials Used.

A series of compatibility tests were done to see if the different materials tentatively chosen would withstand the most stringent

experimental conditions. In all these tests the materials to be studied were equilibrated with copper and cuprous oxide in inert atmospheres at temperatures slightly above 1200°C for various periods of time.

a) Recrystallized Alumina Containers. Alumina crucibles* were held in the previously indicated conditions for 3 to 5 days. No attack on the walls of the crucibles by the melt was observed. This type of container was used in the following compatibility tests and in the experimental work.

b) Zirconia based solid electrolytes. Zirconia 15 mole % CaO** withstood equilibration with Cu-Cu_2O in tests lasting for 48 hours. Zirconia 8 wt% Y_2O_3** (about 9 mole % $YO_{1.5}$) was severely attacked in the same kind of tests. However, the same material resisted the action of unsaturated copper melts with a high oxygen content very well.

c) Copper contact electrode materials. The search for the contact electrode was limited to some ceramics and cermets which looked promising for this purpose. Pure chromium oxide, and a series of chromium and molybdenium cermets were

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* Supplied by Morganite Refractories Ltd.,

** Supplied by Zirconium Corporation of America

tested. The experiments lasted for 2 to 3 days.

Chromium Oxide. The Cr_2O_3 pellets were prepared in the laboratory by pressing Cr_2O_3 powder in a hardened steel die. The pellets were sintered at 1300°C for 5 hours in air. Pellets so obtained were equilibrated with the copper-cuprous oxide melts. The melt crept through the pores of the pellet and was absorbed by it.

50% Cr - 50% Cr_2O_3 Cermet*. The melt crept up the surface of the pellet and covered it completely. There was severe surface reaction.

80% Mo- 20% Al_2O_3 and 60% Mo-40% Al_2O_3 Cermets**. These cermets were completely attacked by the melts. Molybdenum oxide deposited on the cold walls of the furnace.

75% Cr - 25% Al_2O_3 and 72% Cr - 28% Al_2O_3 + SiO_2.** These two materials resisted the action of the melts very well. A very slight coat of chromium oxide was formed on their surfaces which was easily removed afterwards.

On the basis of these results and information on the available commercial forms of the cermets,

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* Supplied by Associated Chemicals Ltd. (Research Department, Harrogate).

** Supplied by Morganite Refractories Ltd. The Commercial names of these cermets are Metamics 519 (80% Mo), 562(60% Mo), 528(75%Cr) and 612 (72% Cr)

the 72% chromium cermet was chosen as the most convenient contact electrode.

The materials used in the present work were the following:

Copper. Spectroscopic pure copper, containing less than 0.001% total impurities. The most important impurities were Ag 3 ppm. and Fe 2 ppm

Solid electrolytes. The lime-zirconia and yttria-zirconia tubes were made commercially* and contained 15 mole per cent lime and 4.5 mole per cent yttria respectively. The wall thickness was 1.0 mm and they were guaranteed as suitable for high vacuum work.

Nickel-nickel oxide pellets. 'Analar' nickel and nickel oxide powders in equimolecular proportions were mixed and pressed at 10 tons / sq. in. The pellets were sintered in purified argon at 900°C for 6 hours.

Chromium cermet. The 72% Cr cermet was obtained as rods of about 4 mm diameter. The electrical resistance of this material, reported by the manufacturer, was around 100 micro ohm cm at room temperature and 250 micro ohm cm at 1200°C.

* Supplied by Zirconium Corporation of America.

Gases. 'Analytical grade' CO_2 was used. The main impurities were H_2O 30 p.p.m., N_2 15 p.p.m. and O_2 5 p.p.m. The CO was guaranteed to be not less than 99% and the maximum impurity contents were 0.2% CO_2, 0.15% O_2 and 0.6% N_2. 'High Purity' Argon was used to flush the reference electrode and the reaction tube when necessary.

III 2.3 Apparatus and Analytical Techniques

a) Gas Train. The gas train is shown diagramatically in Fig. III.4. This consisted of equipment for purifying and metering the gases before use in either electrode of the cell.

The carbon monoxide was passed through a column containing sofmolite (sodium hydroxide plus an indicator supported on an inert base) to remove carbon dioxide and drying towers containing magnesium perchlorate. The argon used to flush the reaction tube and carbon dioxide were dried with silica gel and magnesium perchlorate and the oxygen in argon removed by passing the gas over titanium chips held in a Kanthal furnace at 900°C. Another Kanthal furnace containing copper gauze at 450°C was used to remove the oxygen in carbon dioxide. The reference electrode argon was dried by silica gel and magnesium perchlorate and its oxygen was

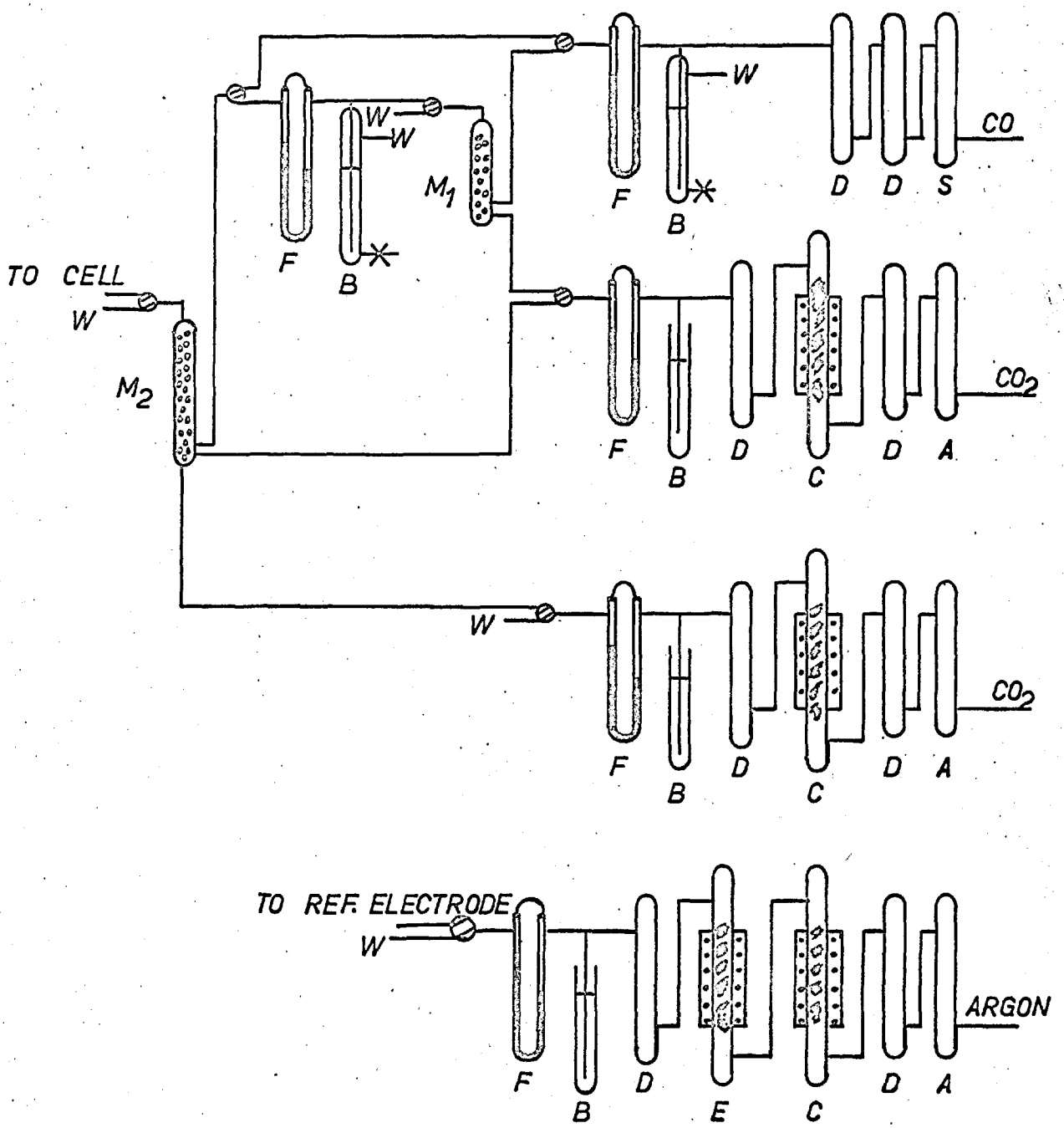


FIG.III.4 GAS TRAIN

Fig. III.4 - Gas Train

A Silica gel tower.

B Dybutyl phtalate blow-off

C Copper gauze furnace

D Magnesium perchlorate tower

E Titanium chips furnace

F Flowmeter

M Mixer

S Sofnolite

W To waste

removed in two stages: first, copper gauze at 450°C and then titanium chips at 900°C.

The gases from the purification trains were maintained at constant pressure by means of the blow-offs B, metered by conventional pattern capillary flowmeters F and mixed in the mixing chambers M. The manometers of the flowmeters and the blow-offs were filled with dybutyl phtalate. Carbon monoxide blow-offs were closed and the waste gas was ejected to the outside atmosphere. Eventually it was necessary to add some mercury to the blow-offs.

The flowmeters were carefully calibrated before each run. Calibration curves were thus obtained at different room temperatures. This was of importance because the temperature had some influence in the gas flowrate at a fixed deflection in the manometer of the flowmeter due to changes in the properties of the dybutyl phtalate.

The maximum gas ratio which it is possible to obtain with accuracy with a system of two flowmeters is 100/1. Double dilution was employed to get higher ratios. If this was the case, the CO_2/CO mixture from mixer M_1 was metered by means of a third flowmeter and diluted with more CO_2, coming

from an independent CO_2 line in mixer M_2. Otherwise, CO_2 and CO were just mixed in mixer M_2. The gas mixture from M_2 was taken directly to the cell through an all glass line.

Both the Argon used for the reference electrode and that one used to flush the reaction tube were also taken to the cell through all glass lines.

b) The Cell. The cell (Fig. III.5) consisted of an alumina crucible, 25 mm i.d. and 40 mm. deep, containing the molten copper. The Cr cermet contact electrode, about 20 mm long, was half inserted at the end of an alumina tube. Electrical contact to the outside was established by a pure Pt lead. There was a very close fit between the cermet and the tube to avoid any copper vapour attacking the Pt. wire. The solid electrolyte was either a calcia zirconia or yttria zirconia tube, $\frac{1}{4}$" diameter. The nickel-nickel oxide reference electrode pellet weighed 0.5 to 0.7 g and its approximate dimensions were 7 to 10 mm long and about 3.5 mm diameter. The reference electrode was machined from a $\frac{1}{4}$" diameter pellet, prepared as described previously, to fit the solid electrolyte tube. A pure Pt lead ending in a Pt disc sitting on the

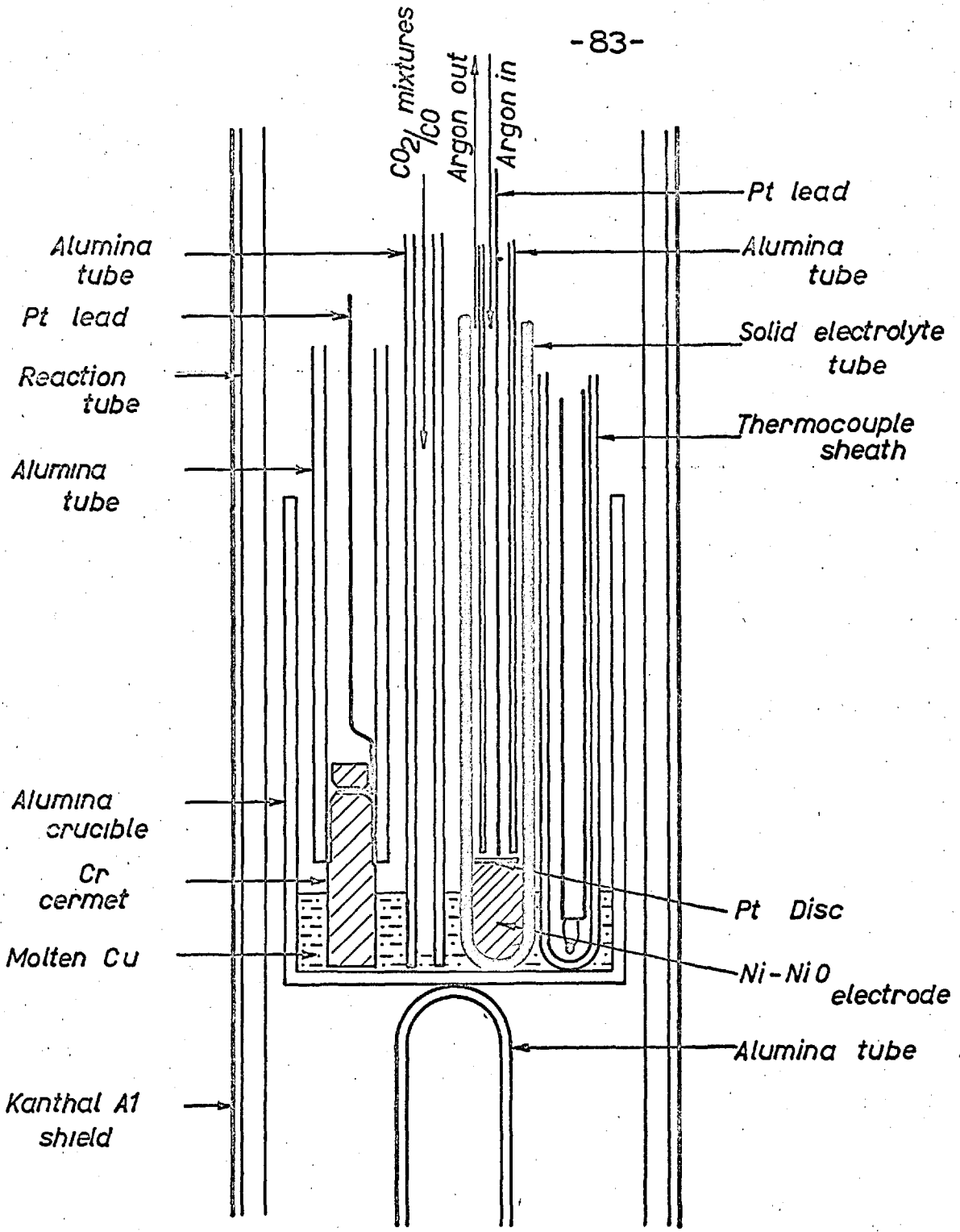


FIG.III.5 CELL USED FOR MEASURING EMF's IN MOLTEN COPPER (scale2:1)

nickel-nickel oxide pellet established electrical contact to the outside. The Pt disc was spring loaded against the pellet through a 3 mm o.d. alumina tube. The same alumina tube carried the argon used to flush the reference electrode. The argon escaped to the atmosphere between the alumina and solid electrolyte tubes. Small slits were cut at the end of the fine alumina tube pressing the pellet to facilitate the flow of argon. When a Pt, O_2 reference electrode was used the Pt lead ended in a small Pt wire ball which was pressed against the bottom of the solid electrolyte tube as described. The alumina tube carrying the CO_2/CO mixtures, which were bubbled through the molten metal, was 5 mm o.d. and 2.5 mm i.d. The Pt, 13% Rh-Pt thermocouple was protected by an alumina sheath, 6 mm diameter.

The alumina reaction tube was 35.5 mm o.d., 28.5 mm. i.d. and 825 mm long. The crucible was supported in the centre of the reaction tube by means of an alumina tube coming from beneath. The lower end of the reaction tube was closed with a water cooled brass cap through which the alumina tube supporting the crucible passed. An entrance for the argon used to flush the reaction tube was

provided in this cap.

Fig. III 6 shows the water cooled brass head which closed the top of the reaction tube, held the different tubes going into the cell and permitted gas and electrical connections. All the tubes were held by means of 'O' rings with the exception of that one carrying the CO_2/CO mixtures which was secured to the brass head with araldite (Section E-F, Fig. III.6). Section C-D in this figure shows the details of assembly of the spring loaded alumina tube which pressed the Pt disc against the nickel-nickel-oxide pellet. The alumina tube was secured with araldite to the brass argon inlet, which was inserted in a bellow sitting on the top of the argon outlet. The springs (not shown in the figure) went from hooks on the argon inlet to hooks on the argon outlet.

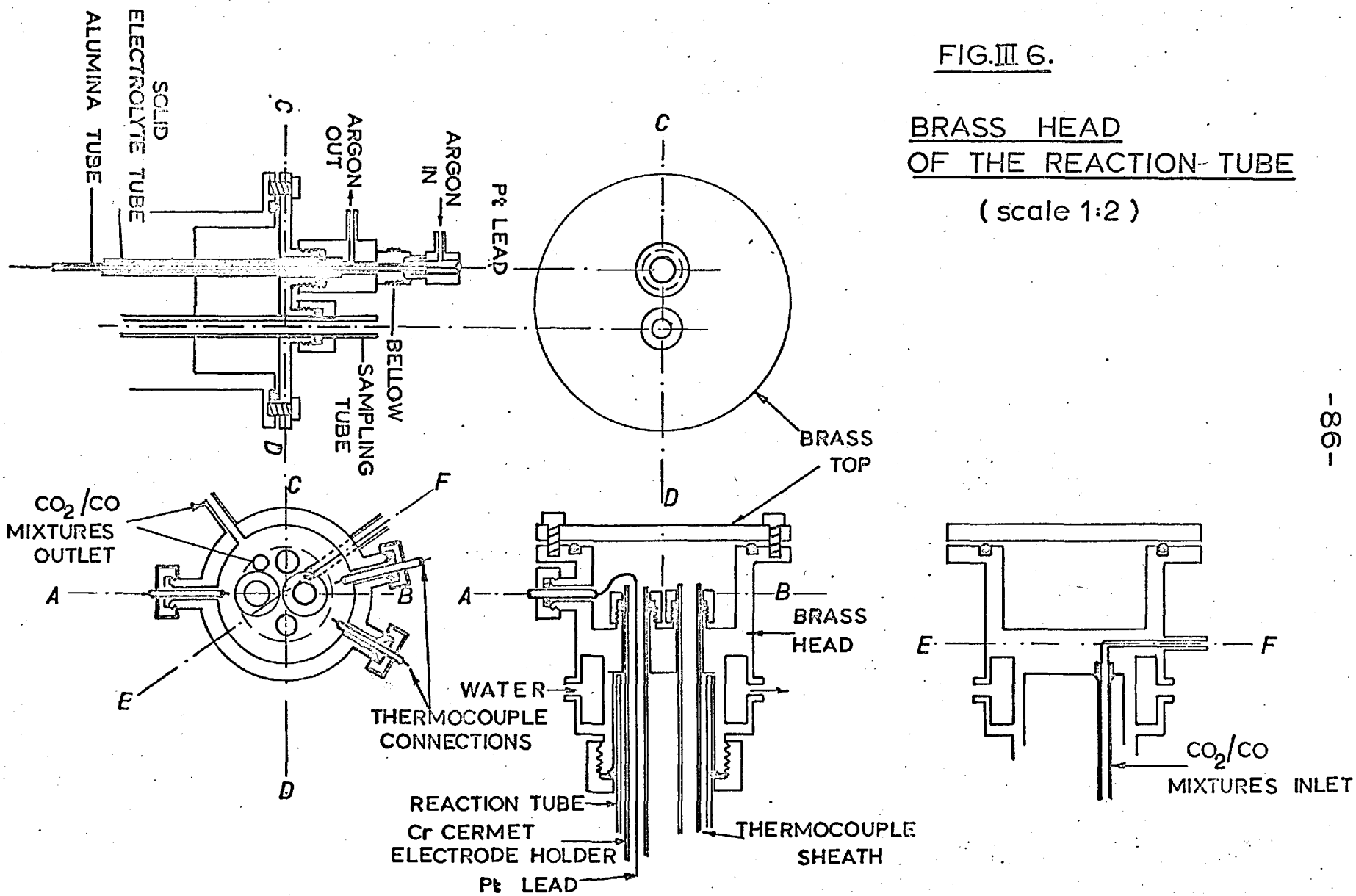
The reaction tube was suspended in a vertical Platinum wound furnace, the temperature of which was controlled to better than $\pm$ 2°C. The controller system used was similar to the one employed in the case of the silver measurements (section II.2,b). The Pt 13% Rh-Pt controller thermocouple was placed beside the furnace winding.

Electrical shielding was effected by means of

FIG. III 6.

BRASS HEAD
OF THE REACTION TUBE

(scale 1:2)



Kanthal Al ribbon wound around the reaction tube from end to end. The brass head of the cell and the exterior casing of the furnace were also electrically grounded. Nitrogen was passed between the furnace and reaction tubes to protect the Kanthal Al winding.

Connections to the electrometer were similar to those used in the silver experiments. The same electrometer used for the silver measurements was employed in this case.

Gas cells of the type:

Pt,Ni-NiO/solid electrolyte/CO_2-CO, Pt

were used in this work. In this case the reaction tube was replaced by a one end closed alumina tube of the same diameter. Fig. III 7 gives the details of the electrodes arrangement in these cells. There is no change with respect to the nickel-nickel oxide reference electrode. The tip of the solid electrolyte tube was wrapped with a piece of Pt foil connected to the outside with pure Pt wire to form the CO_2/CO, Pt electrode. The same brass head used with the molten copper cell was employed in the gas cells.

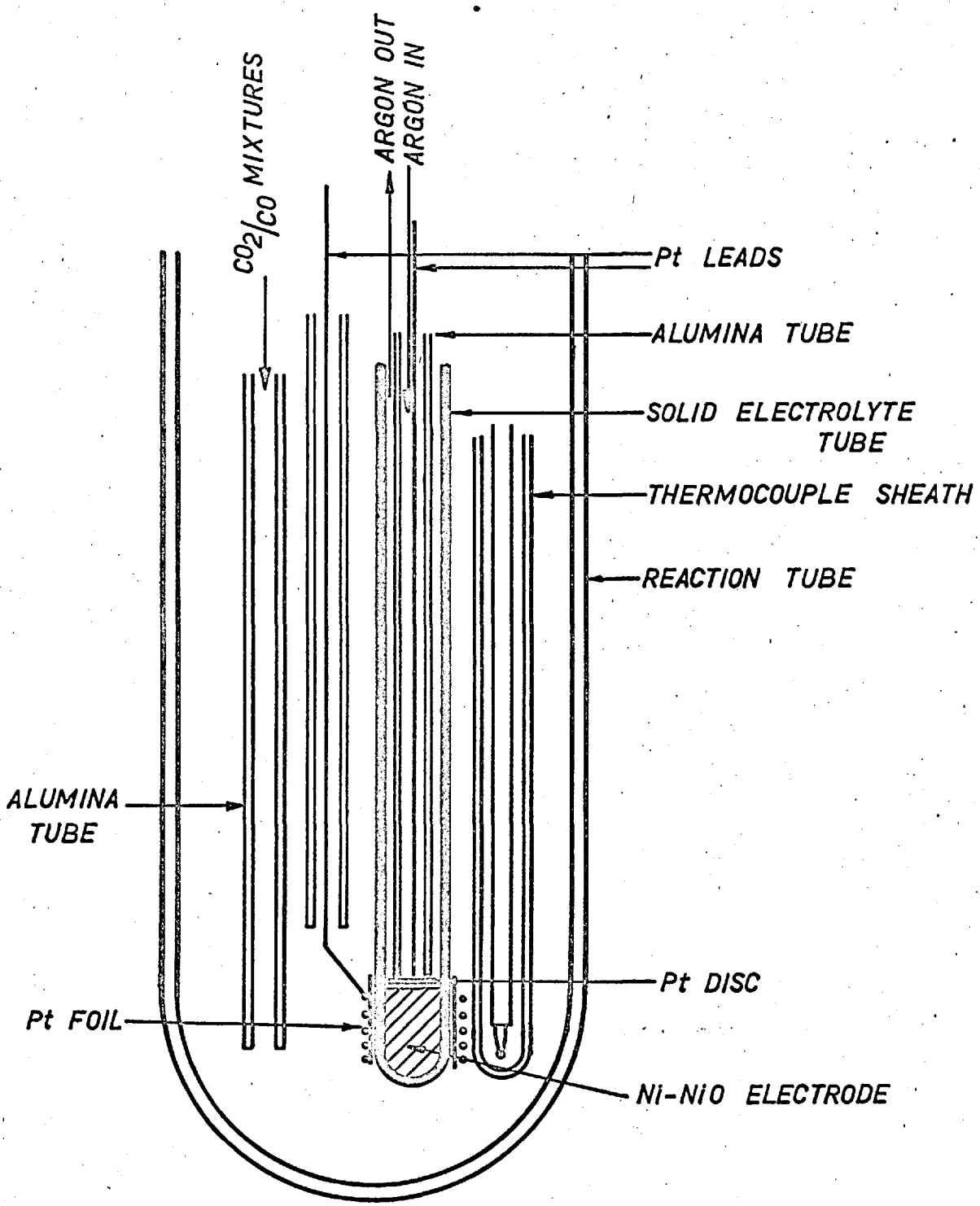


FIG. III.7 Pt, CO_2 - CO / SOLID ELECTROLYTE / Ni-NiO, Pt CELL

C) Gas Analysis

Analysis of the gas mixtures were done when the observed emf's were in discrepancey with respect to the calculated emf's.

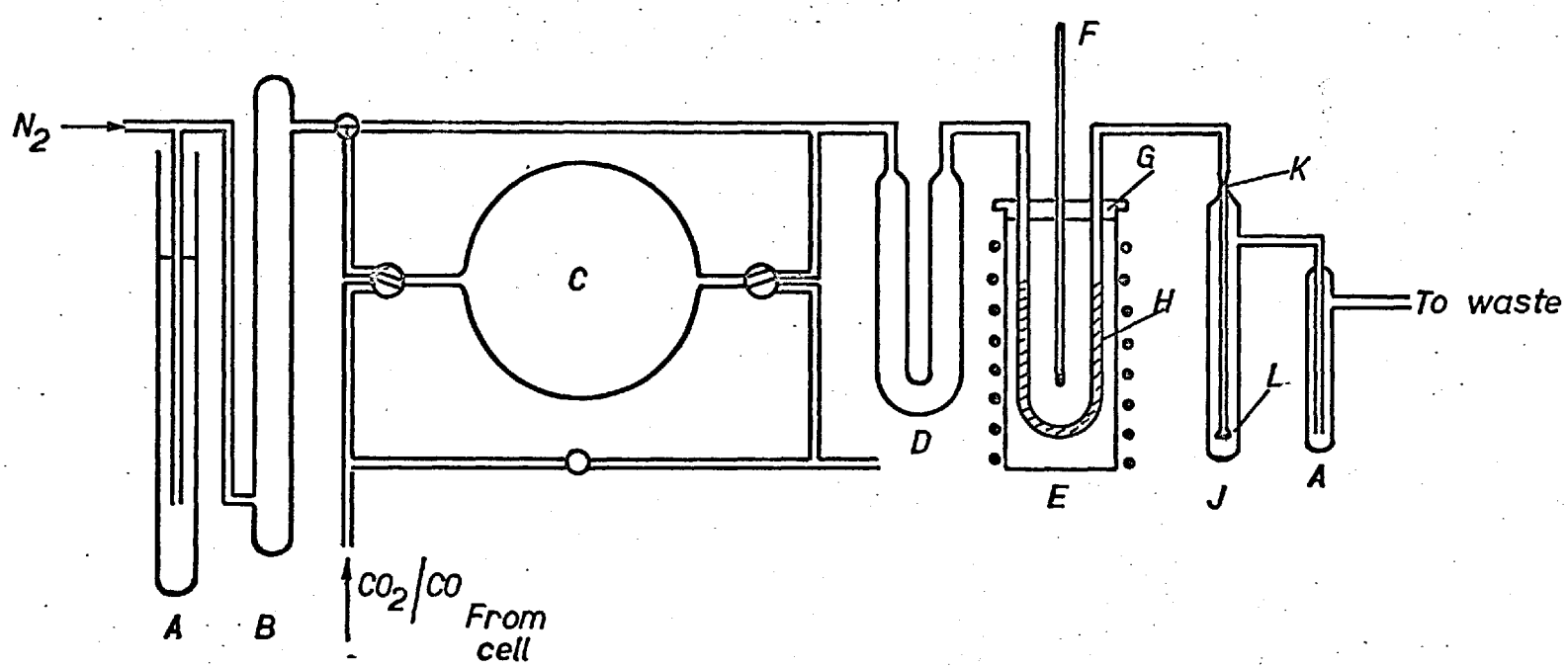
The Iodine Pentoxide method was used to analyse the carbon monoxide content of the CO_2/CO mixtures coming from the cell after equilibration with molten copper. This method has been described[65] as the most accurate for the determination of CO concentrations up to 0.3%.

The Iodine Pentoxide method is based on the reaction of carbon monoxide with granular iodine pentoxide, which is heated at a temperature high enough so that the reaction:

$$5\ CO + I_2O_5 = 5\ CO_2 + I_2 \qquad \text{(III.6)}$$

is rapid and quantitative. The liberated iodine is collected in potassium iodide solution, and determined by a suitable method.

The apparatus is shown diagramatically in Fig.III.8. The furnace E was a $3\frac{1}{2}$" i.d. x 9" long copper cylinder wound with electrically insulated heating wire. The high thermal conductivity of the copper cylinder ensured an even temperature distribution throughout the furnace and at the working temperature of 150°C the maximum deviation in the mean furnace temperature was $\pm$ 3°C. The power to the



○	STRAIGHT BORE TAP
⊜	DOUBLE OBLIQUE BORE TAP
⊖	T-BORE TAP
A	DI-BUTYL PHTHALATE BLOW-OFF
B	MAGNESIUM PERCHLORATE
C	SAMPLING BULB
D	PHOSPHORUS PENTOXIDE
E	IODINE PENTOXIDE FURNACE
F	0-300°C THERMOMETER
G	SINDANYO LID
H	IODINE PENTOXIDE 'U' TUBE
J	POTASSIUM IODIDE SOLUTION
K	B10 GROUND JOINT CONNECTION
L	SINTERED GLASS DISC

FIG. III.8 CO DETERMINATION BY THE IODINE PENTOXIDE METHOD

furnace was controlled by a Variac.

The 'U' tube was made of 4 mm. i.d. pyrex glass following the advice given by the National Coal Board[66]. The tube was filled with iodic acid* to a height of 100 mm in each limb. The absorption bulb J was joined to the 'U' tube by a B10 ground joint. This joint was well ground to form a good seal and left ungreased to prevent the loss of iodine from reaction with grease.

The sample was collected in the sampling bulb C, which had a volume of 511.3 cc in normal conditions. Nitrogen was used as carrier gas for the sample. The nitrogen was dried with magnesium perchlorate and passed through the sampling bulb C for one hour at a flow rate of 75 cc/min. The liberated iodine from the reaction of the carbon monoxide in the gas sample with the iodine pentoxide was absorbed in 5% potassium iodide solution and determined by an amperometric titration technique[67] which was found more accurate then the usual starch end point method, especially when the carbon monoxide concentrations in the gas were below 0.1%.

*Supplied by the National Coal Board.

The main factor controlling the reliability of this analytical method is the quality of the iodine pentoxide used. Big discrepancies between the calculated composition of the gas mixtures and the results of the analysis were observed when a commercial granular iodine pentoxide was used in the first experiments. This is a well known fact. It has been reported[68] that reactivity of commercial iodine pentoxide may be as low as 60-70% and completely unreactive species have been known. Granular iodine pentoxide was obtained from the National Coal Board, where a preparation technique for this reagent has been developed. This sample had already been tested and found satisfactory for carbon monoxide determination in the Scientific Department of the National Coal Board. Tested against known volumes of pure carbon monoxide it proved to be 100% reactive within experimental error. This iodine pentoxide was used in the present work whenever analysis of the gas mixtures were necessary. The chemical analysis showed that the discrepancy between the gas composition and that one predicted from the deflection in the flowmeters was never higher than 2% in the case of CO_2/CO ratios lower than 100/1 and 10% in the case of gas

ratios higher than 100/1 which were obtained by double dilution of CO in CO_2 (see Section III.2.3,a) These fluctuations in the gas composition as obtained from the flowmeters represented an uncertainty in the calculated emf of $\pm$ 1 mv and $\pm$ 5 mv respectively.

An Infra Red Gas Analyser* was used to follow the progress of the gas-liquid metal reaction during the early stages of this work, as a technique independent of the behavior of the cell. However, the need for periodic adjustment of the analyser zero and calibration offset the advantages of the instrument and its use was discontinued. The progress of the experiments was followed by the emf's.

D) Oxygen Determination in Copper

A few samples of copper were withdrawn during experiments with the cell with the purpose of checking existing data on the oxygen solubility in molten copper. The determination of oxygen in copper was made by the hydrogen reduction method using an already existing apparatus for this purpose.

As some of the quartz of the sampling tubes adhered very strongly to the copper samples,

*Infra Red Gas Analyser type SC/LC manufactured by Hilger I.R.D. Ltd.

these were immersed in hydrofluoric acid for over night prior to analysis.

II.2.4 Experimental Procedure

About 40 g of copper were charged in the crucible in each run. The metal was cut from 5 mm diameter 'specpure' copper rods with shears exclusively used for this purpose. The copper was etched with nitric acid and washed with water and alcohol.

The reference and contact electrodes, thermocouple sheath and CO_2/CO mixture carrying tube were inserted in the crucible, which was kept at the top of the reaction tube, before charging the copper. Once the copper had been introduced the whole assembly was lowered down the reaction tube until the brass head was sitting on the top of it. The brass head was secured to the reaction tube by means of an 'O' ring (see Fig.III.6) and all the various gas and electrical connections were made.

The cell was tested for gastightness by passing through it a known gas flow-rate which was checked with the soap bubble technique. The reference electrode and the reaction tube were flushed with purified argon for sometime before heating up the cell. The thermocouple was checked

against the melting point of copper in each run.

Once the experimental temperature had been reached the electrometer was connected to the system and the run started. In most of the experiments oxygen was gradually added to the molten copper by increasing the CO_2/CO ratios in stages. The gas mixture flow-rate was generally kept at about 300 cc/min. The times necessary to reach equilibrium when the CO_2/CO ratio was increased depended on the relative values of the initial and final oxygen equilibrium contents of the molten metal. These times varied from about 20 - 30 minutes to several hours. Due to the complex geometry of the system the gas sometimes found its way out of the crucible without bubbling through the metal. When this was the case the time for equilibrium was longer. The irregularity of the gas flow through the cell altered considerably the CO_2/CO ratio. This proved to be one of the major problems during the various runs. In spite of this difficulty, some of the runs came off very well permitting estimates on the kinetics of oxygen transfer from the gas to the liquid phase (see Section III.3.2,b)

Samples of copper were taken in an argon atmosphere. This was found necessary

because otherwise the CO_2/CO ratio was altered during sampling changing the equilibrium conditions. Furthermore, the inert atmosphere provided a proof that the cell wasactually reacting towards the oxygen content of the metal and not the CO_2/CO gas mixture, because the cell voltage remained constant after replacing the CO_2/CO by argon. The 2 mm. i.d. diameter quartz sampling tube was introduced in the cell through the sampling hole in the top of the brass head (see Fig.III.6) before starting an experiment. Samples of about 2g were drawn by a syringe. The tube was immediately removed and quenched in distilled water, to prevent oxidation. The samples solidified instantaneously so that there was no loss of oxygen.

III.3 RESULTS

III.3.1 Cells with Ni-NiO as reference electrode

a) Calculated emf's

The observed emf's were compared with theoretical emf's which were calculated using available thermodynamic data for the two following reactions:

$$2Ni\ (s) + O_2\ (g) = 2NiO\ (s) \qquad \text{(III.7)}$$

$$\Delta G^\circ_T = -111{,}930 + 40.58T\ (\pm 260\ \text{cal})\ (900°\text{-}1400°k)^{(15)} \qquad \text{(III.8.)}$$

$$2CO(g) + O_2(g) = 2CO_2(g) \qquad \text{(III.9.)}$$

$$\Delta G^\circ_T = -\ 134{,}180 + 41.00T\ (\pm 100\ \text{cal})\ (1300°\text{-}1500°K)^{(68)} \qquad \text{(III.10.)}$$

As the liquid copper was in equilibrium with the CO_2/CO gas mixture, the emf of the cell was given by the relationship:

$$\text{emf} = \frac{4.576T}{4F}\ [\log P_{O_2}(CO_2+CO) - \log P_{O_2}(Ni+NiO)] \qquad \text{(III.11.)}$$

Table III.1 gives calculated emf's for this cell as a function of the composition of the CO_2/CO gas mixture. At the same time the logarithms of the oxygen partial pressure in equilibrium with these mixtures have been included. It may be observed (see Fig.III.2) that the gas mixtures of Table III.1 cover the whole range of oxygen pressures in equilibrium with copper up to the Cu(l) - Cu_2O(s) phase boundary.

TABLE III.1

Calculated emf's for the Cell:

Pt, Ni-NiO/solid electrolyte/(CO_2+CO), Cu(l), cermet, Pt.

	log P_{O_2}-		emf (mv) ± 4 mv	
CO_2/CO	1100°C	1200°C	1100°C	1200°C
20/1	-9.794	-8.344	-58	-44
50/1	-8.998	-7.548	-4	14
100/1	-8.396	-6.946	38	58
250/1	-7.600	-6.150	92	116
500/1	-6.998	-5.548	133	160
1000/1	-6.396	-4.946	174	204
5000/1	-4.998	-3.548	269	306

b) Experiments at 1100°C

Results for two different cells, one with $ZrO_2.Y_2O_3$ and the other one with ZrO_2.CaO solid electrolytes, are shown in Table III.2 and Fig.III.9 The observed emf's correspond to the maximum values obtained for a particular experiment but they were not steady equilibrium readings in the electrometer. If enough time was allowed, the tendency was for the emf's to decrease after reaching the maximum values. This decrease was very slow and even difficult to observe at all when the emf's were low, but faster when the difference in oxygen potentials between

the two electrodes of the cell was big. As an example, the ZrO_2.CaO cell, after reaching a maximum emf of 160 mv in experiment N°9 (Table III.2) was left with the CO_2/CO gas mixture at the constant ratio of 1115/1 for 12 hours. At the end of this period the emf had decreased to 145 mv. It also became evident that the discrepancy observed between the experimental and calculated values was not only a function of the magnitude of the emf but depended at the same time of the previous history of the cell. As experiment N°8 (Table II.2) shows, when equilibrium was approached by reduction of the oxygen content of the molten copper a greater discrepancy between the experimental and calculated emf's occurred than previously experienced for similar oxygen levels in the metal.

In considering the results obtained in the first series of experiments (1-3) using a $ZrO_2.Y_2O_3$ cell various reasons to explain the discrepancy between the experimental and calculated emf's were examined. Errors in the measurement of the cell temperature, in the CO_2/CO gas ratio or oxygen in the argon flushing the reference electrode. All these possible sources of error were carefully examined and discarded as explanations for the phenomenon observed. After experiments with the

TABLE III.2

Observed emf's at 1100°C for the Cell:

Pt, Ni-NiO/solid electrolyte/(CO_2+CO), Cu(l), cermet, Pt.

Cell	Exp.No	CO_2/CO ratio	[O]wt.% in copper*	emf obs. (mv) ± 1%	emf calc. (mv) ±4mv
$ZrO_2.Y_2O_3$	1	74/1	0.009	18.0	20.0
	2	265/1	0.032	89.0	95.0
	3	972/1	0.116	148.0	172.0
ZrO_2.CaO	4	49/1	0.006	-3.5	-4.5
	5	107/1	0.013	39.0	41.5
	6	204/1	0.025	77.5	80.0
	7	302/1	0.036	99.0	103.0
	8	86/1	0.010	25.5	29.0**
	9	1115/1	0.134	160.0	180.0

*Calculated from Young and Tomlinson's(58) expression for dilute solutions of [O] in copper

$$\log \frac{P_{CO_2}}{P_{CO}\,[O]\ \text{wt.\%}} = \frac{10430}{T} - 3.677$$

**Equilibrium approached by reduction of the oxygen content in copper.

Note: the initial emf in both cells was about 50 mv indicating an oxygen content in the copper of 0.015wt.%. The experiments were performed in the order indicated. Times for equilibrium in experiments 1, 2, 4, 5, 6, 7, 8, varied from 15 to 45 minutes and were of the order of several hours in 3 and 9. Cell generally left 1 hour at equilibrium.

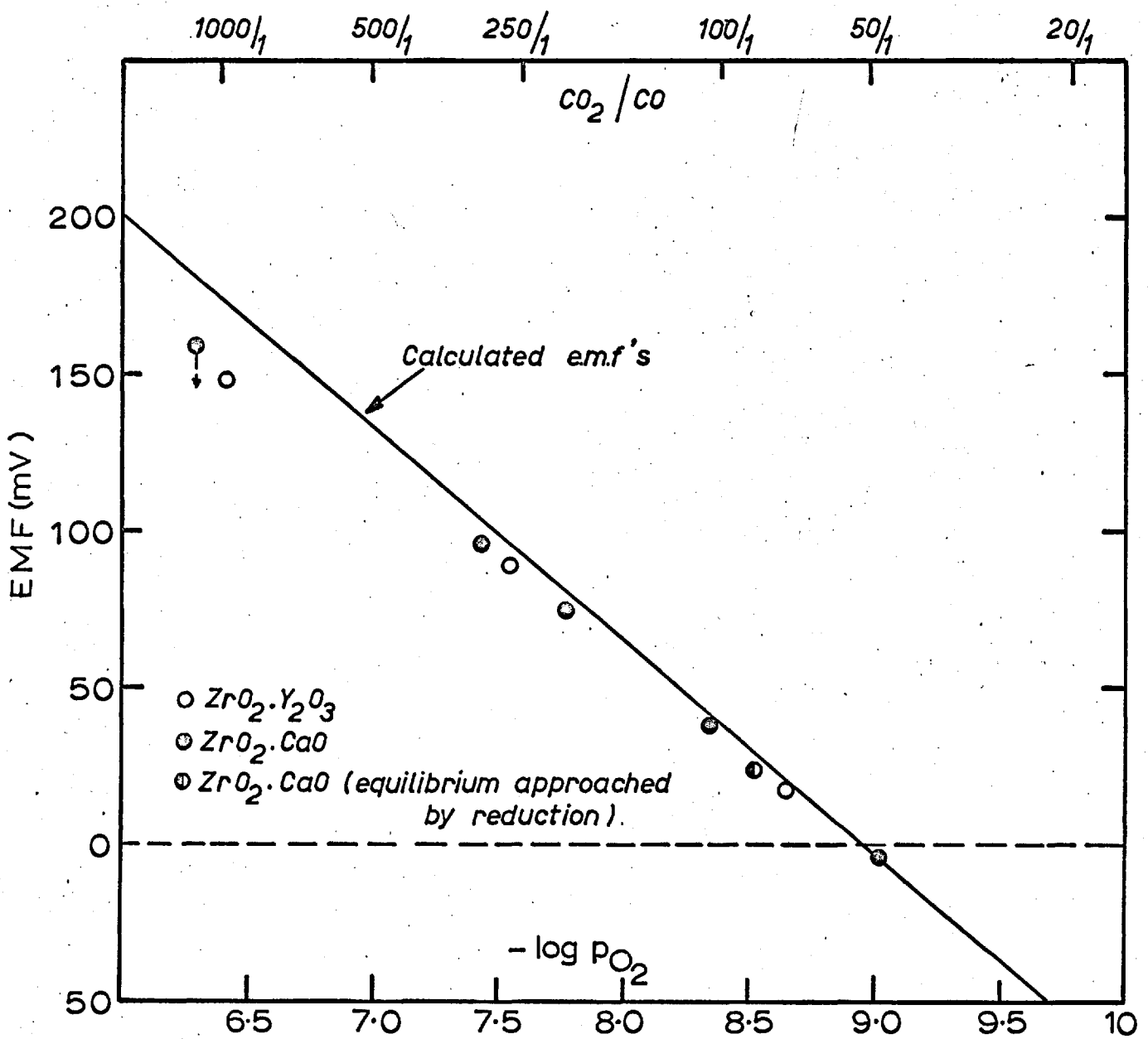


FIG.III.9 RESULTS AT 1100°C FOR THE CELL :

Pt, Ni-NiO / SOLID ELECTROLYTE / (CO_2 + CO), Cu(l), CERMET, Pt

second cell (ZrO_2.CaO), it appeared that polarisation of the cell was the cause of the low emf's being obtained. Oxygen was being transferred from the high oxygen partial pressure electrode [Cu, (CO_2+CO)] to the low oxygen partial pressure electrode [Ni-NiO]. The rate of oxygen transfer would be faster than the oxidation kinetics of the Ni-NiO pellet and thus the equilibrium oxygen pressure could not be maintained. After dismantling the ZrO_2.CaO cell, the Ni-NiO reference electrode was examined and a layer of green NiO was observed covering the pellet.

C) Coulometric Titrations at 1100°C

A series of coulometric titrations using the cell were done to examine the polarisation hypothesis. The technique was to pass a definite quantity of current through the cell to transfer oxygen from the Ni-NiO to the Cu (CO_2 + CO) electrode and subsequently observe the emf as a function of time.

The electrical circuit is shown in Fig.III.10. The current passing through the cell was controlled by the 1M Ω potentiometer and could be varied between a few μA and several hundreds μA. The voltage across the 44 Ω fixed resistance was measured to calculate this current.

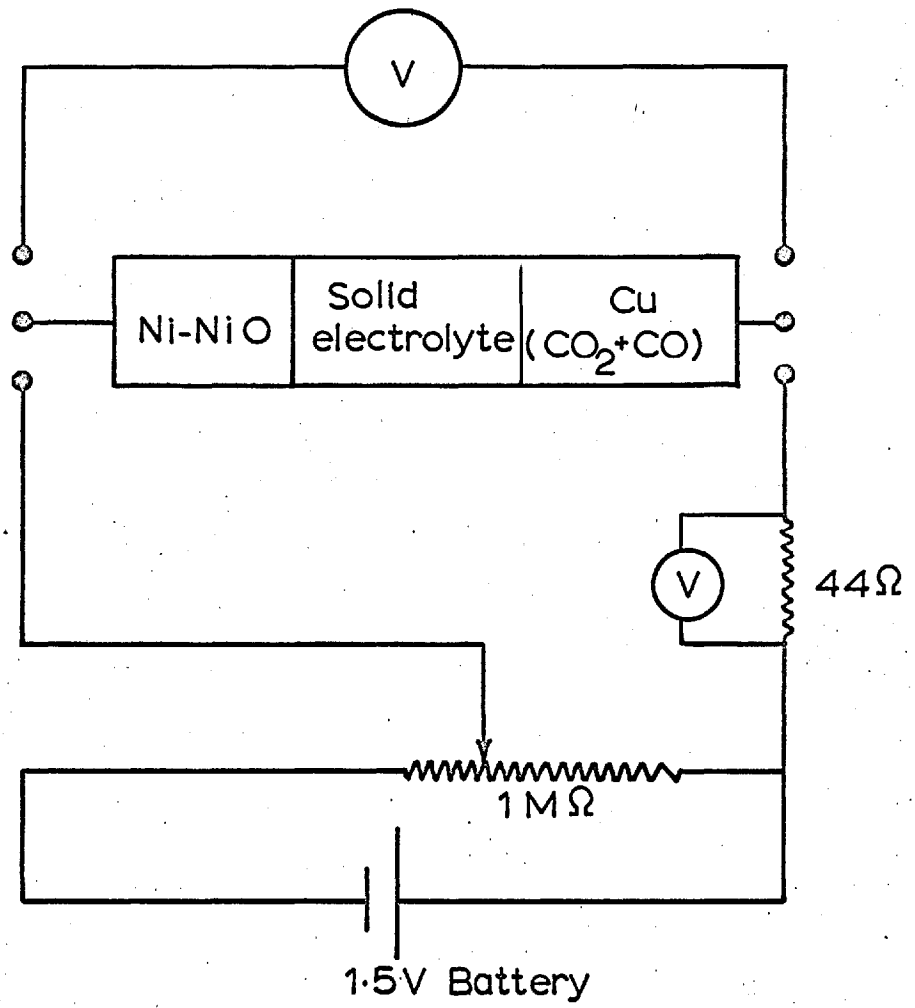


FIG. III.10 ELECTRICAL CIRCUIT FOR COULOMETRIC TITRATIONS

All the coulometric titrations were performed at the same temperature (1100°C) and with a fixed CO_2/CO (1105/1) ratio at the liquid copper electrode. As far as possible all the titrations were commenced when the cell exhibited a similar degree of polarisation (i.e. emf.calc.-emf.obs. = constant) althoigh it was not always possible to fulfill this condition. If the cell was left overnight the emf could decrease to much lower levels. Small fluctuations of the gas ratio were experienced, but they did not alter significantly the calculated value for the equilibrium emf. Table III.3 gives details of the different coulometric titration experiments done. The solid electrolyte in this particular cell was $ZrO_2.CaO$.

Figs.III.11 and III.12 represent the emf of the cell as a function of time after titration. Tables III.4, III.5 and III.6 give the values obtained in three representative decay experiments. The emf's curves as a function of time show that a steady emf was obtained in each case as soon as the applied voltage was removed. This steady emf was only slightly different from the calculated equilibrium vale. The steady emf was maintained for a time which was dependant upon the quantity of current passed

TABLE III.3

Coulometric Titration Experiments of the Ni-NiO/solid elect./Cu, (CO_2 + CO) cell at 1100°C CO_2/CO = 1105/1
Calculated eq. emf (mv) = 180

emf (mv) before titration	Titration current ($\mu A/cm^2$)**	Time of titration (min)
145	29	2
145	29	5
145	29	10
147	29	20
148	364	2
126*	240	2

*After cell was left overnight.

**These figures correspond to current densities calculated on the basis of the Ni-NiO pellet dimensions.

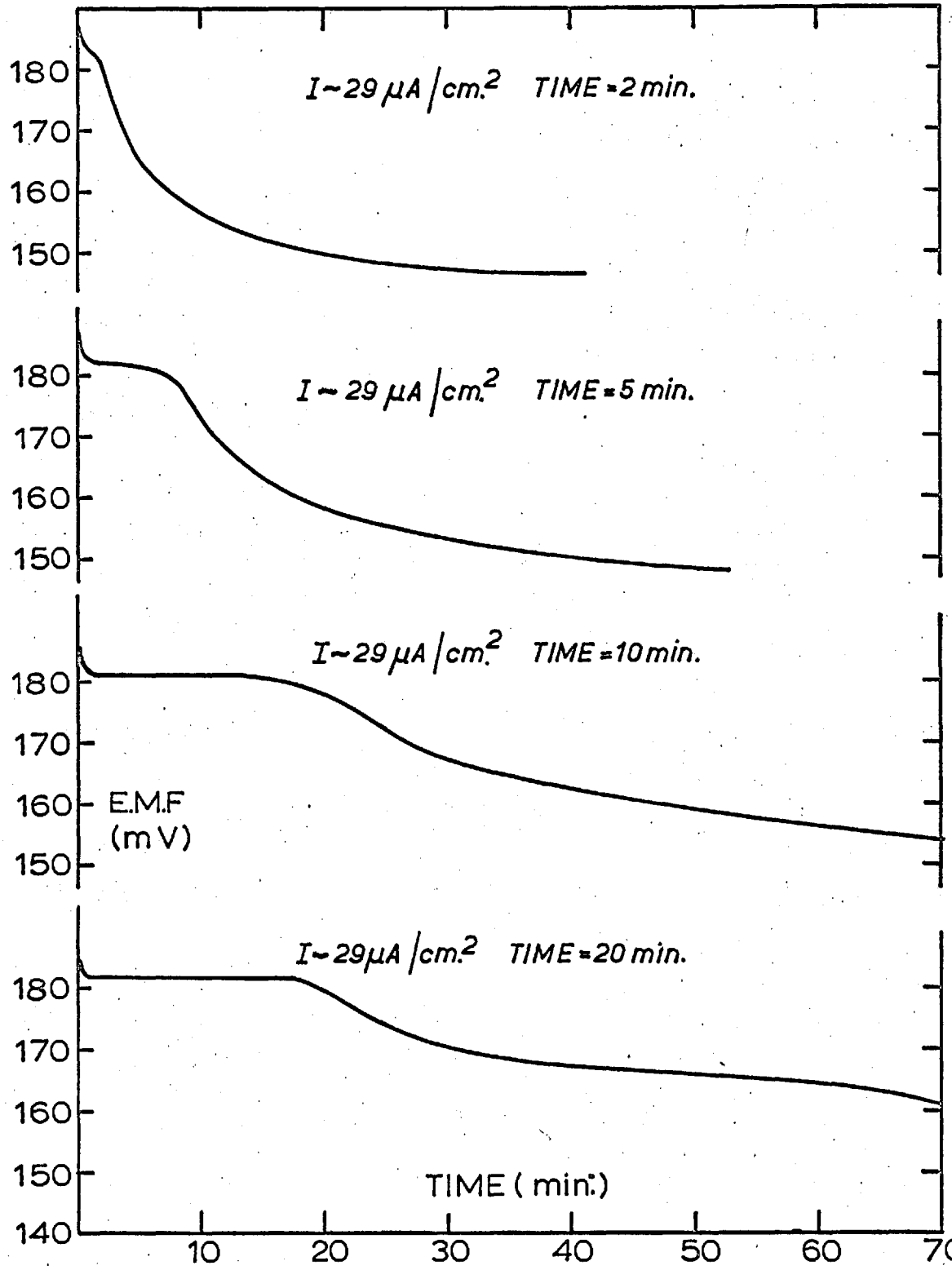


FIG.III.11 E.M.F OF THE CELL Ni-NiO/solid electrolyte/Cu(CO_2+CO) AFTER TITRATION IN THE INDICATED CONDITIONS (1100°C)

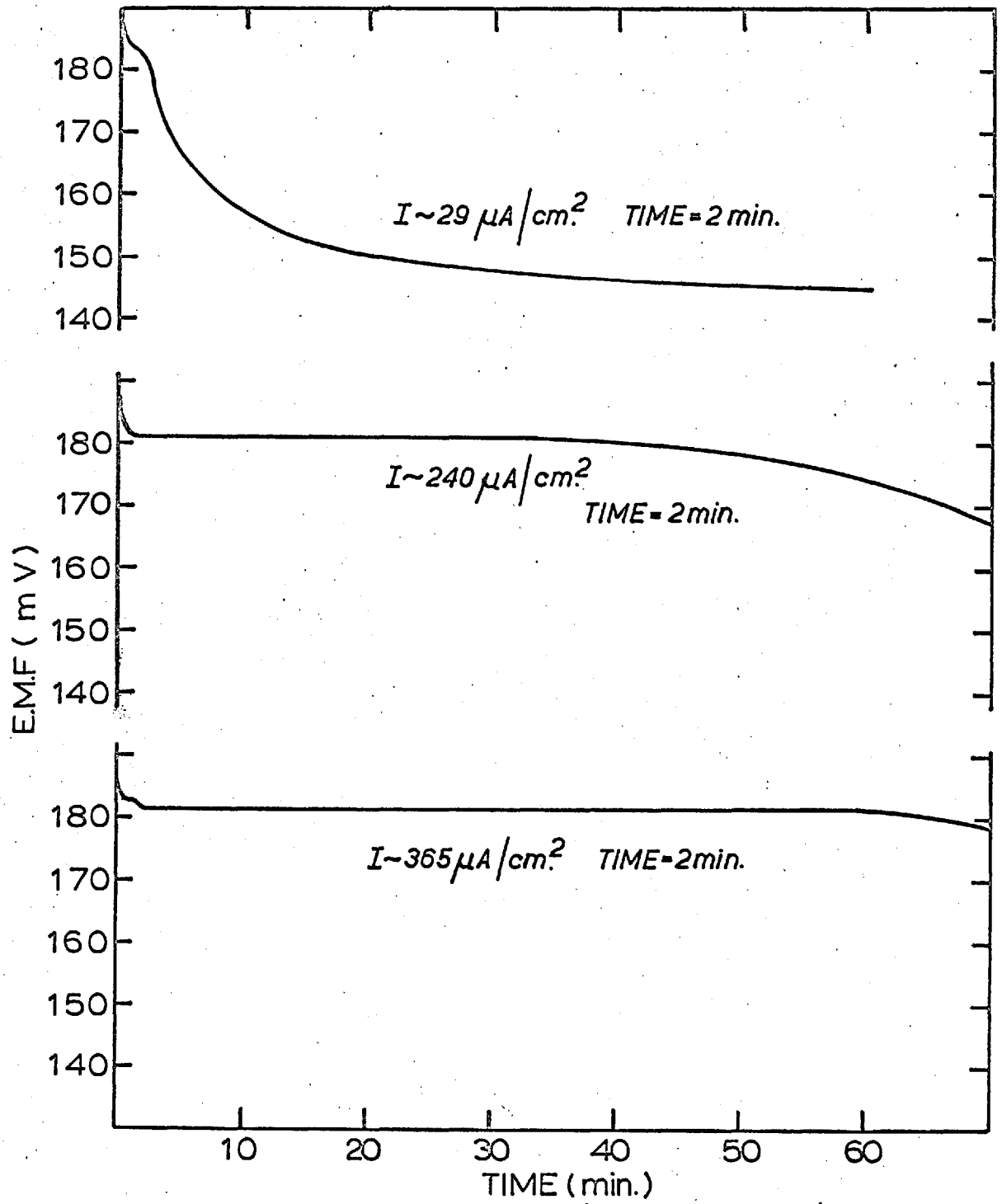


FIG.III.12 E.M.F OF THE CELL Ni-NiO/solid electrolyte/Cu,(CO_2+CO) AFTER TITRATION IN THE INDICATED CONDITIONS (1100°C)

TABLE III.4

Decay of the Ni-NiO/solid electrolyte/Cu, (CO_2 + CO) cell emf, after coulometric titration with a current of 29 $\mu A/cm^2$ passed during 2 min. CO_2/CO = 1105/1; Calculated equilibrium emf = 180 mv.

Time (min)	emf (mv)
0.5	184
1	183
1.5	182.5
2	181.5
3	174
4	168
5	164
6	163
7	161
8	159
11	156
20	150
40	147
60	145

TABLE III.5

Decay of the Ni-NiO/solid electrolyte/Cu, (CO_2 + CO) cell emf, after coulometric titration with a current of 29 $\mu A/cm^2$ passed during 20 min. CO_2/CO = 1105/1; Calculated equilibrium emf = 180 mv.

Time (min)	emf (mv)
0.5	184
1	182.5
2	183
5	183
10	183
13	183
14	182.5
16	182.5
17	182
18	182
19	181.5
20	180.5
22	178.5
25	176
30	173
40	171
50	169.5
70	166
90	160.5
150	154
270	148

TABLE III.6

Decay of the Ni-NiO/solid electrolyte/Cu, (CO_2 + CO) cell emf, after coulometric titration with a current of 365 $\mu A/cm^2$ passed during 2 min. CO_2/CO = 1105/1; Calculated equilibrium emf = 180 mv.

Time (min)	emf (mv)
0.5	183
1	183
1.5	183
2	182.5
3	182.5
5	182.5
8	182.5
9	182
15	182
18	182
19	181.5
21	182
24	182
27	181.5
29	181
35	181
45	181
60	181
65	180
70	179
75	175
80	170
95	165
(left overnight) 12 hours later	126

through the cell during titration.

A series of experiments were planned in order to get a deeper understanding on the nature of the polarisation phenomena. These experiments will be described in the following sections.

D) Experiments with cells of the type Pt, Ni-NiO/solid electrolyte/(CO_2 + CO), Pt.

A cell using Ni-NiO as reference electrode and a simple gas electrode (Fig.III.7) has the advantage of much greater experimental flexibility than the cell with liquid copper. Considerable information could be obtained on the behaviour of the Ni-NiO electrode with this type of cell in a short time.

Several solid electrolyte tubes were tested, both ZrO_2.CaO and $ZrO_2.YO_{1.5}$. All of them showed exactly the same behaviour. Tables III.7 and III.8 summarise the results for two of these cells. Correct emf's were obtained when the cell was quickly taken through a range of increasing CO_2/CO ratios, provided that the equilibrium oxygen partial pressure corresponding to the gas mixtures was not too high. It was never possible to get right emf's for CO_2/CO mixtures about or above 1000/1. If the cell was left a long time with a particular gas mixture, even small, the emf decreased

TABLE III.7

Emf's for the cell Pt,Ni-NiO/$ZrO_2.YO_{1.5}$/(CO_2+CO), Pt at 1100°C

Exp.No.	CO_2/CO	emf obs.(mv)±1%	emf calc. mv)±4mv	Observations
1	50/1	-2	-4	Experiments done one after the other. Cell left for one hour at equilibrium
2	100/1	38	38	
3	250/1	90	92	
4	100/1	37	38	Cell left for 20 hours. Emf decreased to 35 mV
5	250/1	88	92	Cell left for 12 hours Emf decreased to 84 mV
6	1005/1	162	174	After reaching this maximum the emf began to decrease immediately. In one hour decreased to 155 mV.
7	50/1	-12 - 7.5 - 6.5 - 6.0	-4	Decreasing immediately. After 2 hours " 3 " " 4 "
		-1.0	-4	Left for 15 hours After 19 hours Cell dismantled.

Note: The times necessary for equilibrium were about 10-15 minutes after changing the composition of the gas mixture.

TABLE III.8

Emf's for the cell Pt,Ni-NiO/$ZrO_2.YO_{1.5}$/(CO_2+CO), Pt at 1200°C

Exp.No.	CO_2/CO	emf obs(mV)±1%	emf calc(mV)±4mV	Observations
1	20/1	-43	-44	Experiments done one after the other. Cell left for one hour at equilibrium.
2	50/1	14	14	
3	100/1	58	58	
4	250/1	114	116	
5	20/1	-44	-44	Cell left for 15 hours, emf decreased to -36 mV.
6	100/1	57	58	Cell left for 12 hours, emf decreased to 52 mV.
7	Pure CO_2	212	347	
8	100/1	50	58	Cell dismantled.

Note: The times necessary for equilibrium were about 10-15 minutes after changing the composition of the gas mixture.

to values substantially lower than the calculated emf's. Some of the experiments indicated in Tables III.7 and III.8 have been plotted in Fig. III.13. This graph shows that the cell polarisation occurs in both directions, depending on the sign of the emf. These experiments also indicate the importance of the previous history of the cell on the magnitude of the polarisation effect. Experiments 5 and in particular experiment 7 in Table III.7 are good examples in this respect. In the case of experiment 7, the high emf initially obtained shows the remaining effect of the high polarisation of the Ni-NiO electrode in the previous experiment. However, the situation reverted after 19 hours to the correct polarisation sign.

The gas cells exhibited a pattern of behaviour similar to the liquid copper cells already discussed and produced evidence to support the polarisation hypothesis. The experimental emf's of the gas cell appeared to be in better agreement with the calculated emf's than in the case of the liquid copper cell. Discrepancies between observed and calculated emf's occurred in the liquid copper cell at lower CO_2/C_O ratios than in the gas cell in times not very much longer.

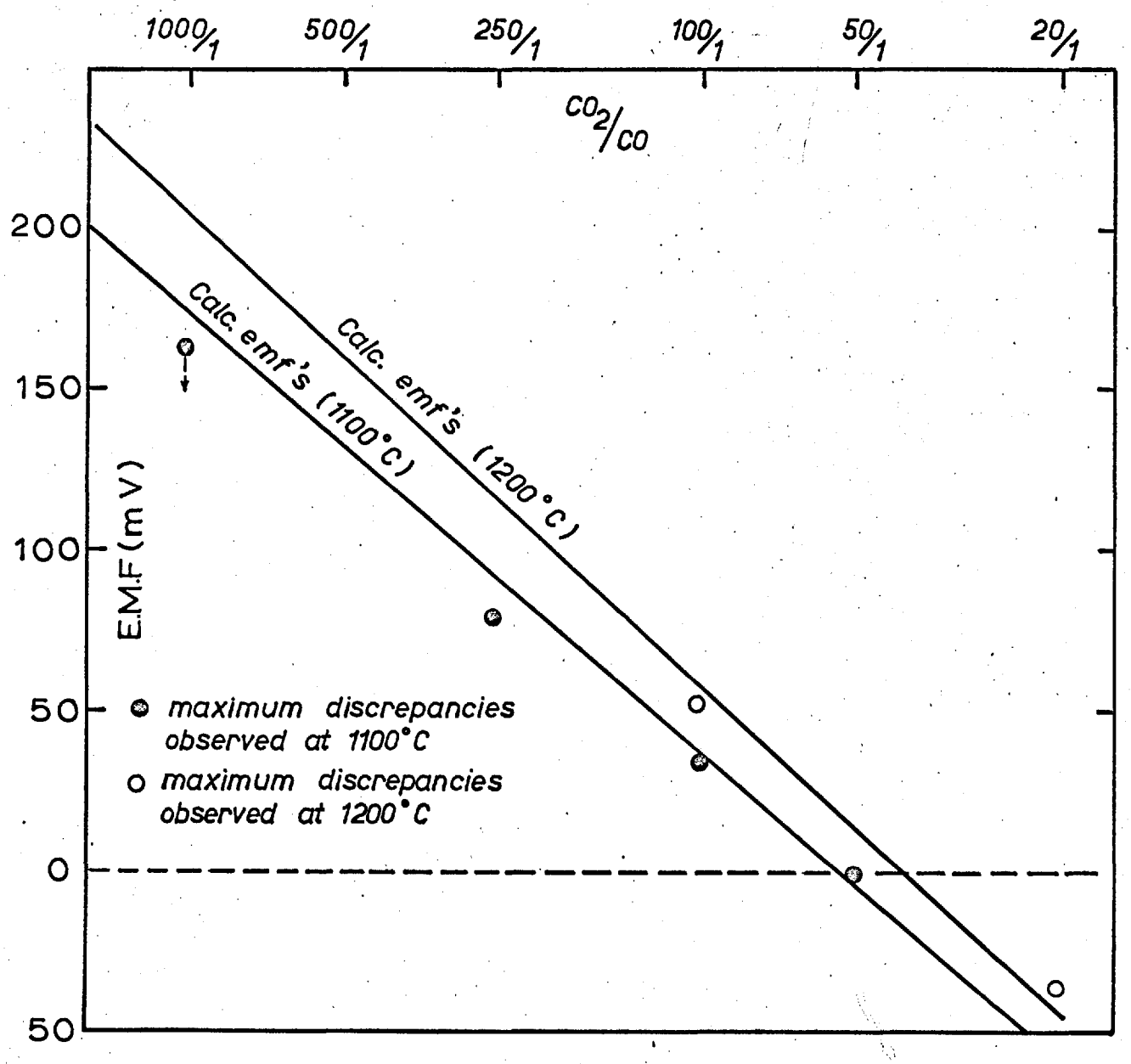


FIG. III.13 RESULTS FOR THE CELL Pt, Ni-NiO / $ZrO_2.YO_{1.5}$ / (CO_2+CO), Pt

If the gas cell was left enough time after equilibrium had been reached, the magnitude of the polarisation phenomena was of the same order in both types of cell.

e) Nature of the Polarisation Phenomena

The possible causes of polarisation could be solid electrolyte tube permeability, electronic conduction or a combination of both. The better behaviour of the gas cell suggested that electronic contribution to the conductivity of the zirconia tubes was the most likely cause of the observed polarisation phenomena. This idea was supported by Roberts studies of oxygen permeability through zirconia stabilised oxide solutions[45] (Section I.3. 1,d). However, previous work[10][12] on cells of the type:

$$\text{Ni-NiO/solid electrolyte/Cu,[O]}_{\text{(inert atmosphere)}}$$

where an inert atmosphere was maintained over the liquid copper, appeared to show that polarisation of the Ni-NiO was not observed during measurements. Unfortunately the lack of experimental details made it difficult to draw any conclusions about the behaviour of the cells, but if it was assumed that these cells were maintained in the reported

experimental conditions for long periods of time without exhibiting any polarisation at all, it would mean that the gas phase at the liquid copper electrode was certainly an important factor in the polarisation process. A few experiments were done to try to clarify this rather confused point.

The first series of experiments with the liquid copper cell consisted of two coulometric titrations, followed by observation of the emf as a function of time, to study the influence of the gas phase on the polarisation process of the cell. In one experiment the CO_2/CO mixture was kept bubbling through the molten copper all the time. In the other experiment the CO_2/CO atmosphere was replaced by argon coming from the bottom of the reaction tube as soon as the applied voltage was removed. The flow of argon was high in the first three minutes (about 500 cc/min) to sweep out of the cell the CO_2/CO mixture as quickly as possible. Then, it was reduced to about 50 cc/min to avoid losses of oxygen from the copper in the inert gas stream. The emf decay curves for both experiments are shown in Fig. III.14. Practically no difference was observed. It is difficult, however,

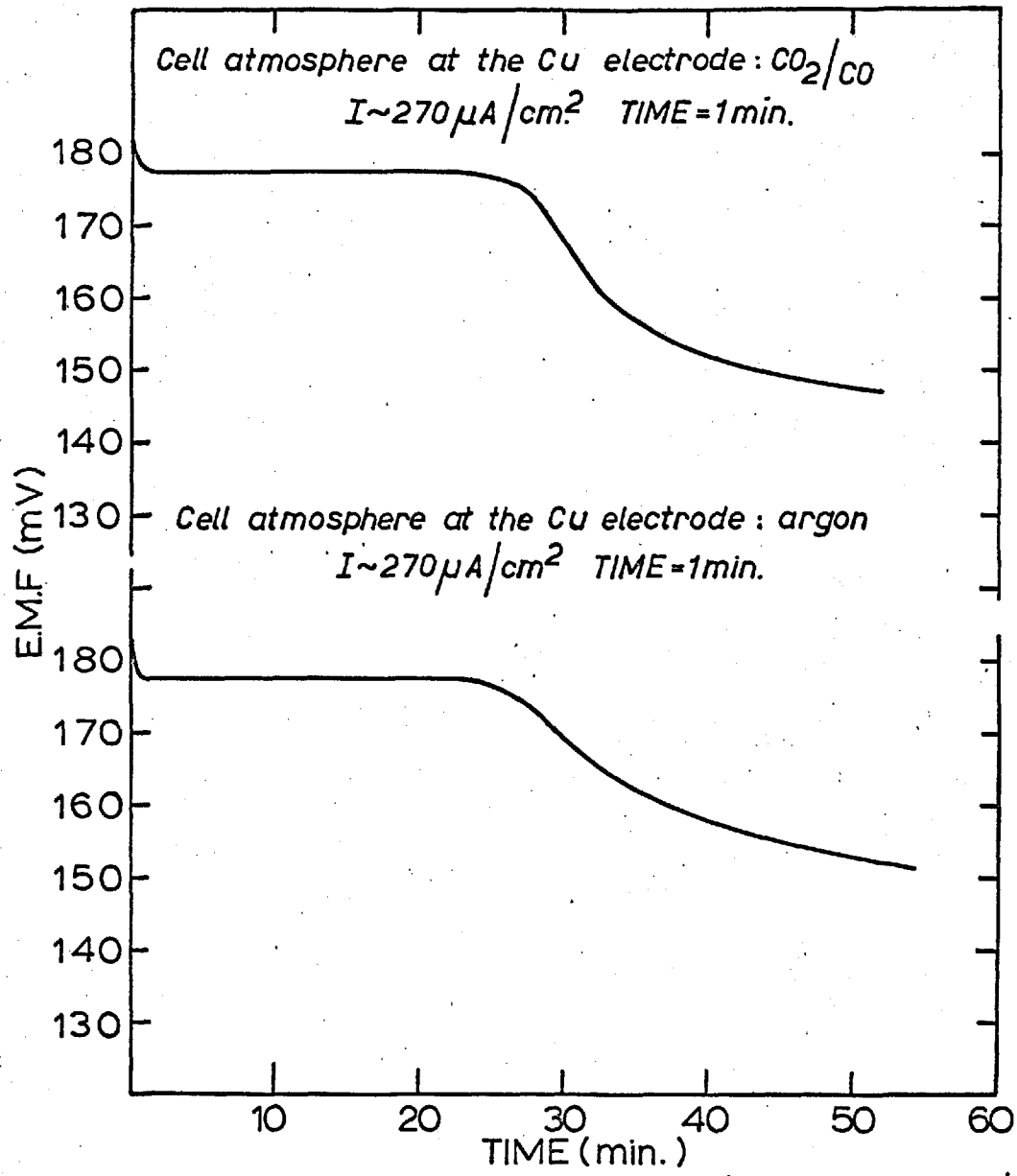


FIG.III.14 E.M.F OF THE CELL Ni-NiO/solid electrolyte/Cu,[O] AFTER TITRATION IN THE INDICATED CONDITIONS (1100°C)

to say how effectively the argon changed the CO_2/CO atmosphere inside the alumina crucible and consequently the experiment was not considered conclusive.

The magnitude of the short circuiting current due to the electronic contribution to the solid electrolyte conductivity is inversally proportional to the resistance of the electrolyte. In practice, the actual magnitude of this current will also depend upon the electrode kinetics which will determine the rate of oxygen to be transferred from one electrode to the other. Having in mind this limitation, it was thought that if it was possible to demonstrate a dependance of the polarisation phenomena upon the resistance of the electrolyte, this would be a direct proof of the importance of the electronic conduction in this respect. The simplest way of increasing the low resistance of the zirconia based solid electrolyte being used was by placing another solid electrolyte with a high resistivity (i.e. a thoria based oxide solution) between the zirconia tube and the molten copper. The following cell was built:

$Pt,Ni\text{-}NiO/ZrO_2.YO_{1.5}/ThO_2.YO_{1.5}/Cu,(CO_2+CO),cermet,Pt$

The cell arrangement is shown in Fig. III.15. A flat end $ZrO_2.YO_{1.5}$ tube was pressed against the bottom of a ThO_2 10 mole % $YO_{1.5}$* crucible whose dimensions were 12 mm i.d., 15 mm o.d. 10 mm height and 1.5 mm. wall thickness. The resistivity of the ThO_2 10 mole % $YO_{1.5}$ electrolyte is about 25 times bigger than the resistivity of the ZrO_2.9 mole% $YO_{1.5}$. The alumina tube carrying the CO_2/CO gas could not be brought down the bottom of the alumina crucible due to the considerable space occupied by the $ThO_2.YO_{1.5}$ crucible. Otherwise the cell was just like any other liquid copper cell used previously.

The cell was taken to 1100°C under argon and then a $^{CO_2}/_{CO}$ mixture $^{1228}/_{1}$ was passed through the cell. Nearly 36 hours were necessary to reach a steady emf of 163 mV which was 23 mV lower than the calculated emf of 186 mV. It was evident that the Ni-NiO electrode was again polarised even though the magnitude of the polarisation was less than in an ordinary cell where emf obs - emf calc was about 40 mV The cell was

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* The crucible had been made from spectroscopic pure reagents and was already available.

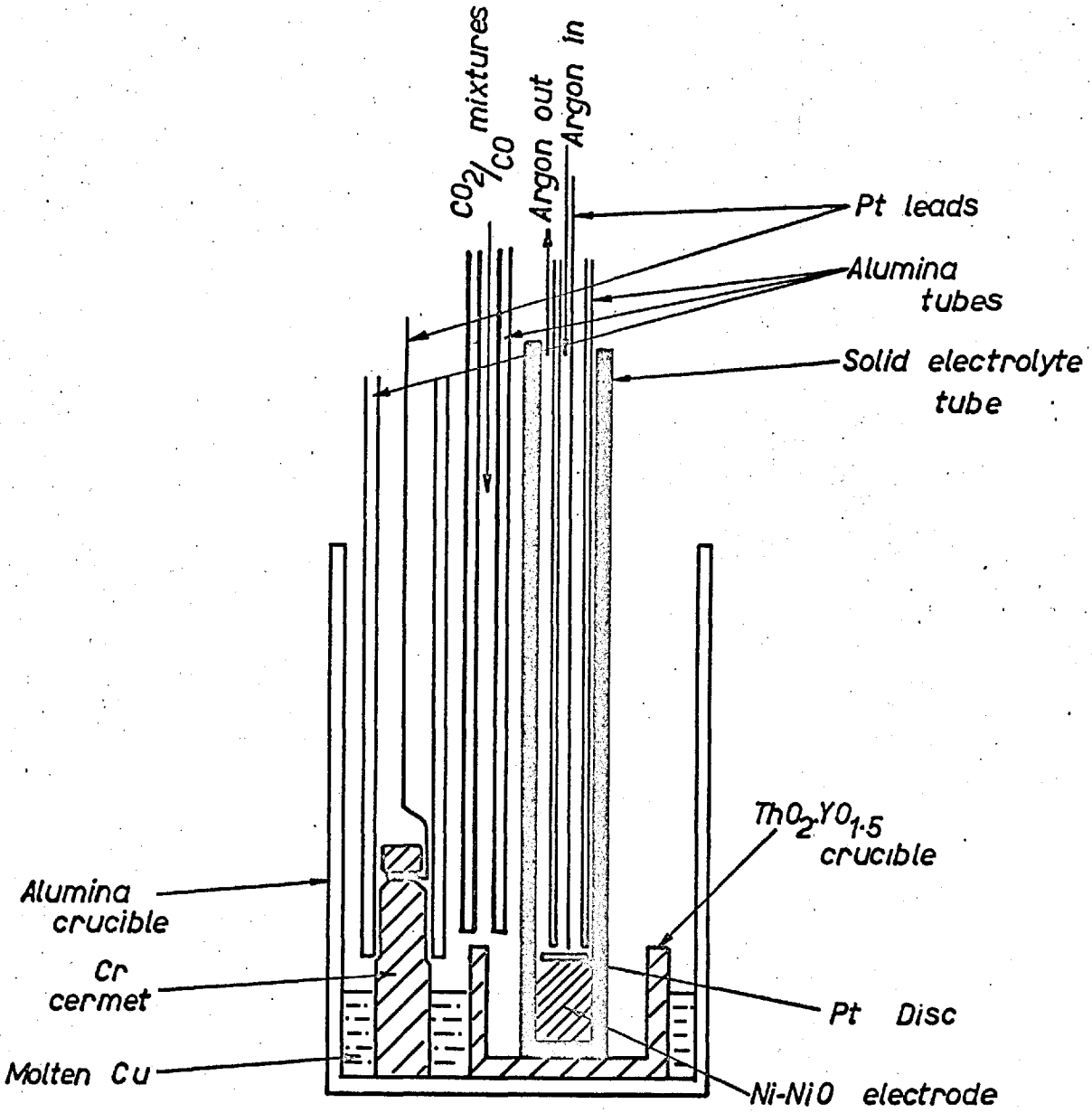


FIG.III.15

Cell : Pt, Ni-NiO / $ZrO_2.YO_{1.5}$ / $ThO_2.YO_{1.5}$ / Cu, (CO_2+CO), cermet, Pt.

left in this condition for 24 hours, but no significant decrease of the emf was observed (emf = 161 mV after 24 hours). A coulometric titration was done to compare the emf decay curve of the cell with those of the simple zirconia cells. The details of the experiment are given in Table III.9 and the emf decay curve, together with two selected emf decay curves of the zirconia cells, is shown in Fig. III.16.

The improvement in the behaviour of the cell with the $ThO_2.YO_{1.5}$ electrolyte was not substantial Several reservations have to be done with respect to the experiment itself. It would have been desirable to have increased the resistance many more times (100 or 1000). Furthermore, the behaviour of the $ThO_2.YO_{1.5}$ electrolyte in the oxidizing conditions of the experiment ($^{CO_2}/_{CO}$ = 1228/1 corresponding to $P_{O_2} = 10^{-6.22}$) was unknown. It is possible that its additional resistance has been offset by a significant electronic conduction (see Fig. I.3). On the other hand a high oxygen chemical potential in the copper electrode was necessary if any change in the polarisation phenomena was to be observed.

A further attempt was made to study the

TABLE III.9

Decay of the Ni-NiO/$ZrO_2.YO_{1.5}$/$ThO_2.YO_{1.5}$/Cu,(CO_2 + CO) cell emf, after coulometric titration with a current of ~55 $\mu A/cm^2$ passed during 2 min. (Tempt. 1100°C) CO_2/CO = 1228/1; calculated equilibrium emf = 186 mV

Time (min)	emf(mV)
0.5	188
1	187
5	187
15	187
25	187
35	187
38	187
40	186.5
41	186
43	184
47	178
50	176
54	173
60	170
66	168
73	167
95	165
120	164

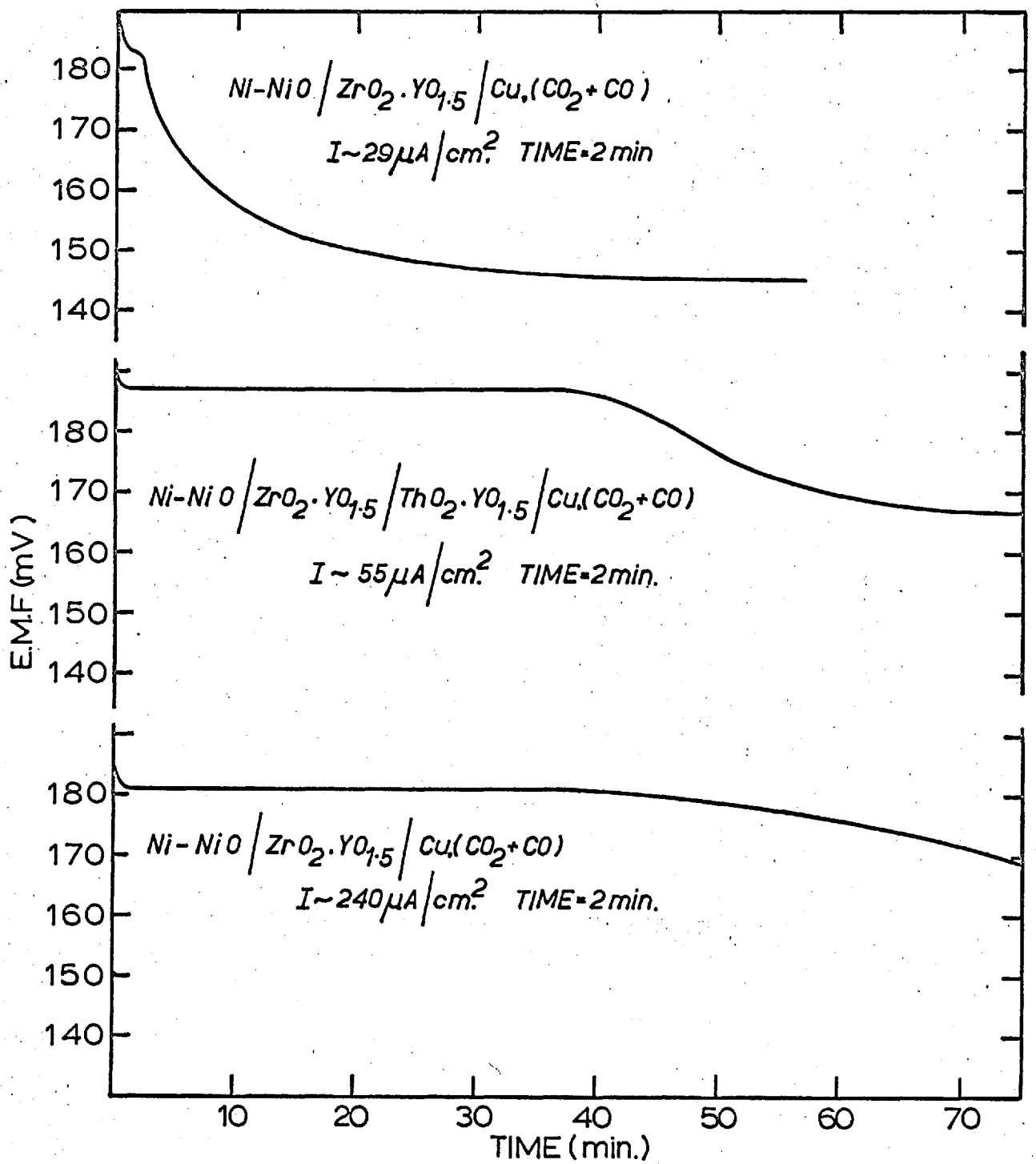


FIG.III.16 E.M.F OF CELLS WITH & WITHOUT $ThO_2.YO_{1.5}$ AFTER TITRATION (1100°C)

dependance of polarisation upon resistance of the electrolyte. The end of a $ZrO_2.YO_{1.5}$ tube was coated with a paste of ThO_2 2 mole % $YO_{1.5}$. The $ThO_2.YO_{1.5}$ layer was 1 to 1.5 mm thick. This layer should have increased the resistance of the solid electrolyte tube about 100 times. Unfortunately the $ZrO_2.YO_{1.5}$ tube became porous during sintering of the $ThO_2.YO_{1.5}$ coat (2000°C in vacuum) and finally cracked.

The two experiments described give once more some indication that electronic conduction would be mainly responsible for polarisation, but they are not conclusive. This problem needs further investigation.

Although the uncertaintly about the cause of polarisation remains, it is possible to give an idea about the nature of the polarisation phenomena. The equilibrium in a perfectly reversible cell may be represented by Fig. III.17a.

If the solid electrolyte tube is permeable, molecular oxygen goes from the side of higher oxygen partial pressure to the other. If the electrolyte exhibits electronic conduction electrons flow from the left to the right electrode and O^{2-} pass in the reverse direction. The kinetics of the Ni-NiO

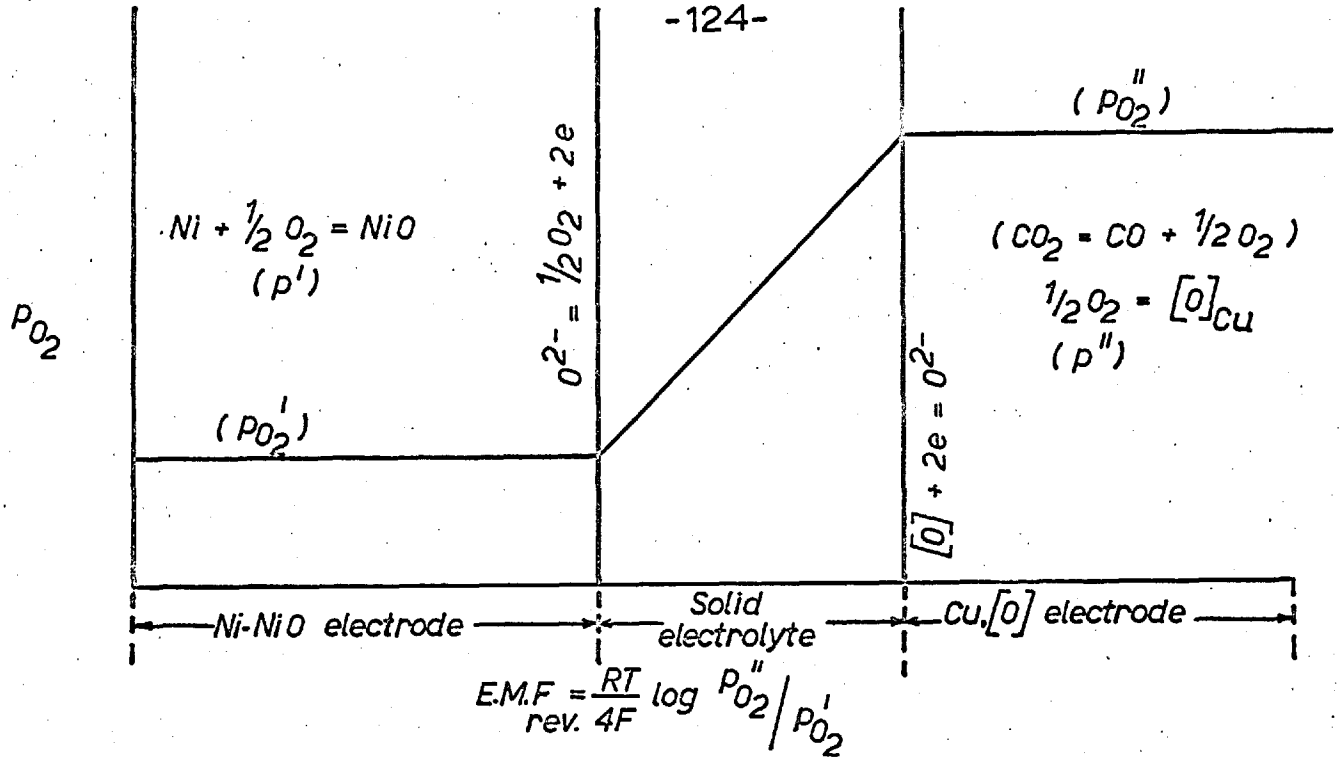


FIG.III.17a REVERSIBLE CELL

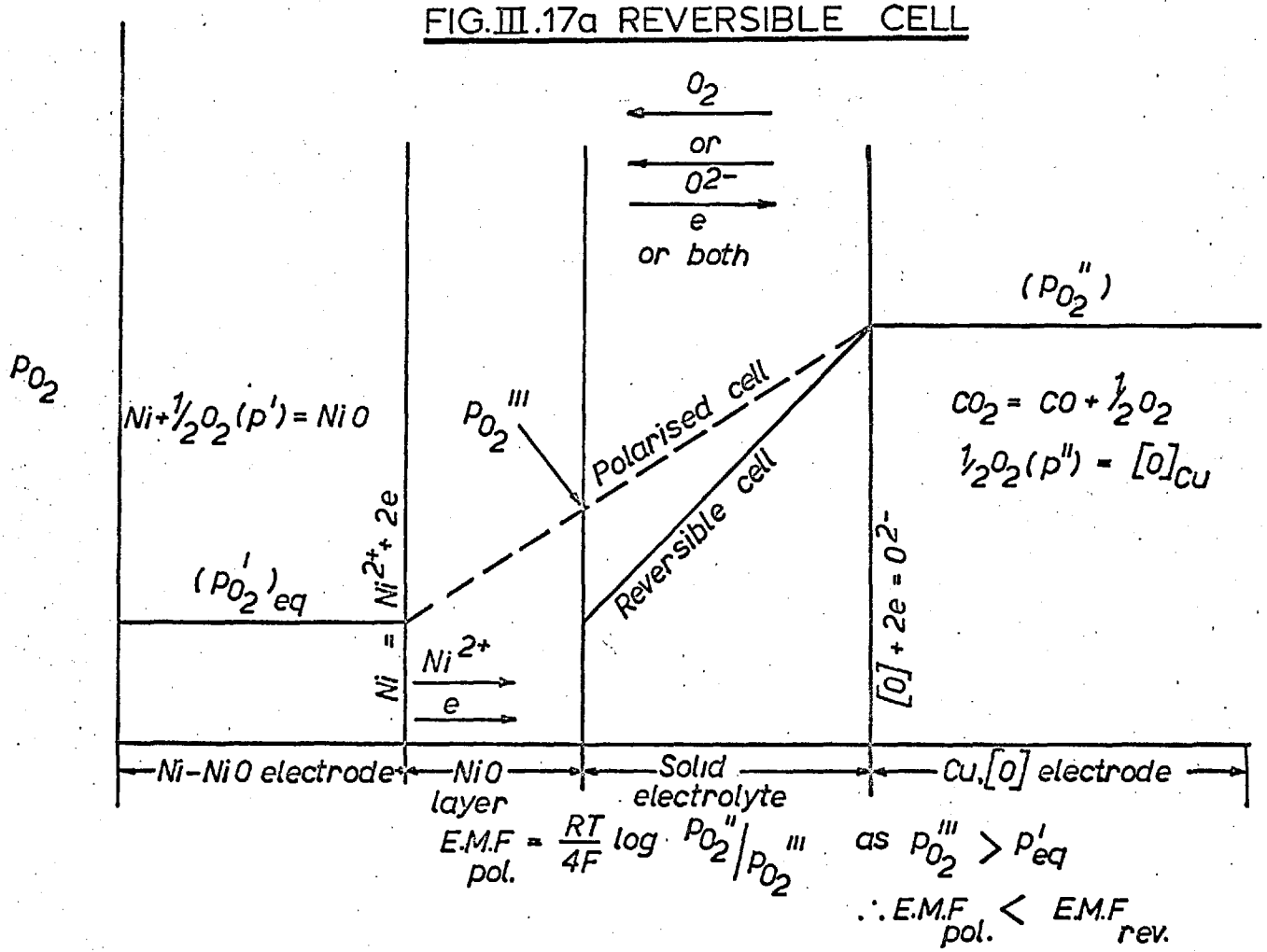


FIG.III.17b POLARISED CELL

electrode are too slow to cope with the oxygen coming through the electrolyte and the equilibrium oxygen pressure corresponding to the reaction:

$$Ni + \tfrac{1}{2}O_2(g) = NiO$$

cannot be maintained. A layer of NiO forms on the surface of the pellet and after a while the situation in the cell may be represented by Fig. III.17, b.

It is difficult to make a more quantitative approach to the polarisation problem with the information available. An idea of the magnitude of the resultant internal 'short-circuiting' current can be obtained making the following assumptions: i) The electronic contribution to conductivity in the solid electrolyte is of the order indicated in Chapter I (i.e. 0.5% of the total ionic conductivity);ii) The resistivity of the ZrO_2.9 mole % $YO_{1.5}$ and ZrO_2.15 mole % CaO materials is given by Fig. 1.2 (i.e. about 20 ohm cm in both cases). Assuming that the transfer of oxygen across the electrode/electrolyte interface at the high oxygen chemical potential electrode is not rate determining, then it follows that the 'short-circuiting' current varies from 400-500$\mu A/cm^2$ at the maximum emf's found (i.e.

180-200 mV). Even if it is accepted that 0.5% for the electronic conductivity is a maximum, the 'short-circuiting' currents may thus be big enough to produce polarisation of the Ni-NiO pellet. As already said in Section I.4 currents of 10 $\mu A/cm^2$ have been found to polarise Ni-NiO electrodes[15].

f) Experiments at 1200°C

Results for one cell, with a ZrO_2.CaO solid electrolyte, are shown in Table III.10. The general pattern of behaviour of the cell is similar to that observed at 1100°C and it would be difficult to say that the polarisation process was more or less evident at the higher temperature. Small differences between the cells at 1100° and 1200°C could be attributed to differences in the solid electrolyte tubes and Ni-NiO pellets used. The important fact is that significant polarisation occurred again when big differences in the oxygen chemical potential at the electrodes were established.

Coulometric titrations were performed using the cell in the experimental condition corresponding to experiments 4 and 5 of Table III.10. The results show that the emf decay at 1200°C was faster than at 1100°C if similar titration currents and

TABLE III.10

Observed emf's at 1200°C for the cell

Pt, Ni-NiO/$ZrO_2.YO_{1.5}$/(CO_2+CO), Cu(l), cermet, Pt

Exp.No.	CO_2/CO ratio	[O]wt% in copper*	emf obs(mv)±1%	emf calc(mv)±4mv
1	63/1	0.025	26.5	28
2	110/1	0.043	62	64
3	161/1	0.063	86	88
4	979/1	0.386	181	202
5	296/1	0.117	120	127**

* Calculated from Young and Tomlinson's solubility results[58] (see Table III.2)

** Equilibrium approached by reduction of [O] in copper.

Note: The times necessary for equilibrium were of the same order of magnitude of those observed at 1100°C.

times were employed(see Fig. III.18). These results tend to contradict the observation that the magnitude of the polarisation process was not worse at 1200°C than at 1100°C and indicate that the whole problem of electrode kinetics and electrolyte properties needs very careful consideration if better understanding of these phenomena is desired.

III.3.2 Cells with Pt, O_2 as reference electrode

a) Results at 1100° and 1200°C

One cell, with ZrO_2.CaO as solid electrolyte, was operated using a gas electrode (i.e. Pt, pure oxygen at atmospheric pressure) as a reference electrode. The difference in oxygen partial pressures between the electrodes and consequently the emf's developed in this case would be much larger than when Ni-NiO was used as reference. Oxygen transfer under these conditions would be from the gaseous oxygen towards the copper electrode and thus any polarisation would be expected to depend upon the kinetics of the Cu(l),(CO_2+CO) electrode.

The results at 1100° and 1200°C are shown in Table III.11. Good agreement was found between the observed and calculated emf's. However, the trend was for the observed emf's to be lower than

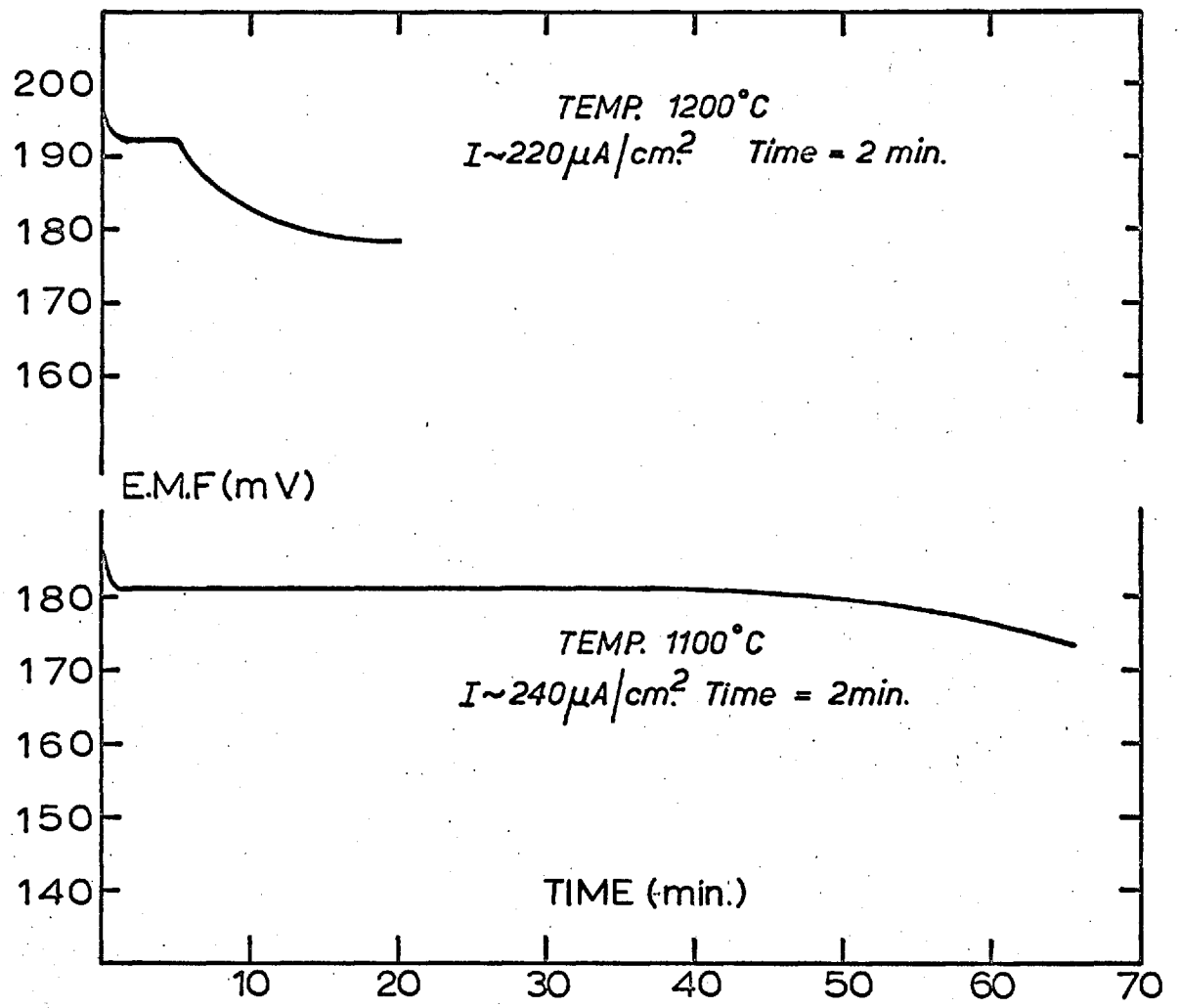


FIG.III.18 EMF OF THE CELL Ni-NiO/solid electrolyte/Cu,(CO_2+CO) AFTER TITRATION IN THE INDICATED CONDITIONS

TABLE III.11

Observed emf's for the cell

$Pt,O_2(Patm)/ZrO_2.CaO/(CO_2+CO),Cu(l),cermet,Pt$

Temp°C	Exp	CO_2/CO ratio	[O]wt% in copper*	emf obs(mv)±1%	emf calc(mv)±1mv
1100°	1**	87/1	0.010	577	580
	2**	472/1	0.057	476	480
	3**	1180/1	0.149	420	425
1200°	4**	960/1	0.420	360	364
	5**	93/1	0.037	509	512

* Calculated from Young and Tomlinson's results. [O]wt% for experiments 3 and 4 have been calculated from their experimental log P_{CO_2}/P_{CO}x[O]wt% values as given in Fig. III. 21.

** Copper samples taken for oxygen analysis. Results reported in section III.3.3

the theoretical emf's, but this could not be attributed to polarisation. In fact currents of about 100$\mu A/cm^2$ were passed for 1 and 2 minutes in both directions and the emf came back rapidly to the equilibrium value.

If the molten copper was left under purified argon, interrupting the CO_2/CO mixture flow, for a long time, the emf decreased. This phenomena indicated that oxygen transfer from the high to the low oxygen partial pressure side also occurred in this case, as expected. An attempt was made of measuring the magnitude of this transfer leaving the copper under argon for 13 hours. The emf's were read and samples of copper taken at the beginning and end of the experiment. Table III.12 contains the details of this experiment.

TABLE III.12

Oxygen transfer through the electrolyte in the cell Pt, cermet, Cu(l), $(CO_2+CO)/ZrO_2.CaO/O_2$(Patm), Pt, at 1100°C

	Weight of Copper(g)	emf(mv) ± 1%	[O]wt%	[O] in equivalents
Initial	42.83	515	0.0285	0.00153
Final	39.61	482	0.0479	0.00237

The total number of oxygen equivalents passed in 13 hours was 0.00084, which correspond to a constant current of about 1700 $\mu A/cm^2$. If the oxygen transfer were only due to electronic conduction the magnitude of this calculated current is 0.7% of the total conductivity, which is not very far from the figure given by various authors.

b) Kinetics of oxygen transfer from the CO_2/CO Mixture to the metal

During experiments with this cell a constant regular bubbling of the CO_2/CO gas mixture through the molten metal was observed. It was decided then to make readings of the emf as a function of time to get some information on the kinetics of oxygen transfer from the gas to the metal. The results of two experiments at 1100° and 1200°C respectively are given in Tables III.13 and III.14.

The oxygen transfer to the metal from the gas phase may be either gas, metal or chemically controlled. The following expressions have been derived for each one of these cases:(63)

i) Gas-controlled Oxygen Transfer

The transfer of oxygen may be represented by the equation

TABLE III.13

Oxygen transfer to molten copper (1100°C) from a CO_2/CO gas mixture = 1180/1. (Gas flowrate = 340 cc/min)

Time(min)	emf(mV) ±1%	[O]wt% *
0	476	0.061
10	467	0.072
25	463	0.077
45	457	0.085
60	452	0.094
90	447	0.102
115	445	0.106
140	442	0.111
200	436	0.124
290	429	0.140
330	428	0.143
345 **	427	0.145
equil **	420	0.165

* [O] wt% calculated from the emf's using Young and Tomlinson values for log $P_{CO_2}/P_{CO}x[O]$ wt %. Samples of copper were taken at the beginning and end of the experiment. The oxygen contents were 0.0588 and 0.160 wt % respectively.

** Time necessary for equilibrium not exactly known. Equilibrium was reached overnight.

TABLE III.14

Oxygen transfer to molten copper (1200°C) from a CO_2/CO gas mixture = 960/1 (Gas flowrate = 345 cc/min)

Time (min)	emf (mv) ± 1%	[O] wt.%*
0	418	0.165
30	408	0.195
55	403	0.212
75	398	0.231
90	395	0.243
120	391	0.261
140	388	0.277
180	384	0.294
295	374	0.350
375	371	0.371
equil.**	360	0.452

*[O] wt.% calculated from the emf's using Young and Tomlinson values for log P_{CO_2}/P_{CO} [O] wt.%. Samples of copper were taken at the beginning and end of the experiment. The oxygen contents were 0.160 and 0.468 wt.% respectively.

**Time necessary for equilibrium not exactly known. Equilibrium was reached overnight.

$$CO_2 \rightleftharpoons CO + [O]_{Cu} \qquad \text{(III.12)}$$

If the rate of oxygen transfer to the metal is considered to be controlled by the rate of removal of CO formed at the metal surface then a mass transfer equation may be written as:

$$\frac{dn}{dt} = \frac{W}{1600}\frac{d[O]}{dt} = \frac{kA}{RT}\left[P_{CO_{Surface}} - P_{CO_{Bulk}}\right] \qquad \text{(III.13)}$$

where dn/dt is the rate of transfer of gram moles of CO from the metal surface or the rate of transfer of gram atoms of oxygen to the metal per second, W is the weight of the metal specimen in grams, [O] is the weight percent oxygen dissolved in the metal, k is the mass transfer coefficient (cm/sec), A is the area of the specimen (cm^2), P is the pressure of CO (atmospheres) and R is $82^{c.c.\ atm}/$ degree mole.

Equation III.13 may be integrated after some transformations, between the limits $[O]_o$ when $t = 0$ and $[O]_t$ at time t. The integrated form is given by:

$$-[O]_{eq} \times \ln\frac{[O]_{eq} - [O]_t}{[O]_{eq} - [O]_o} - ([O]_t - [O]_o) = \frac{1600\ k\ A\ t\ P_{CO_B}}{R\ T\ W} \qquad \text{(III.14)}$$

ii) Metal-controlled Oxygen Transfer

If it is assumed that the surface of the metal specimen is in equilibrium with the bulk of the gas at all times and that the diffusion of oxygen into the metal is rate controlling (metal phase control) the mass transfer equation becomes

$$\frac{dn}{dt} = \frac{W}{1600}\frac{d[O]}{dt} = kA\left[\frac{n_{eq}}{V} - \frac{n}{V}\right] \qquad \text{(III.15)}$$

where

$$\frac{n}{v} = \frac{\text{gram atoms oxygen}}{\text{Volume metal}} = \frac{[O]\delta}{1600} \qquad \text{(III.16)}$$

and δ is the density of the metal.

If III.15 is integrated between $[O]_o$ and $[O]_t$, the following expression is obtained:

$$-\ln\frac{[O]_{eq} - [O]_t}{[O]_{eq} - [O]_o} = \frac{k A \delta t}{W} \qquad \text{(III.17)}$$

iii) Chemical-controlled Oxygen Transfer

If the rate of oxygen transfer represented by reaction III.12 is considered to be chemically controlled, a chemical rate equation may be written as follows:

$$\frac{dn}{dt} = \frac{W}{1600}\frac{d[O]}{dt} = k_1 P_{CO_2} A - k_2 P_{CO} A N_O \qquad \text{(III.18)}$$

where N_o is the atom fraction of oxygen dissolved in the metal

The integration of III.18 between the limits $[O]_o$ and $[O]_t$ gives:

$$- \ln \frac{[O]_{eq} - [O]_t}{[O]_{eq} - [O]_o} = \frac{1600\ k_1\ A}{W\ K} \times P_{CO} \times t \qquad \text{(III.19)}$$

The data of Tables III.13 and III.14 have been used to investigate which of these three alternatives apply in the present case*. Plots of $-\ln ([O]_{eq} - [O]_t)/([O]_{eq} - [O]_o)$ against time produced good straight lines (Figs. III.19 and III.20). Plots of $-\{[O]_{eq} \ln ([O]_{eq} - [O]_t)/([O]_{eq} - [O]_o) - ([O]_t - [O]_o)\}$ against time failed to give straight lines. Considering that during these experiments the metal was subjected to strong stirring, it appears that oxygen transfer to the metal from a CO_2/CO mixture is a first order chemical controlled process, which is in perfect

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* The error introduced in these calculations by any oxygen transferred from the pure oxygen electrode to the molten copper during these experiments is less than 10% and has been neglected because of the impossibility of a correct estimate under dynamic conditions.

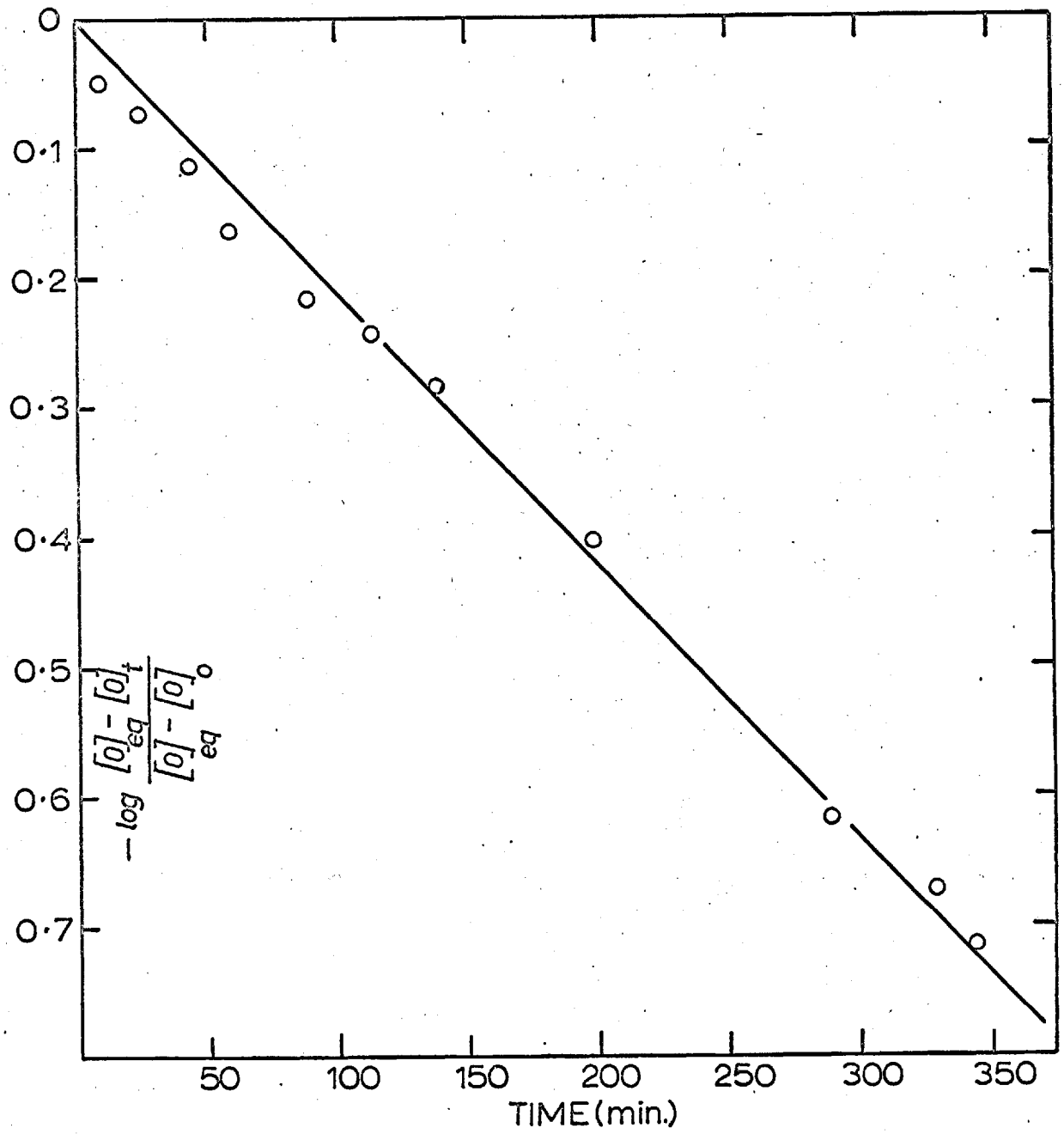

0
0·1
0·2
0·3
0·4
0·5
0·6
0·7
$-\log \frac{[0]_{eq} - [0]_t}{[0]_{eq} - [0]_o}$
50
100
150
200
250
300
350
TIME (min.)

FIG. III 19

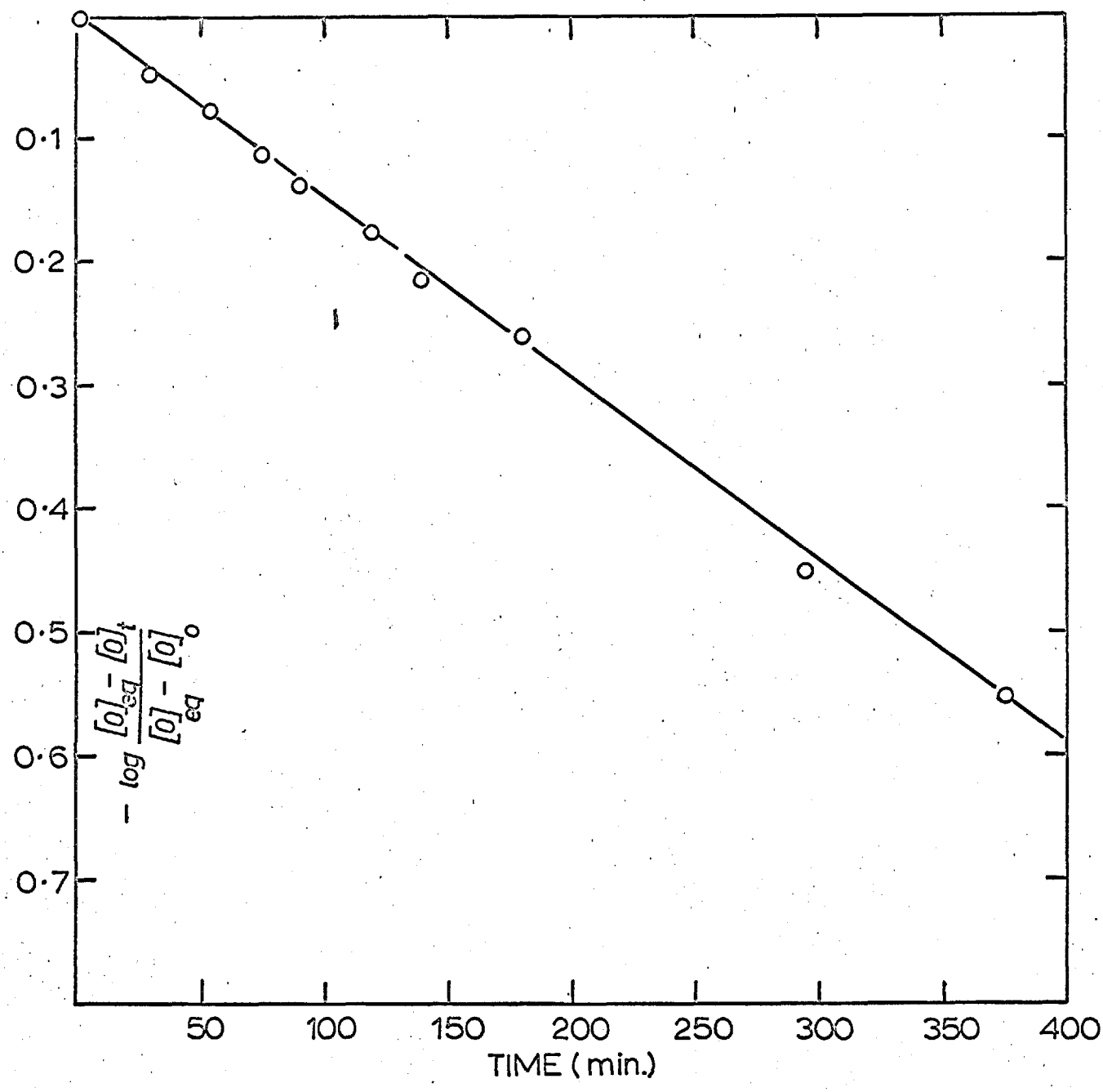

0·1
0·2
0·3
0·4
0·5
0·6
0·7
$-\log \frac{[o]_{eq} - [o]_t}{[o]_{eq} - [o]_o}$
50
100
150
200
250
300
350
400
TIME (min.)

FIG. III.20

agreement with results obtained by levitation of copper drops in CO_2/CO gas streems[63].

III.3.3 Oxygen Solubility in Molten Copper

A few samples of copper were taken in the course of the present work to check previous oxygen solubility data. The results of these analyses and the calculated values of log P_{CO_2}/P_{CO} x atom % [O] are given in Table III. 15 and Fig.III.21. The small number of samples do not permit any firm conclusions to be drawn about the liquid Cu-Oxygen equil, but it appears from Fig.III.21 that the results confirm Young and Tomlinson's[58] reported data. The values of these authors for the mentioned equilibrium seem to be reliable and the best at present available.

Further discussion on the liquid oxygen system is given in the appendix.

III.4 Previous Measurements of Oxygen in Molten Copper with Solid Electrolyte Galvanic Cells

All the previous work done with solid electrolyte galvanic cells for measuring oxygen in molten copper has been summarised in Table III.16. A common feature of all the cells studied is the inert atmosphere maintained at the Cu,[O] electrode during the experiments. None of the authors reported polarisation occuring during the measurements but neither did they test the reversibility of the cell being used.

TABLE III.15

Experimental results for the equilibrium:

$$CO(g) + [O]_{Cu} = CO_2(g) \quad K' = \frac{P_{CO_2}}{P_{CO} \times \text{atom \% [O]}}$$

Exp. No.	CO_2/CO	[O] wt.%	Atom % [O]	log K'
		1100°C		
1(Table III.11)	87/1	0.0109	0.0433	3.303
2(Table III.11)	472/1	0.0588	0.2329	3.307
3(Table III.11)	1180/1	0.160	0.6319	3.271
Sample 1 (Table III.12)	261/1*	0.0285	0.1130	3.364
Sample 2 (Table III.12)	456/1*	0.0479	0.1899	3.380
		1200°C		
4(Table III.11)	960/1	0.468	1.832	2.720
5(Table III.11)	93/1	0.0346	0.1371	2.832
3(Table III.10)	161/1	0.0553	0.2193	2.866
5(Table III.10)	296/1	0.1327	0.5249	2.751
4(Table III.10)	979/1	0.512	2.0025	2.689

*CO_2/CO ratios calculated from the observed emf's. Experiments actually done under argon.

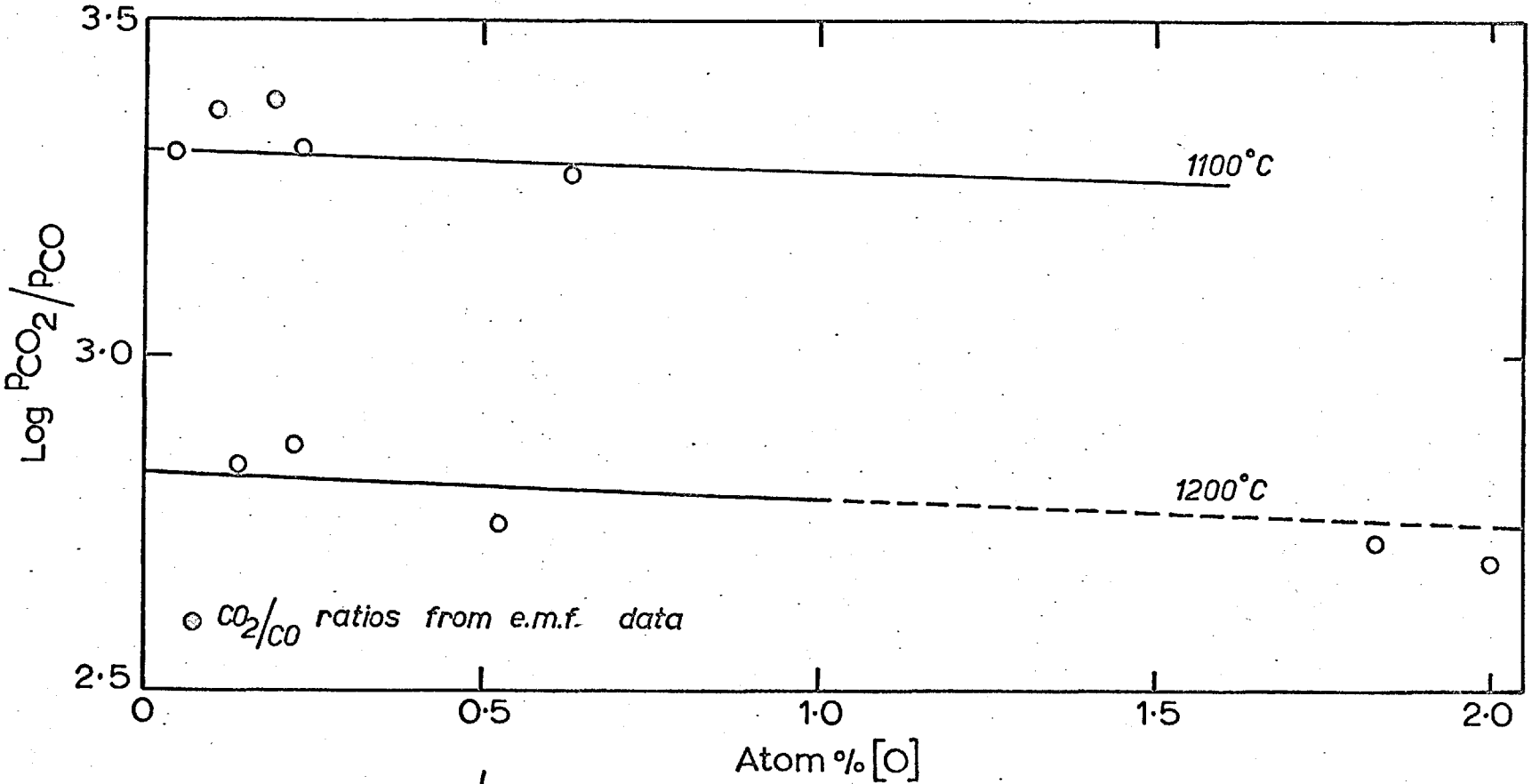


FIG. III. 21 LOG P_{CO_2}/P_{CO} x Atom % [O]. THE LINES REPRESENT THE RESULTS OF YOUNG & TOMLINSON[53]

TABLE III.16

Previous investigation with a cell of the type Cu[O]/solid electrolyte/reference electrode

Reference	Temp.°C	Technique	Solid Electrolyte	Reference Electrode	Contact Electrode
(8)	1100°-1300°	Addition of copper oxide to Cu(l) in inert gas atm.	ZrO_2.MgO	Air,Pt	Cr_2O_3
(9)	1150°	"	ZrO_2.CaO	Air,Pt	Molybdenum
(10)	1145°	"	ZrO_2.MgO	Ni-NiO	Cermet (not specified)
(11)	1100°-1420°	"	Stabilised ZrO_2 (not specified)	Air,Pt	Pt
(12)	1100°-1200°	"	ZrO_2.CaO	Ni-NiO	Ta

Considering the results of the present work, cells with a gaseous electrode[8][9][11] (i.e. Pt, oxygen or Pt. air) should have given emf's in close agreement with theoretical values. However, the discrepancy of Osterwald's results for the equilibrium $CO(g) + [O]_{Cu} = CO_2(g)$ (see Fig.III.3) suggest lower emf's than expected for the corresponding oxygen contents in the metal. Fischer and Ackermann[11] dip the solid electrolyte in the copper only at the time of making a measurement. Their results for the oxygen liquid copper equilibrium are in very good agreement with values obtained using equilibration techniques[58][62].

The lack of experimental details makes it very difficult to discuss work done using Ni-NiO as a reference electrode[10][12]. The time necessary for equilibrium with the copper oxide addition technique appears to be very short, but no information at all is given about how long a particular solid electrolyte tube was kept in direct contact with the metal. The fact is that calculated values for the equilibrium liquid copper-oxygen using emf's obtained with one of these cells[12] are in close agreement with Young and Tomlinson's[58] and Sano and Sakao's[61] results. If gas permeability of the solid electrolyte was the main cause of pol-

arisation, experiments done with both electrodes under inert atmosphere should give correct results, but as already discussed the cause of the polarisation has not been definitely established.

III.5 General Discussion and Conclusions

The results of the present work indicate that a cell with a gaseous reference electrode (i.e. Pt. pure oxygen or Pt. air) is a reliable instrument for measuring oxygen contents in molten copper. Furthermore, gaseous electrodes of this type appear to be the simplest reference electrodes which could be used for this purpose.

Chromium cermets have proved very convenient materials as contact electrodes in molten copper at different oxygen levels. The superficial oxidation of the cermet does not affect the response of the galvanic cell. Only a very small amount of chromium dissolves in the liquid copper*

The reliability of this cell permitted the study of the kinetics of oxygen transfer to molten copper from a CO_2/CO gas mixture. It was established that the process is chemically controlled confirming

*Chemical analysis done at the Service Laboratory of the Department showed that the Cr content in Cu of cells which had been continuously operated at high temperatures for 10-12 days was less than 0.02%.

the findings of previous research done with a levitation technique. These results are the clearest demonstration of the rapidity of response of the cell to any change of the oxygen content in the molten metal.

Cells using Ni-NiO as a reference electrode became polarised. The causes of this phenomena need further investigation. There is some indication, however, that the oxygen transfer through the solid electrolyte is mainly due to electronic conduction. It is known that all the so called solid electrolyte materials exhibit some electronic conduction. Two important factors should be considered then in the selection of solid electrolytes and reference electrodes to be used in galvanic cells of the type discussed. The first one is the resistivity of the electrolyte and the second the kinetics of the reference electrode. Known solid electrolytes (i.e. thoria based oxide solutions) with high resistivity start to exhibit a significant electronic contribution at 1000°C and at oxygen pressures, which are of the order of magnitude of those corresponding to the liquid copper-oxygen equilibrium.

It may be concluded that the technological application of these high temperature galvanic oxygen meters is handicaped by the present general lack of information about the characteristics of solid state electrochemical cells.

ACKNOWLEDGEMENTS

The author wishes to express sincere gratitude to Professor F. D. Richardson for supervision and suggestions received throughout the course of this work. He extends thanks to Professor C. B. Alcock and is also grateful to Dr. B.C.H. Steele for valuable discussions and helpful suggestions in the course of preparing this thesis.

Sincere appreciation is extended to the staff and members of the Nuffield Research Group, and in particular to fellow researchers in Room 401, for their help. Thanks are due especially to Mr. L.E. Leake, for his continuous co-operation and Mr. C. G. Glen for the oxygen analyses. All of them have made his stay in the Nuffield Group very enjoyable.

The author is indebted to the British Council and the University of Chile for making this visit to the Imperial College possible.

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APPENDIX

BEHAVIOUR OF OXYGEN IN MOLTEN METALS

Oxygen solubility studies have been done for a number of liquid metals of industrial interest in the very dilute range of melts. The behaviour of oxygen in these metals have been summarised in Table A. This gives the free energy equation for the process $\frac{1}{2}O_2=[O]$ at 1 atom percent concentration, and the heats of formation of the oxides from O_2 gas per oxygen atom at 25°C.

Oxygen in silver obeys Henry's law even above 1 atm. of oxygen pressure. Young and Tomlinson[a] found that oxygen solubility in copper deviates positively from Sievert's law. Sano and Sakao[b] also observed a deviation of this kind. Recent studies with cells support the view that Henry's law appears to be obeyed by oxygen in molten copper up to at least[c] 0.3 wt%. If this was the case the activity

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(a) Reference (58) in the text
(b) Reference (62) in the text
(c) Reference (12) in the text

TABLE A

Behaviour of Oxygen in Elementary Metals

Solvent	ΔG° (cal)	Reference	$\Delta H^\circ_{f25^\circ C}$ in cal/mole for oxide[h]
Silver	- 3,380+1.3T	This Work	(Ag_2O) - 7,300
Copper	-20,650+1.9T	Young & Tomlinson[a]	(Cu_2O) - 40,000
Nickel	-12,030-4.7T	Tankins, Gokcen and Belton[d]	(NiO) - 57,500
Cobalt	-14,840-4.8T	"	(CoO) - 57,100
Iron	-27,980-3.1T	Chipman & Floridis[g]	(FeO) - 63,200
Lead	-28,540-3.4T	Alcock & Belford[e]	(PbO) - 52,400
Tin	-43,870-6.6T	" " [f]	(SnO) - 68,400

(h) Kubaschewski, O and Evans, E.Ll. 'Metallurgical Thermochemistry,' Third Edition Pergamon Press (1958).

coefficient of oxygen taking pure oxygen gas at 1 atm as reference state, would be equal to 0.13 and 0.22 at 1100° and 1200°C respectively, indicating a negative deviation from ideality.

A similar situation exists for all the metals in Table A. Henrian behaviour[d] has been established for oxygen in nickel (up to 0.3 wt%) and cobalt (up to 0.2 wt%) and for lead[e] (0.008 wt%) and tin[f] (0.003 wt%). There is discrepancy with respect to oxygen in iron. Chipman and Floridis[g] have confirmed previous measurements by one of the authors and give an activity coefficient for oxygen in molten iron expressed by the following relationship:

$$\log f_o = -0.20[O]\text{wt\%}$$

Tankins, Gokcen and Belton[d] have found Henrian behaviour for oxygen in molten iron up to 0.20 [O] wt%.

The principal fact is that in all these cases there is a negative deviation from ideality.

(d) Tankins, E.S., Gokcen, N.A. and Belton G.R: Trans. AIME, 230, (1964), 820-827.

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The limiting partial molar heats of solution of oxygen in the metals of Table A are negative showing a tendency of the solution for 'short range order'. This tendency has been taken sometimes as evidence of compound formation in the melt, but actually the negative heat of solution is only an indication of a preference for [O]-M bonds compared to M-M or [O]-[O] bonds. This preference is so strong that for most of the metals in Table A it is possible to observe the separation of a second phase at relatively low oxygen concentrations with the formation of miscibility gaps in the phase diagram. The second phase in the liquid state has a composition slightly richer in metal than the stoichiometric oxide.

One would expect that a metal would have greater affinity for oxygen in dilute solution the more negative the heat or free energy of formation of the metal oxide. There is a general correspondence between the partial molar heats of solution and the heats of formation of the oxides in Table A. An exact correspondence is not to be expected due to differences in co-ordination numbers of the oxygen and metal atoms in the oxide and the solution.