A THERMODYNAMIC STUDY OF OXYGEN IN MOLTEN COPPER ALLOYS

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Abstract.

The dilute solutions of oxygen in molten copper and copper alloys have been investigated by studying the equilibrium between these melts and a gas phase of known oxygen pressure. The oxygen pressure of the gas was controlled either by circulating a CO_2/CO gas mixture in a closed system over Ni + NiO at a certain fixed temperature or metering a $CO_2/CO/A$ gas mixture. The gas-circulation apparatus was used for studies between 1085°C and 1300°C and the flowmeter apparatus for studies in the temperature range 1300°C to 1500°C. The equilibrium reaction can be written as

$$CO_2 = [O]_{Melt} + CO$$

The above equilibrium has been studied for pure copper over the temperature range 1085°C to 1500°C, dilute solutions of gold, platinum, silver and nickel at 1200°C, and over the entire composition range of copper + nickel and copper + cobalt alloys at 1500°C.

The CO_2/CO ratio in equilibrium with Ni + NiO over the temperature range 550°C to 800°C was also determined in the studies with the circulation apparatus and by a slight alteration of the technique used in this apparatus it has been possible to establish the CO_2/CO ratio in equilibrium with copper saturated with oxygen

and cuprous oxide over the temperature range 1000°C to 1188°C.

The results of the studies on the alloy systems have been compared with the thermodynamic behaviour of dilute solutions of sulphur in the same alloy systems and two simple models based on the random and quasi-chemical theories. The integral excess free energies of mixing of the Cu + Ni and Cu + Co systems calculated by means of the random solution model from the ternary data with oxygen as the solute were found to be much more positive than the values obtained from the sulphur data.

Consideration of these results indicates that the energies associated with the pairwise interaction between atoms in a ternary metallic solution may differ from those for the separate binaries and that simple configurational models are only of limited applicability in predicting the thermodynamic properties of ternary metallic solutions from knowledge of the three respective binaries.

TABLE OF CONTENTS

Chapter 4. COPPER-CUPROUS OXIDE SYSTEM

Chapter 5. DILUTE SOLUTIONS OF OXYGEN IN MOLTEN COPPER

Chapter 6. DILUTE SOLUTIONS OF OXYGEN IN LIQUID COPPER ALLOYS

INTRODUCTION

The major part of the world's supply of copper is obtained from the smelting of low grade copper sulphide ores. The sequence of operations from smelting to fully oxidised copper ready for poling in refining involves a series of systems characterised by decreasing sulphur activity and increasing oxygen activity. Metallurgists have also recognised for a long time that the presence of oxygen in liquid copper has an important effect on its casting and physical properties (ref. 1). For these reasons the quantitative relationships between oxygen in liquid copper and the gases present during processing are important.

The present research was carried out to resolve the large discrepancies in the experimental data for the solution of oxygen in molten copper and to provide information on the effect of alloying elements on the activity coefficient of oxygen in dilute solution in liquid copper. The information gained from these studies is particularly relevant to refining and alloy making and might help towards the better understanding of the atomic interactions between the components of metallic solutions.

In the last decade a large number of studies have been carried out in an attempt to develop a satisfactory theory to explain the thermodynamic behaviour of metallic solutions (ref. 2). In order to test fully the validity of the proposed theories, or formulate new generalisations, data on the thermodynamics of a wide range of solutions are required. Therefore, any steps undertaken to provide more experimental thermodynamic data are worthwhile from both the theoretical and practical point of view.

At the time of the commencement of this research studies by Alcock and Richardson (ref. 3) in this department had led to the development of a semi-quantitative relationship to explain the effect of an alloying element on the activity coefficient of a dilute solute in a ternary alloy system. They showed that if two solutes S and Y are dissolved in a metal X

$$\ln \gamma_{S(X+Y)} = N_X \ln \gamma_{S(X)} + N_Y \ln \gamma_{S(Y)} - \Delta G^{M,XS}_{X+Y}/RT \quad (1.1)$$

where $\gamma_{S(X+Y)}$ is the activity coefficient of solute S in the solution, N_X and N_Y are the atom fractions of X and Y, $\gamma_{S(X)}$ and $\gamma_{S(Y)}$ are the activity coefficients of S in pure X and Y, and $\Delta G^{M,XS}_{X+Y}/RT$ is the excess free energy of mixing of X and Y. The equation is based on the assumption that the distribution of the atoms in the solution is random, the co-ordination number of all three types of atoms is equal, and the energy of interaction between atom pairs is independent of concentration. For the same model the following equation was also derived;

$$\left[\frac{\partial \ln \gamma_{S(X+Y)}}{\partial N_Y}\right]_{N_Y \to 0} = \ln \gamma_{S(Y)} - \ln \gamma_{S(X)} - \ln \gamma_{Y(X)} \quad (1.2)$$

Alcock and Richardson showed that the preceding equations were approximately applicable to dilute solutions of sulphur in copper alloys which they studied and to a substantial number of others for which data were available.

It was evident from equation (1.1) that for the regular model to be generally applicable the calculated values of $\Delta G^{M,XS}_{X+Y}$ should be the same for different solutes, S. For this reason it was decided to try and study the behaviour of oxygen in the same copper alloys as used by Alcock in his studies with sulphur (ref. 4). The systems selected for study were, Cu-O, Cu-Ni-O, Cu-Co-O, Cu-Fe-O, Cu-Ag-O, Cu-Au-O and Cu-Pt-O.

Subsequent published work after the commencement of this research on the solution of oxygen and sulphur in various liquid alloys proved certain limitations in the proposed theory of Alcock and Richardson (ref. 5). The limitations of their original proposed model and the further developments will be discussed in the following chapter.

CHAPTER 1

STATISTICAL THERMODYNAMICS OF METALLIC SOLUTIONS

1. Solutions

Solutions may be classified according to their thermodynamic behaviour. A component in a liquid solution is said to behave ideally if its vapour pressure is proportioned to its mole fraction, or

$$p_i = p_i^o N_i$$

where p_i is the vapour pressure of component i over the solution, p_i^o is the vapour pressure of pure i at the temperature, and N_i is the mole fraction of component i. This equation defines Raoult's law explicitly, which may be written as,

$$a_i = N_i = \frac{p_i}{p_i^o}$$

where a_i is the activity of component i in the liquid solution.

The free energy, activity and activity coefficient of component i in a solution can be expressed by the relation,

$$\Delta \bar{G}_i = \bar{G}_i - G_i^o = RT\ln a_i = RT\ln \gamma_i N_i$$

where $\Delta \bar{G}_i$ is the relative partial molar free energy change accompanying the addition of one mole of component i in its chosen standard state to an infinite amount of the solution, $\overline{G}_i$ and G_i^o are the partial molar free energy of component i and the standard molar free energy of pure component i respectively, γ_i is the activity coefficient of component i which becomes unity if the solution is ideal.

An ideal solution can be defined thermodynamically as,

$$\Delta H^{M,id} = 0$$
$$\Delta S^{M,id} = -R\ (N_1 \ln N_1 + N_2 \ln N_2 + \ldots)$$
$$\Delta G^{M,id} = RT\ (N_1 \ln N_1 + N_2 \ln N_2 + \ldots)$$

where $\Delta H^{M,id}$, $\Delta S^{M,id}$ and $\Delta G^{M,id}$ are the ideal molar enthalpy, ideal molar entropy and the ideal molar free energy of mixing respectively. R is the gas constant. Ideal solutions are seldom encountered, deviations from Raoult's law are usually the case.

A more general concept of solutions is that of the "regular solution" originally formulated by Hildebrand (ref. 6). He postulates that,

$$\Delta S^M = \Delta S^{M,id} = -R\ (N_1 \ln N_1 + N_2 \ln N_2 + \ldots)$$

but, $\Delta H^M \neq \Delta H^{M,id} \neq 0$

and since $\Delta G^{M,xs} = \Delta G^M - \Delta G^{M,id}$

$$\Delta G^{M,xs} = RT\ (N_1 \ln \gamma_1 + N_2 \ln \gamma_2 + \ldots)$$

where ΔS^M, ΔH^M, ΔG^M and $\Delta G^{M,xs}$ are the entropy change, enthalpy change, free energy change and the excess free of mixing of components 1 and 2 respectively. Under the conditions assumed in this model, the excess entropy $\Delta S^{M,xs}$ is zero, therefore

$$\Delta G^{M,xs} = \Delta H^{M}$$

In a binary solution whose mole fractions of components are N_1 and N_2, the following parabolic equation occasionally holds;

$$\Delta H^{M} = RT\alpha N_1 N_2$$

where α is assumed to be constant, though, in general it is a function of composition (ref. 7).

In a dilute solution, that is a solution in which N_i approaches zero, the following equation usually holds;

$$a_i = kN_i$$

where k is a constant for the system. This equation is called Henry's law. Both Raoult's and Henry's laws are ideal limiting laws; the former applies to a solvent containing a small percentage of total solute in the solution and the latter to the solute at very low concentrations. In deriving Henry's law it is assumed that the solute atoms are so far apart that interactions between these atoms no longer need to be considered; only interactions between solvent atoms and interactions between solvent and solute atoms are of importance. The range over which Henry's law is obeyed depends on the temperature, the strength of the atomic interactions in the next nearest neighbour position, and the accuracy of the experimental method for small values of N_i. Furthermore, positive deviations from Henry's law are to be regarded as due to the effect of repulsive forces between solute atoms, and negative deviations due to attractive forces.

Darken and Smith (ref. 8) have shown how interactions between solute atoms in dilute solutions may be taken approximately into account. Their model leads to the following relationship;

$$\log \gamma_i = kN_i + \log \gamma_i^o$$

where γ_i is the activity coefficient of the solute in the solution, γ_i^o is the activity coefficient of the solute in the infinitely dilute solution and k a constant.

A few general statements describing the properties of metallic solutions have been outlined by Oriani (ref. 2). They can be summarised as follows:

(i) All the excess thermodynamic properties of solution are small therefore the maximum of the enthalpy of solution ΔH^M, usually lies within the limits of about $\pm$ RT; the entropy of solution ΔS^M is usually no further from zero than $\pm$ R, but less than that for an ideal solution;

(ii) The change of volume upon mixing is only a few per cent different from zero.

(iii) Every solid solution examined by diffuse X-ray scattering has been found to be characterised by a deviation from random distribution of atomic species upon the lattice sites, and usually by a static displacement of the mean positions of the atoms from the exact points of the geometric lattice.

(iv) The thermodynamic properties, co-ordination number, electrical resistivity, paramagnetic susceptibility of the simpler metals change very little in the melting process.

Many different approaches have been made to the theory of solutions, but as yet there is no theoretical model to explain the behaviour of metallic solutions. To elucidate the complexity of this problem a brief discussion of the important approaches is given in the remainder of this chapter.

2. Quasi-Chemical Theory

This statistical model (ref. 9) assumes the energy of a solution may be characterised as the sum of constant pairwise interaction energies, E_{ij}, between neighbours i and j, and that the volume and vibrational changes upon formation of the solution from the pure components may be neglected. In its simplest form, the quasi-chemical method considers the distribution of nearest-neighbour pairs as affected by non-zero values of $w = E_{ij} - \frac{1}{2} (E_{ii} + E_{jj})$, assuming non-interference of pairs, i.e., that the relative probabilities for a pair of neighbouring sites to be occupied in any one of several possible ways are independent of the manner of occupation of all other sites. The theory is such that when the sign and magnitude of w is fixed, the signs and magnitudes of the degree of short range order, and excess entropy of solution are also fixed.

The immediate short-coming of this theory is that it gives wrong signs for the excess thermodynamic quantities. The comparison of the experimental values of $\Delta S^{M,xs}$, the excess molar entropy with those calculated clearly indicates that the neglect of the non-configurational factor is a serious deficiency in quasi-chemical treatment. The assumption that E_{ij} is independent of composition, even within any one phase, has been discussed by Guttman (ref. 10) and found to be inconsistent with the experimental results for the activity coefficients (ref. 11) and short range order parameters (ref. 12, 13) in disordered Au-Cu solid solutions and for the same two properties for aluminium-zinc alloys (refs. 14,15). The variation of E_{ij} with composition is perhaps not entirely unexpected in concentrated solutions. However, studies by Oriani on liquid tin solutions of less than 2 atomic percent solute (ref. 16) can also be interpreted, in terms of a composition-dependent E_{ij}. If the variation of the pairwise interaction energies between the atomic species are taken into consideration (ref. 16), a modified form of the Bragg-Williams approximation for the integral molar enthalpy is obtained,

$$\Delta H = \frac{Z}{2} (x_i \Delta E_{ii} + x_j \Delta E_{jj}) + zwx_i x_j$$

where, ΔE_{ii}, is the change in the i-i bond energy in going from the pure ith component to the solution of solute concentration x_j, z is the co-ordination number and $w = E_{ij} - \frac{1}{2}(E_{ii} + E_{jj})$ is an interaction parameter. E_{ii}, E_{jj} and w are functions of composition. The Bragg-Williams approximation may adequately describe the variations with concentration of the partial molar heat of solution of the solute in dilute solutions.

3. The Average-Potential Model

The serious deficiencies in the quasi-chemical treatment are the neglect of vibrational and volume changes during the solution process. Pairwise inter-action energies must also be considered as functions of composition.

The average-potential model developed by Prigogine and co-workers (ref. 17) explicitly incorporates the above factors as natural consequences of its basic assumptions. The basic premises of the average-potential model are that the pure components obey the theorem of corresponding states, and that the mean average potential acting on a molecule in the solution is of the same form as that in the pure components. Average interactions, between one molecule and all its neighbours are introduced, and these are taken to be composition-dependent and of the same form as the Lennard-Jones 6-12 intermolecular potential. When the theory is applied (ref. 2) the degree of agreement found between the calculated enthalpies of solution of many binary alloys and the experimental values is poor, even though the disparity of the atomic size is taken into consideration.

From the general assumptions of the theory, Shimoji (ref. 18), derived a modified form of the interaction energy expression which includes the effect of difference in the atomic radii and the power indices of the distance from the centre of the model cell. This expression is only useful in predicting the excess functions of solutions when the ionic character of the bonds can be neglected.

4. Chemical Bond Theory

Deficiencies in the quasi-chemical and average-potential models indicate that it is necessary to investigate the nature of the chemical bond, or electron interaction between solvent and solute atoms in the alloy. Alcock (ref. 19) and Shimoji (ref. 20) have summarised the hypotheses proposed to deal with this problem. An abstract of their discussions is presented below.

The simplest form of the chemical approach is that for a regular solution. The heat of formation of an alloy is related to the difference between the bond energies of unlike atom pairs and like pairs, and to the co-ordination number of each atom. In the strictly regular solution, where the integral heat of formation has a parabolic dependence on alloy composition, it is assumed that the co-ordination number is the same for each pure metal and does not change in the process of alloying over the whole composition range. Further, it is assumed that only nearest neighbour interactions are important, and that the alloying atoms are randomly distributed.

At present, the bond energies can be deduced only from the experimental data. The energy of the bond between two atoms in a pure metal is deduced from the energy of vapourisation of the metal, and the co-ordination number of each atom.

Based on some concepts of the band theory of metals Friedel (ref. 21) attempts to calculate the excess thermodynamic properties of alloys. He can only partially account for the heat term arising from the screening effect of conduction electrons in alloys, but not the absolute values, ΔH^{M} or $\Delta S^{M,xs}$.

Varley (ref. 22) extended another approximation of the band theory in order to calculate the value of ΔH^{M}. In his model, electrons in a solution are transferred from the band of a higher Fermi level to that of a lower one, filling up the hitherto unoccupied levels, at the top of the latter band. This charge transfer necessarily leads to a negative heat of mixing only. This, of course, does not agree with experimental observation. In order to have a better correlation between the observed heats of formation and the alloy characteristics of element, Varley concluded that the changes of the boundary conditions imposed on the electrons during alloying process and the limitations of assumed completely free electron theory should be taken into consideration.

5. Ternary Solution's

Wagner's investigations on ternary amalgams had led him to summarise a few general statements as follows:

> "Under certain conditions, the interaction between positively charged metal ions in an alloy may be considered to be of minor importance as compared to the interaction between conduction electrons and metal ions. Then it follows that the activity of a solute metal 2 dissolved in metal 1 will be increased by a third component if metals 2 and 3 change the valence electron/atom ratio in the same direction. Conversely the activity of a solute metal 2 will be decreased by a third component if metals 2 and 3 change the valence electron/atom ratio in opposite

directions ....."

(ref. 23). Wagner's hypothesis is contradicted by Alcock's results for the effect of nickel and platinum on the activity coefficient of sulphur in molten copper. Both nickel and platinum decrease the electron/atom ratio, but whereas nickel decreased the activity coefficient of sulphur platinum raised it.

Alcock showed the results could be better explained by chemical theory and developed the equations shown on page two. The first equation was found to be reasonably accurate in cases where the difference between $\ln \gamma_{s(x)}/\gamma_{x(x+y)}$ and $\ln \gamma_{s(y)}/\gamma_{y(x+y)}$ were less than unity. The second gave values of the interaction parameter ε, defined by the first term in equation two which were correct in sign but between two and three times smaller than the measured values. It was suggested that these differences might be partly or entirely caused by clustering about the solute atoms of that component of the alloy which interacted more strongly with the solute. An extreme example of clustering may occur in mixtures of iron and aluminium where oxygen is the solute. Gokcen and Chipman (ref. 24) have derived a value of -780 for ε from their measurements at 1760°C whereas an estimate based on the likely thermodynamics of oxygen in aluminium, and the known properties of solutions of oxygen in iron and of aluminium in iron leads via equation (1.2) to values of the order of -10.

In an attempt to account for this behaviour Alcock and Richardson (ref. 5) derived equations based on the quasi-chemical model,

$$\ln \gamma_{s(x+y)} = \ln \frac{\gamma s(x)}{\gamma x(x+y)} - z\ln(kN_y + N_x) \qquad (1.3)$$

and $$\left[\frac{\partial \ln \gamma s(x+y)}{\partial N_y}\right]_{N_y \to 0} = \frac{-z(k-1)}{N_x+kN_y} \qquad (1.4)$$

where z is equal to the co-ordination number and

$K = \frac{\gamma s(x)\ \gamma y(x+y)}{\gamma s(y)\ \gamma x(x+y)}$. If z is taken as 8, equation (1.4) gives a value of -17 for ε for the iron - aluminium - oxygen system. It is evident that although equation (1.4) looks a better proposition than equation (1.2), it falls far short of accounting for the experimental value of ε .

Alcock compared the values of ε which can be derived from equations (1.2) and (1.4) with the experimental values that were available. The results for z = 8 are given in Table 1.

TABLE 1

System*	Temp. (°C)	Exptl.	Values of ε Quasi-chemical	Random
Cu(S + Fe)	1500	-4.6	-3.5	-3.0
Fe(S + Cu)	1500	-0.8	-2.5	-1.6
Fe(O + Al)	1760	-780	-17	-9
Fe(O + Ni)	1600	+0.5 to 0.9	+3.1	+4.6
NI(O + Fe)	1600	-7.4	-3.7	-2.8
Fe(O + Co)	1600	+1.7	+2.4	+2.9
Co(O + Fe)	1600	-3.5	-3.5	-2.9

* The element outside the brackets corresponds to element "x" in equation (1.2) and (1.4).

From these data Alcock concluded that the quasi-chemical approach was a slight improvement on his original model but still fell far short of accounting for the measured values of ε. He suggested the following possible reasons for the discrepancies in the calculated and measured values of ε.

(a) The energies associated with the pairwise interactions between the atoms of the ternary may differ from those for the three separate binaries.

(I) The solute-solvent interactions may vary with the proportions of each solvent atom about the solute.

(II) The interactions between unlike neighbouring solvent atoms in the co-ordination shell around each solute atom may be different from those between unlike solvent atoms in the remainder of the solution.

(b) The co-ordination number for the solute z_s may be different from those for the other atoms of the solution.

(c) The number of strong pairwise interactions about any solute atom may be much less than the co-ordination number.

From consideration of the above possibilities Alcock concluded that the extent to which the pairwise interaction energies change with composition depends on the chemical properties. If this is correct the next task would seem to be to relate these changes in interaction energy with the positions of the components in the periodic table.

Ohtani and Gokcen (ref. 25) plotted the interaction parameters, ε , for the iron-oxygen-x, iron-carbon-x, iron-nitrogen-x, iron-sulphur-x and iron-hydrogen-x, where x is a dilute element, against the atomic number of element x. These plots showed that the interaction parameters for dilute ternary solutions of "2" and "x" in liquid iron followed a regular periodic pattern. By means of this periodic pattern it is possible to discard certain sets of data for an element if they are completely discordant and thus select the better fitting data, provided that the periodic correlations are based on adequate and reliable data. In addition, either by extrapolation or interpolation it is possible to make approximate predictions of the parameters of elements for which there are no experimental results.

From the discussion in this chapter it can be recognised that more variable parameters than originally anticipated must be included in the theoretical development of a model for ternary metallic solutions. Furthermore the complicated theoretical treatment required to include the variation of these parameters would appear to preclude the development of a model at the present time. Until a better understanding of the nature of these interactions has been obtained the most fruitful approaches for metallurgists appear to be those suggested by Alcock and Richardson (ref. 5) and Gokcen (ref. 25). The results of this investigation will be examined by means of the relationships suggested by the above workers.

CHAPTER 2

EXPERIMENTAL METHODS

1. Selection of Method

The object of this research as previously stated was to study the equilibrium;

$\frac{1}{2} O_2 (g) = [O]$ Molten copper or one of its alloys.

The oxygen potentials required in this investigation were too low for direct determinations by Sievert's method (ref. 26) and an indirect method such as;

$CO_2 (g) = [O]$ Copper or alloy $+ CO (g)$

had to be used. The points outlined by Richardson and Alcock (ref. 27) were considered in selecting the gas mixture. These points can be summarised as follows:

1. The thermodynamic properties of the gas mixture should be well known.

2. Other factors introduced into the system, such as a second potential, should be negligibly small and unimportant.

3. The making, controlling and analysing of the gas mixture should be as simple as possible.

4. The gas mixture should have a reasonable capacity for transporting the desired element to and from the

condensed phase.

These considerations were best satisfied for this investigation by a gas mixture of carbon monoxide and carbon dioxide.

The design of the apparatus was considerably simplified by previous work in this department by Tomlinson and Monro (ref. 28). They had shown that small beads of molten copper could be equilibrated with a circulating gas mixture of carbon monoxide and carbon dioxide. This apparatus was found to be suitable for investigations up to 1300°C and CO_2/CO ratios from 100/1 to 1000/1: (corresponding to oxygen pressures of $10^{-5.7}$ and $10^{-3.7}$ atm. respectively at 1300°C). At higher temperatures and lower oxygen pressures this method was unsatisfactory and a second apparatus was designed for these conditions.

Conventional pattern capillary flowmeters were used in the second apparatus to obtain the required CO_2/CO ratios. The gases were bubbled to waste after equilibration with the molten metal.

The description of the experimental procedures used in this research can be broadly divided into two parts. The first part covers the methods used to equilibrate the molten copper or alloys with the CO_2/CO gas mixture, and the second the analytical techniques used for determining the CO_2/CO ratio, the oxygen content of the equilibrated metal, and the chemical composition of the alloys. After a preliminary section on the materials used and their preparation, the experimental apparatus and procedures will be described in the above order.

2. Preparation of Materials

All the metals used in this research were spectrographically standardised materials supplied by Johnson, Matthey and Co. Ltd.

The copper beads were prepared from spectrographically pure 7 mm diameter rods. The surface layer of the rods was removed with a clean file and small lengths were cut off with a clean high speed hacksaw blade. The copper beads produced in this manner weighed one to two grams. The beads were always handled with clean tweezers to avoid contamination and stored in a desiccator if not used immediately.

The alloys were made by weighing small pieces of the pure metals and placing in close contact in the wells of the fired alumina boat used in the equilibration apparatus. The small pieces of metal were obtained by cutting 1 mm thick spectrographically pure sheet with strong tin-snips. This method of producing alloys was found to be successful and was simpler than trying to prepare an homogeneous alloy.

Great care was taken during the preparation of the samples to avoid any contamination. This was very important since the metal specimens used in this investigation weighed only one or two grams and any introduced impurities could have a large effect on the purity of the metal beads and significantly change the equilibria.

3. Circulation Apparatus

The apparatus (Fig. 1) consisted of a vacuum tight circulation system in which the gas flow rate and composition could be varied. The apparatus could be evacuated and filled or flushed with carbon dioxide. Two furnaces were required, the first F2 for heating the nickel + nickel oxide regenerator which controlled the gas mixture composition and the second F1 for heating the metal beads to an accurately known and controlled temperature.

a) The Equilibration Furnace. The horizontal furnace F1, in which the metal beads were brought to equilibrium with known CO_2/CO gas mixtures, was a platinum wound furnace (Type T68, Johnson and Matthey Ltd.) capable of operating up to 1500°C. The furnace winding tube was 2" i.d. x 20" long. An inner, gas tight, mullite tube, 1½" i.d. x 25" long, acted as the reaction tube. The tube was positioned centrally so

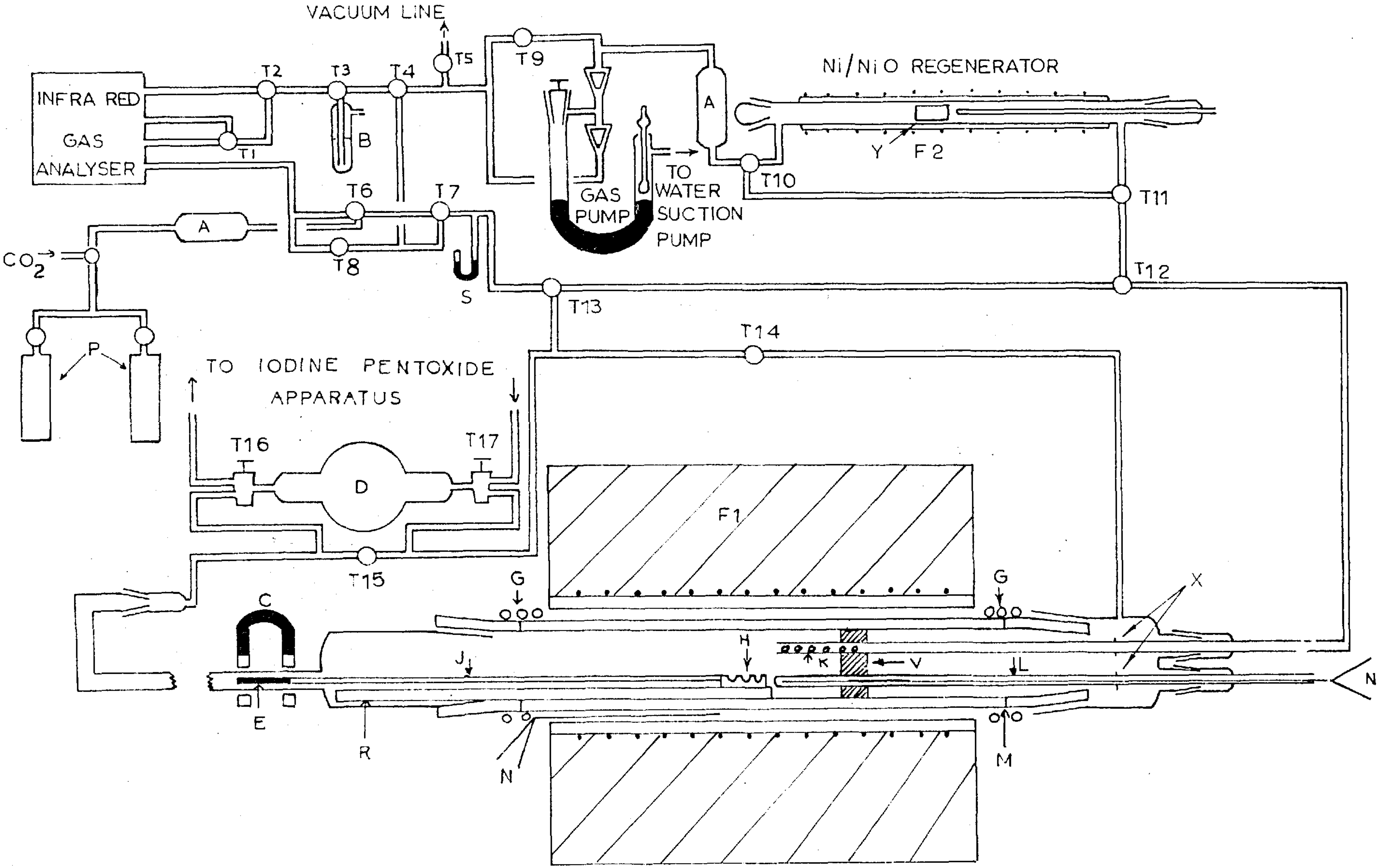


FIG. 1 GAS CIRCULATING APPARATUS

LEGEND TO FIGURE 1

A	Drying agent, magnesium perchlorate
B	Blow-off, dibutyl phthalate
C	Magnet
E	Soft iron rod
F1	Equilibrium reaction furnace
F2	Regenerator furnace
G	Compo water cooling coil
H	Specimen holder
J	Specimen holder rod
K	Mullite gas inlet
L	Mullite thermocouple sheath
M	Glass to mullite joint (Araldite)
N	Pt/Pt+13% Rh thermocouple sheath
P	CO_2/CO standard gas mixture cylinders
R	Alumina "gutter"
S	Mercury manometer
T	High vacuum taps
V	Alumina support and radiation shield
X	Glass to mullite joint
Y	Ni+NiO for generating CO_2/CO gas mixture

that 2½" projected beyond each end of the wound tube and was held firmly in place by a clamp at each end. Convection currents between the two tubes were reduced by packing asbestos wool into the annular gap at the ends. In order to join the remainder of the apparatus to the reaction tube, a B45 pyrex cone was sealed with Araldite to one end and a B45 socket to the other. The joints were cooled by water passing through compo tubing wound on copper foil. A pyrex B45 socket with two B14 cones blown on the end and a gas outlet on the top, fitted onto the B45 cone of the reaction tube. The gas inlet tube (K) was a 5 mm i.d. mullite tube. The inside of this tube was packed with small pieces of mullite to stir and preheat the incoming gas mixture. At the cool end of the furnace the tube (K) was joined by a'glass to mullite seal' (X), to a short length of similar bore pyrex tubing which in turn was internally sealed to a B14 socket. Similar tubing was blown on the other side of the socket and joined the equilibration furnace with the remainder of the circulation system. The measuring thermocouple sheath (L) was a closed 5 mm i.d. mullite tube and was fitted into the reaction tube in a similar manner to that described for the gas inlet tube, (K). The thermocouple and gas inlet sheaths extended ½" into the uniform temperature zone of the reaction tube. A fired alumina cement block (V) was used as a support and radiation shield. At the other end of the reaction tube an 8 mm i.d. x 27" long pyrex tube was sealed onto a B45 cone which fitted into the outlet socket. The last 6" of the pyrex tubing was bent through 180^{o} and joined to a B10 cone which connected to the remainder of the circulation system. The pyrex tubing was used for holding the rod (J) of the specimen holder and had to be carefully aligned with the reaction tube.

A length was cut from a clean discarded alumina tube to form a "gutter" (R) which lay along the bottom of the reaction tube. The "gutter" protected the reaction tube from thermal shocks when the specimen holder was introduced and removed from the furnace.

The specimen holder was constructed from a RR alumina boat and a 3 mm o.d. x 18" long mullite sheath. The end of the boat was cut off by means of a diamond wheel and the rod (J) cemented into the boat with pure alumina cement. Three ½" dia. x ¼" deep holes were drilled in the dried cement and the assembly fired at 1400^{o}C for 12 to 18 hours. After cooling a 3 mm o.d. x 2" long rod of soft iron (E) was sealed with Araldite to the end of the mullite rod.

The temperature of the furnace was controlled by a Kent "Multilec" controller operating from the E.M.F.

of a thermocouple (N) positioned in the hot zone of the annulus between the reaction and furnace tubes. The controller opened or closed a Sunvic hot wire vacuum switch depending on the temperature of the furnace. To improve control, a resistance of approximately $\frac{1}{4}$ that of the furnace winding was placed across the terminals of the vacuum switch so that when the switch was open the furnace winding was not completely disconnected from the power supply, but 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 64% of that in the ON position. This gave temperature control such that the temperature of the furnace varied less than $\pm$ 2°C at 1300°C. The uniform temperature zone of the furnace was found to be $1\frac{3}{4}$" long and the mean temperature variation of this zone was not more than ± 2°C.

b) <u>Regenerator</u>. The regenerator utilized the reaction:

CO_2 (g) + Ni (s) = NiO (s) + CO (g) for which $K_p = P_{CO}/P_{CO_2}$, where K_p is dependent only on temperature.

The regenerator furnace was a 1" i.d. x 20" long horizontal gas tight mullite tube wound with kanthal wire and thermally insulated by asbestos rope. The uniform temperature zone of this furnace was improved by wiring a sixty watt electric light bulb in parallel with the central four inches of the windings. A B29 pyrex socket with a short length of pyrex tubing blown on one side was joined by a "glass to mullite seal" to the gas inlet end of the furnace and on the other end a B19 socket with a short pyrex sidearm was similarly attached.

The regenerator was closed by a sealed B29 cone on the inlet side. The outlet side was closed by a B19 socket joined to a mullite thermocouple sheath. The mullite sheath extended ½" into the uniform temperature zone and protected a Pt/13%Pt/Rh thermocouple.

The regenerator source (Y) consisted of 20 gauge nickel wire coiled inside a 7/8" o.d. x 2" long open ended cylinder of pure nickel sheet. A few lumps of solid nickel oxide were interspersed amongst the coils. The source was placed in the uniform temperature zone and positioned so that it just touched the end of the thermocouple sheath.

The furnace temperature was controlled to ± 2°C by a Sunvic "TYB" regulator which operated a Sunvic vacuum switch. The Sunvic "TYB" regulator is a simple ON-OFF control whose cycle is determined by the expansion of a bifiliar element which on heating, bends and breaks contact between the furnace and the power supply. The time to bend the bifiliar strip a given amount depends on the quantity of heat supplied to it, and since this depends on the heat generated in a fixed resistance by the mains voltage, the On-OFF time cycle varies with, and compensates for variations in the mains voltage. The "TYB" regulator was used to open and close the Sunvic vacuum switch which made or broke contact between the furnace windings and the output of a variac transformer. The temperature of the regenerator was thus determined by the voltage supplied by the variac and made insensitive to small changes in this voltage by the "TYB" regulator.

c) Gas Circulation System. This constituted the rest of the apparatus. It can be seen from Fig. 1 that it consisted of equipment for moving, analysing, and measuring the pressure of the gas phase, and gave facilities for evacuating the apparatus, introducing carbon dioxide and drying the moving gas during an experiment.

The gas pump was of conventional design and is described in (ref. 29). The mercury column of the pump oscillated with an amplitude of about ¾" and flowrates of up to 750 c.c./min at N.T.P. could be achieved despite the resistance presented by the many taps in the system.

The circulating gases were dried by magnesium perchlorate placed in a drying tower (A) positioned between the gas pump and regenerator.

The gas sample bottle (D) was a glass bulb of known volume which was connected to the circulation system via taps T_{16} and T_{17}. These two-way taps permitted either the circulating gas mixture or pure nitrogen to pass through the bulb. The pure nitrogen was used to flush the contents of the bulb into the Iodine Pentoxide Apparatus. Tap T_{15} permitted the circulating gas to by-pass the analysis volume while the above operation was carried out.

Tap T_5 connected the system to an Edwards, two-stage, rotary vacuum pump. This could reduce the pressure in the apparatus to 10^{-2} mm in about twenty minutes. The mercury manometer (S) was used as an approximate vacuum gauge and for checking the rate of gas leakage into the sealed evacuated system.

The taps T_3, T_6 and T_8 permitted the Infra Red Gas Analyser to be flushed with carbon dioxide or one of the standard gas mixtures while the remainder of the apparatus was being evacuated or an experiment was in progress. The evacuated part of the apparatus was filled with carbon dioxide via tap T_8. The blow-off (B) was filled with di-butyl phthalate and indicated when atmospheric pressure was reached.

The remaining taps T_4, T_7, T_9, T_{10}, T_{12}, T_{13} and T_{14} were used for by-passing the various pieces of apparatus in the circulation system. The by-passes simplified leak testing by allowing the various pieces of apparatus to be tested in turn.

d) Experimental Procedure. Three beads of copper, or the weighed alloys, were loaded into the small wells of the fired alumina boat. The boat holder was placed in the glass container which joined the reaction tube to the circulation system. The boat was carefully positioned on the "gutter" of the reaction tube before pressing the cones of the glass container into their respective sockets on the apparatus. These cones were cleaned before each experiment and covered with a thin layer of silicone grease to obtain a vacuum tight seal.

The Infra Red Analyser was isolated from the circulation apparatus by taps T_3, T_6 and T_8 and flushed with carbon dioxide. After approximately five minutes the zero of the analyser was adjusted and the instrument calibrated with the standard gas mixtures. The analyser was reflushed with carbon dioxide and the vacuum pump started. The apparatus, with the exception of the Infra Red Analyser and the gas circulation pump, was then evacuated by opening tap T_5 to the vacuum pump. A "Tesla" coil was used to check the evacuated apparatus for leaks and to obtain an approximate indication of the pressure. After sealing any leaks, the gas-pump was evacuated in the following manner. The valve of the float-chamber was sealed with "Q" - compound and the rubber line joining this chamber to the water suction pump was closed by a clip. The water suction pump was started and the clip carefully opened until the mercury in the float chamber reached the float. The clip was retightened and the tap of the gas pump opened until the mercury was level again. The tap was closed and the cycle repeated. The pressure in both limbs of the pump was progressively reduced in this manner and after four cycles the gas tap and steel clip could be left fully open without any danger of the mercury being sucked out of the pump. When the "Tesla" coil discharge indicated a pressure less than 0.01 mm Hg the gas pump tap was closed and the vacuum pump isolated by turning tap T_5. The absence of leaks was frequently checked by ensuring that there was no change in the mercury manometer over a period of six hours.

The evacuated apparatus was slowly filled with carbon dioxide by opening tap T_8. The blow-off (B) indicated when atmospheric pressure was reached. The chamber of the gas pump was filled with carbon dioxide by tightening the steel clip on the rubber tubing, disconnecting the water suction pump and using the reverse of the evacuation procedure. The apparatus, now filled with carbon dioxide at one atmosphere pressure, was isolated from the carbon dioxide supply line by turning tap T_6 through 90°.

The taps of the apparatus were positioned so that the gas mixture would circulate through the analyser, gas pump, regenerator, reaction tube and gas sample bottle.

The gas circulating pump was set in operation by removing the "Q" - compound from the valve and reconnecting the rubber tubing to the water suction pump. The alumina boat was moved along the "gutter" into the uniform temperature zone of the furnace by means of a magnet (C) which formed a magnetic couple with the soft iron rod (E) of the speciment holder. After fifteen minutes the temperatures of the regenerator and reaction furnace were measured and the control settings adjusted to obtain the required values. The temperatures of the regenerator and reaction furnace were checked at half hourly intervals. The reading of the Infra Red Analyser was recorded every fifteen minutes. The dead space of the reaction tube was flushed out at regular intervals by opening tap T_{14}.

When the Infra Red Analyser showed a constant reading, the regenerator was by-passed by turning taps T_{10} and T_{11} and the analyser carefully observed to detect any change in the reading. In the initial experiments the furnace was then by-passed and the regenerator reintroduced into the circulating system and the analyser observed to detect any changes in the gas mixture composition. This procedure was a very good check that equilibrium had been established. The Infra Red Gas Analyser was isolated from the circulation system and the calibration checked with the standard gas mixtures. The original circulation pattern was then restored and the temperatures of the regenerator and reaction tube, and the reading of the analyser were carefully recorded for a further half hour. At the end of this period the temperature of the gas sample bottle was recorded and the gas-pump stopped. Taps T_{16} and T_{17} were closed and tap T_{15} opened. The alumina boat was then quickly withdrawn into the cool end of the reaction furnace by means of the horse-shoe magnet. The metal specimens solidified very rapidly and were allowed to cool for fifteen minutes. The gas-pump tap was then closed and the apparatus opened to the atmosphere by removing the glass chamber containing the specimen holder. The metal specimens were removed from the wells of the fired alumina boat with clean tweezers and placed into clean platinum cups. The platinum cups were placed on a brass block inside a desiccator. The specimens were then analysed for oxygen by a method which will be described in a later section.

The atmospheric pressure at the end of the experiment was measured with a barometer and the carbon monoxide content of the gas sample determined by the Iodine Pentoxide method described in the gas analysis section.

4. Flowmeter Apparatus

a) Equilibration Furnace. A diagram of the apparatus is shown in Fig. 2. The horizontal furnace T, in which the metal beads were brought to equilibrium with known CO_2/CO gas mixtures was the same as F1 previously described on page 22. An inner, gas-tight RR alumina tube, 1½" i.d. x 25" long, acted as the reaction tube and was positioned so that 2½" projected beyond each end of the wound furnace tube. A pyrex B45 cone was sealed with Araldite to one end of the reaction tube and a heavy water cooled brass vessel, which acted as a quenching block, to the other end. The joints were cooled by passing water through compo tubing (G) wound on copper foil. A B45 socket with two B14 sockets blown on one end and a pyrex tubing side-arm at the top, fitted onto the B45 cone of the reaction tube. The gas inlet tube (C) was a 5 mm i.d. R.R. alumina tube and contained a few pieces of broken alumina to stir and preheat the incoming gas mixture. This tube (G) and the thermocouple sheath (E), which was a 5 mm i.d. closed end RR

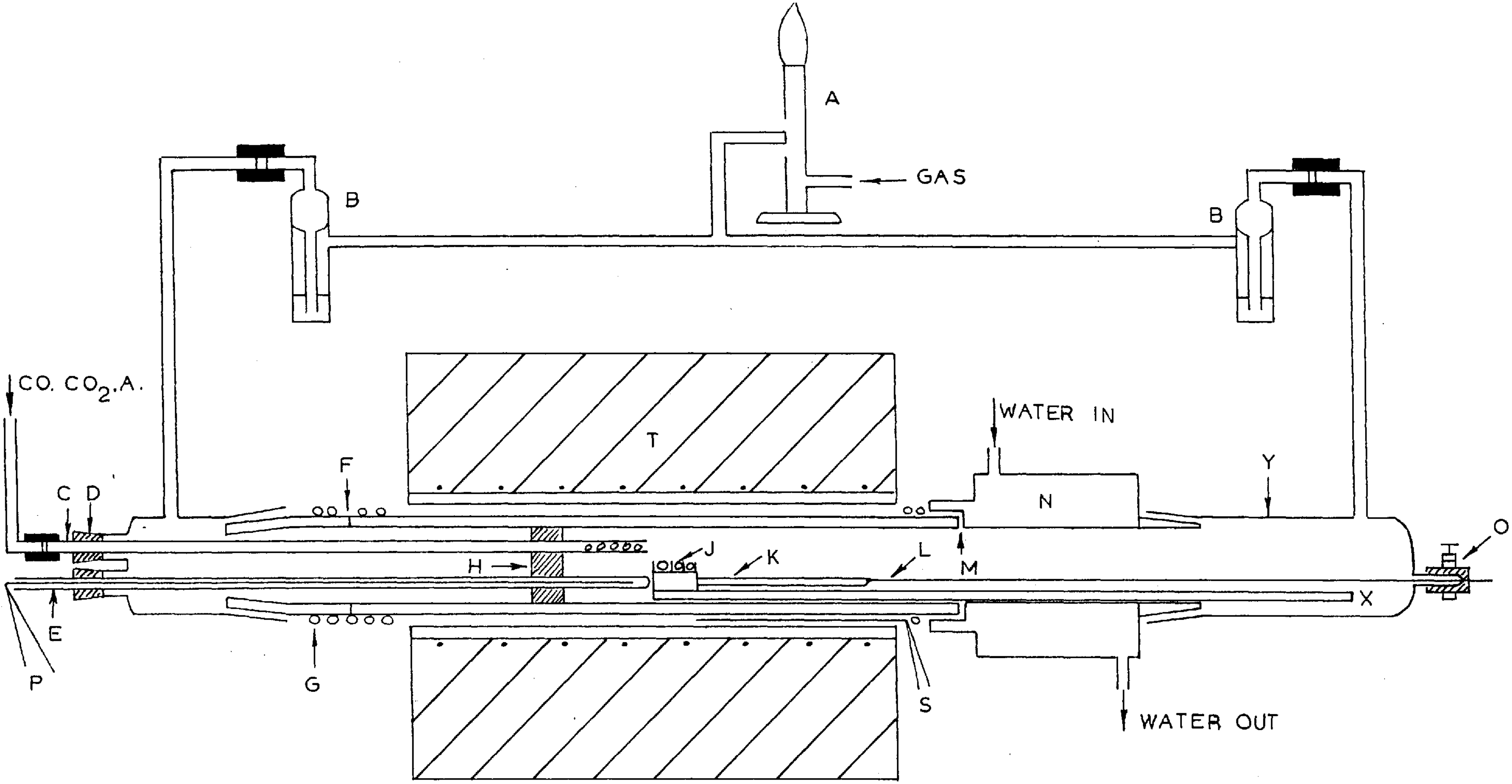


FIG. 2. EQUILIBRATION FURNACE

LEGEND TO FIGURE 2

A	Bunsen burner
B	Bubbler
C	Alumina gas inlet tube
D	Rubber bung
E	Alumina thermocouple sheath
F	Glass to mullite joint (Araldite)
G	Compo water cooling coil
H	Alumina support and radiation shield
J	Specimen holder
K	Specimen holder rod
L	Platinum wire
M	Mullite to brass joint (Araldite)
N	Water cooled brass block
O	Steel screw-up clip
P	Pt/Pt+13% Rh thermocouple sheath
S	Control thermocouple
T	Equilibration furnace
X	Alumina "gutter"
Y	B45 socket

alumina tube were sealed into the reaction tube by two rubber bungs (D) which fitted into the B14 sockets. The rubber bungs were coated with "Silastomer" to form a gas tight seal. The two tubes were supported in the reaction tube by a fired alumina cement block (H) which also acted as a radiation shield. The end of the brass quenching chamber was machined to give a gas-tight fit with a B45 socket. This socket had a 1 mm capillary blown on the end and a pyrex tubing side-arm at the top. The side-arms at each end of the furnace allowed the reacted gases to pass to waste. The waste gases were passed via bubblers (B) to a bunsen burner (A) where the carbon monoxide was burned. The reaction tube was protected from thermal shocks by a RR alumina "gutter" (X).

The specimen holder was constructed from a RR alumina boat and a 3 mm o.d. x 7" long alumina rod. The end of the boat was cut off by means of a diamond wheel and the rod cemented onto the boat with pure alumina cement. Three ½" dia. x ¼" deep holes were drilled in the dried cement and the assembly fired at 1400°C for 12 to 18 hours. After cooling a long length of platinum wire (L) was attached to the end of the alumina rod (K) and the specimen holder was ready for use. The platinum wire from the specimen holder passed through the capillary of the B45 socket which fitted onto the brass quenching block. A short length of rubber tubing fitted onto the capillary and a fairly efficient gas seal was obtained by using a steel screw clip (O).

b) Gas Train. The gas train is shown diagrammatically in Fig. 2A. This consisted of equipment for purifying and metering the gases before use in the equilibration furnace. The gases carbon dioxide, carbon monoxide and argon, were obtained from cylinders and maintained at constant pressure by means of the blow-offs (B). Pure commercial gases were used. The carbon dioxide contained on average 99.5% of carbon dioxide, the remainder being mostly air. The carbon monoxide was guaranteed to be not less than 99%, and the maximum impurity contents were 0.2% carbon dioxide, 0.15% oxygen and 0.6% nitrogen. The carbon monoxide gas was passed through a column containing Sofnolite (sodium hydroxide plus an indicator supported on an inert base) to remove carbon dioxide and a drying tower containing silica gell and magnesium perchlorate to remove water. The carbon dioxide and argon were dried by silica gell and magnesium perchlorate. The oxygen in the argon was removed by passing the gas over titanium granules held in an alumina tube heated to 800°C by a small Kanthal furnace (H). The oxygen in the carbon dioxide was removed by

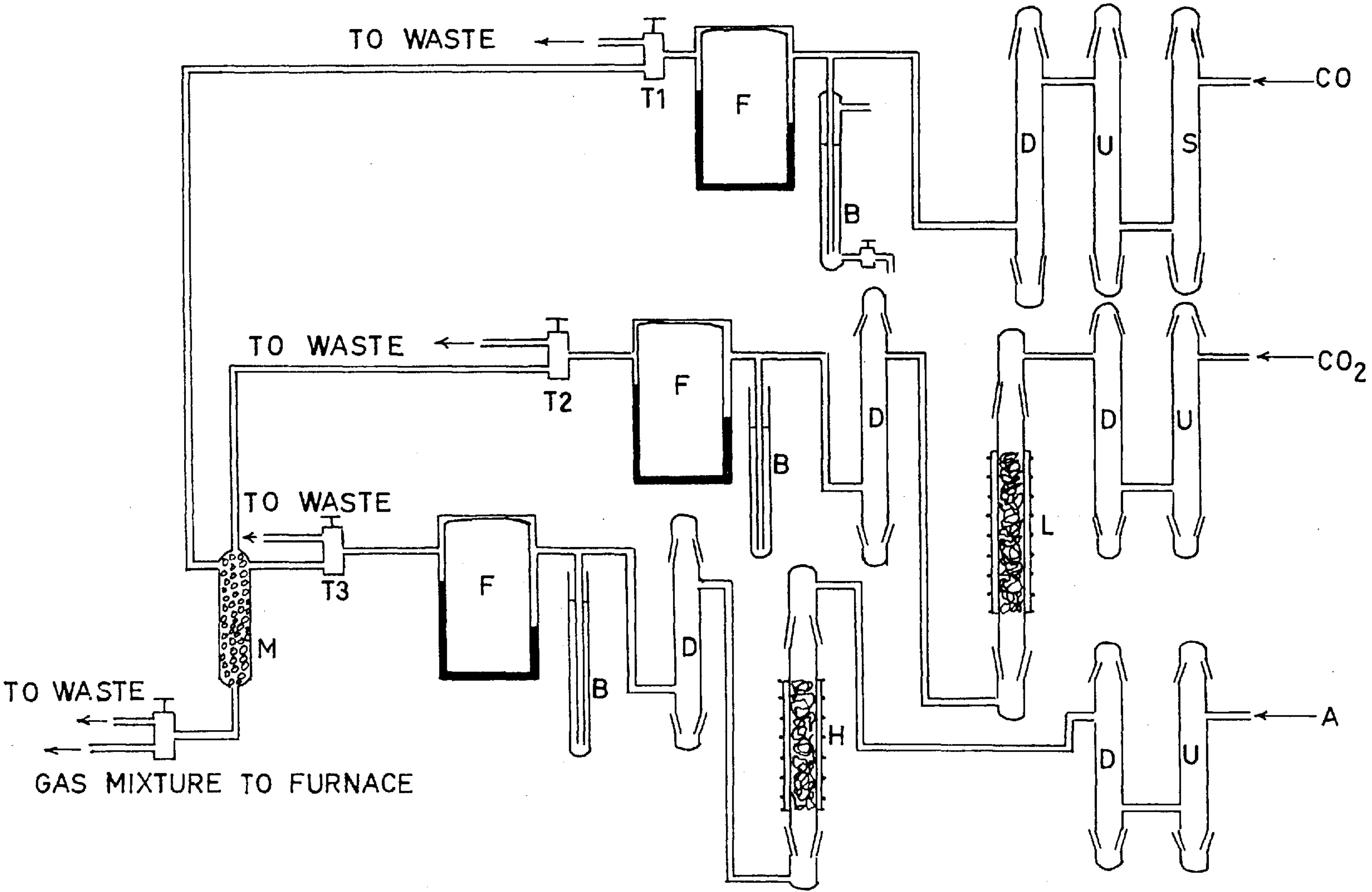


FIG. 2A GAS TRAIN

LEGEND TO FIGURE 2A

B	Blow-off, dibutyl phthalate
D	Drying agent, magnesium perchlorate
F	Flowmeter
H	Titanium granules furnace
L	Copper furnace
S	"Sofnolite" tower
U	Drying agent, silica gel

passing the gas over copper turnings held in an alumina tube heated to 600°C by a small Kanthal furnace.

The gases from the purification trains were metered by conventional pattern capillary flowmeters (F) and mixed in the mixing chamber. The manometers of the flowmeters and the "blow-offs" were filled with di-butyl phthalate. The carbon monoxide "blow-off" was sealed from the atmosphere to allow the "blown-off" gas to be burned in a bunsen burner.

The number of joints in the apparatus was kept to a minimum and all joints and leads were made with P.V.C. (polyvinyl chloride) tubing. The apparatus was checked at frequent intervals for leaks.

c) Experimental Procedure. The copper beads and alloys were prepared in the same manner as previously described for the circulation apparatus experiments.

Single copper beads, approximately three grams in weight were used for the copper oxygen experiments at 1300°C. 1400°C and 1500°C. The copper was loaded into the well of the fired alumina specimen holder. The B45 socket was removed from the quenching chamber and the specimen holder placed on the "gutter". Argon was passed through the furnace at 500 ml./min. and the specimen holder pushed into the centre of the furnace with an alumina push-rod. The push-rod was then removed and the platinum wire attached to the specimen holder threaded through the capillary of the B45 socket. The socket was replaced and the capillary made gas tight by screwing up the steel clip on the rubber tubing. The carbon monoxide and carbon dioxide were then connected to the equilibration apparatus by turning taps T_1 and T_2. The flowmeter manometers were checked and corrected by adjusting the heights of the dibutyl phthalate in the "blow-offs". The gas flowrate was 500 ml./min. and contained 50% argon. The argon was used to decrease the carbon potential of the mixture and to help in reducing the demixing of the gases by thermal diffusion. These effects were negligible for the CO_2/CO ratios used in the pure copper investigations but became increasingly important in the transitional metal-copper alloy studies where much lower CO_2/CO ratios had to be used.

At the end of the equilibration period the carbon monoxide and carbon dioxide flow was stopped and the screw-clip attached to the rubber tubing on the capillary unscrewed. The boat was pulled into the quenching chamber by means of the platinum wire and the screw-clip quickly retightened. The boat was allowed to cool for fifteen minutes before the B45 socket was removed. The equilibrated metal beads were then removed from the boat with clean tweezers and placed in small platinum cups seated on a heavy brass block inside a desiccator.

The procedure for the alloys was similar in that the metals forming the alloys were weighed and placed into the small wells of the boat. Three alloy beads of approximately the same composition were equilibrated at the same time. After quenching, two of the beads were used for oxygen analysis and the third for chemical analysis to determine the change in composition of the alloys.

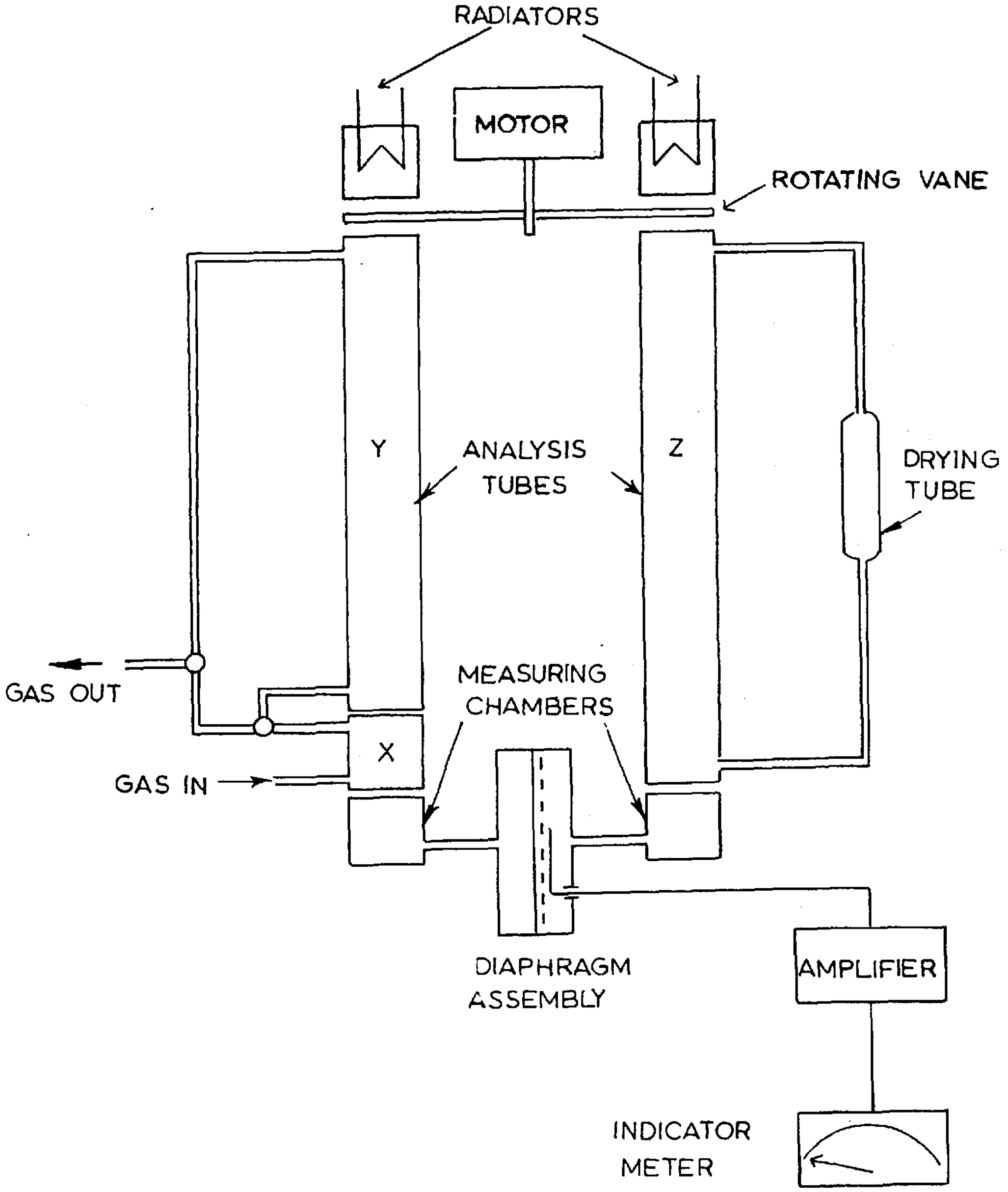
The changes in weight of the alloys equilibrated at 1200°C were found to be negligible with the exception of the copper-silver series. The weight losses of the copper-silver alloys were assumed to be silver and the final alloy compositions corrected on this basis.

5. Gas Analysis.

a) Infra Red Gas Absorption Analyser. The Infra Red Gas Analyser used in this investigation was the standard commercial type (SC/L5028) manufactured by the Infra Red Development Co. Ltd., Welwyn, Garden City. The method of identification and measurement of the carbon monoxide is absorptiometric in the infra red region between wavelengths of 3 and 15μ. The radiation source is a hot filament; and the portion of the spectrum examined is determined by a radiation detector. The detector is limited in response to that part of the spectrum in which the absorption bands of carbon monoxide fall, by consisting of a sample of carbon monoxide.

The instrument is shown diagramatically in Fig. 3. The radiation from one source is reflected down the absorption tube through which the gas mixture to be analysed flows at one atmosphere pressure and from the second source down a reference tube which contains dry air. The interior surfaces of the absorption tubes (X) (Y) and (Z) are rhodium plated and highly polished. Transparent mica mirrors are mounted at the ends of the tubes. To overcome the problem of measuring the small displacement of the diaphragm of the detector without errors due to zero change, the cycle of events is made to repeat itself rapidly by using a revolving shutter. The shutter is positioned between the radiation sources and the absorption tubes. The residual radiation from the absorption tubes falls onto the detector which consists of two cylindrical chambers sealed at the top by transparent mica windows. The two chambers have outlets which join to a central compartment. Across the centre of the compartment a separate assembly is mounted. This consists of a perforated and insulated plate and held close to it a stretched aluminium diaphragm which is electrically connected to the body of the unit. The two sides of the assembly are filled

FIG. 3 INFRA RED GAS ANALYSER



with pure dry carbon monoxide by the manufacturer.

The gas samples of the detector are heated by absorption of the residual radiation, and, being contained in closed chambers exhibit the increases in temperature by increases in pressure.

The diaphragm of the detector is moved by the excess of pressure on the reference side over that on the analysis side. The movement occurs periodically at the rate of "chopping" of the radiation by the shutter. The diaphragm forms one plate of a polarised electrical condenser, which consequently, by the periodic variation of its capacity produces an alternating voltage output across a load resistance. The signal is amplified to provide an indication of the difference in absorption in the two tubes. The meter of the instrument is calibrated to give a direct reading of the carbon monoxide content.

In order to increase the range and sensitivity of the instrument the analysis absorption tube is divided into two chambers, (X) and (Y) by a mica window. The gas mixture can be passed through either chamber (X) or chambers (X) and (Y) in series by means of the two three-way taps. The amplifier circuit is also designed to provide two ranges by a switch which changes the polarising voltage to the detector. The above modifications increase the sensitivity of the instrument and any of the following four scales can be used.

Range A both analysis tubes	0 - 0.03% carbon monoxide
Range B both analysis tubes	0.02-0.1% carbon monoxide
Range A small tube X	0 - 0.35% Carbon monoxide
Range B small tube X	0.2-1.2% carbon monoxide

Before the instrument can be used it has to be zeroed and calibrated with a known carbon monoxide gas sample. The instrument is zeroed by flushing dry carbon dioxide through the absorption chambers (X) and (Y) and adjusting the zero control until the meter indicates zero. The flushing is then stopped and the large chamber (Y) isolated. A known carbon monoxide gas provided by the manufacturers is flushed through the small chamber (X) and the gain of the amplifier adjusted until the correct reading is indicated on the meter. The zero setting is altered by changing the amplifier settling and the above procedure of zeroing with carbon dioxide and then calibrating with a standard gas mixture has to be carried out three to four times to obtain satisfactory accuracy. The instrument is then switched to range B and a second standard gas sample, suitable for this range, is flushed through the small tube (X). The gain control for range B is adjusted to obtain the correct reading on the indicating meter. The instrument is now ready for use.

The range of carbon monoxide determination by this instrument was ideal for this investigation and the non-destructive, instantaneous nature of the method offered several advantages over the conventional methods of gas analysis used by previous workers in this field. The stability of the CO_2/CO gas mixture could be checked by circulating the gases through the regenerator and round the apparatus until the analyser reading was constant and then by-passing the regenerator and observing the analyser for any change in reading. The time to reach equilibrium could be determined by recording the time required for the analyser to reach a constant value when an equilibration experiment was carried out. The exchange of oxygen from the metal to the gas phase on quenching could also be estimated by by-passing the regenerator a few minutes before quenching the metal sample. When the pressure in the apparatus had returned to atmospheric the gases were recirculated and the analyser reading recorded. The amount of oxygen exchanged could then be estimated from the difference in the analyser readings before and after quenching and the volume of the gas in the apparatus. The information gained by the above operations permitted the equilibrium to be closely studied and simplified the detection of faults in the apparatus.

The above advantages of the Infra Red Gas Analyser were considerably offset by the amount of time spent in maintaining and repairing the instrument. The detector unit was in frequent need of repair either from a perforated diaphragm or from leakage of carbon monoxide from the two chambers. The zero and calibration of the instrument was very sensitive to the condition of the surface of the mica windows and reflectors of the radiation sources. To overcome these problems the instrument had to be dismantled and cleaned at frequent intervals and the detector returned to the makers. The absorption cells had to be attached to the glass circulation apparatus by short lengths of high pressure rubber tubing. This was found to become permeable after a short length of time and had to be replaced. The agreement of scales A and B for the two lower carbon monoxide ranges was very poor and it was suspected that the calibration of the amplifier for range B was faulty. It was found in practice that the instrument had to be calibrated every 20 minutes and that the makers accuracy claim of 2-3% was optimistic, 5-6% being found in practice. For these reasons it was decided to place a gas sample bottle in the equilibration apparatus and use a conventional method to determine the final equilibrium CO_2/CO ratio.

b) Determination of Carbon Monoxide by the Iodine Pentoxide Method.

As previously stated in the last section, the performance of the Infra Red Gas Analyser for determining carbon monoxide concentrations, especially those less than 0.1%, was unsatisfactory and it was decided to search the literature for a suitable chemical method. Beatty (ref.30) gives a good survey of the various methods for determining carbon monoxide. This survey indicated that the Iodine Pentoxide method was the most accurate method of determining carbon monoxide concentrations up to 0.3%. From the extensive literature on this method, the apparatuses of Teague (ref.31) and Vandaveer and Gregg (ref.32) were selected for modification to meet the requirements of this investigation.

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 oxidation is rapid and quantitative.

$$5CO + I_2O_5 = 5CO_2 + I_2$$

The liberated iodine is collected and determined by a suitable method.

The apparatus is shown diagrammatically in Fig. 4. The furnace (D) was a 3½" i.d. x 9" long copper cylinder wound with electrically insulated heating element wire (F).

The bottom of the furnace was sealed off by a brazed copper plate and the space at the top with a split "Sindanyo" ring (C) which formed a close fit around the glass tubes of the "U" - tube and thermometer stem. 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 ± 3°C. The power to the furnace was controlled by a Sunvic bi-metallic strip regulator.

The "U" - tube was made of pyrex and filled with 40 gms. of granular iodine pentoxide arranged in alternate layers with glass wool. The absorption bulb (G) was 25 ml. in capacity. A sintered glass disc (H) dispersed the flowing gas into a series of fine bubble streams. The drying tubes (K) and (B) were filled with phosphorus pentoxide and magnesium perchlorate respectively. The carrier gas nitrogen was obtained from cylinders and the flowrate was controlled by means of the di-butyl phthalate "blow-off" (A).

The taps T_1 and T_2 allowed the apparatus to be flushed with nitrogen when an experiment was in progress in the equilibration apparatus. The taps and sockets before the iodine pentoxide "U" - tube were greased to obtain a good seal. The socket of the absorption bulb was

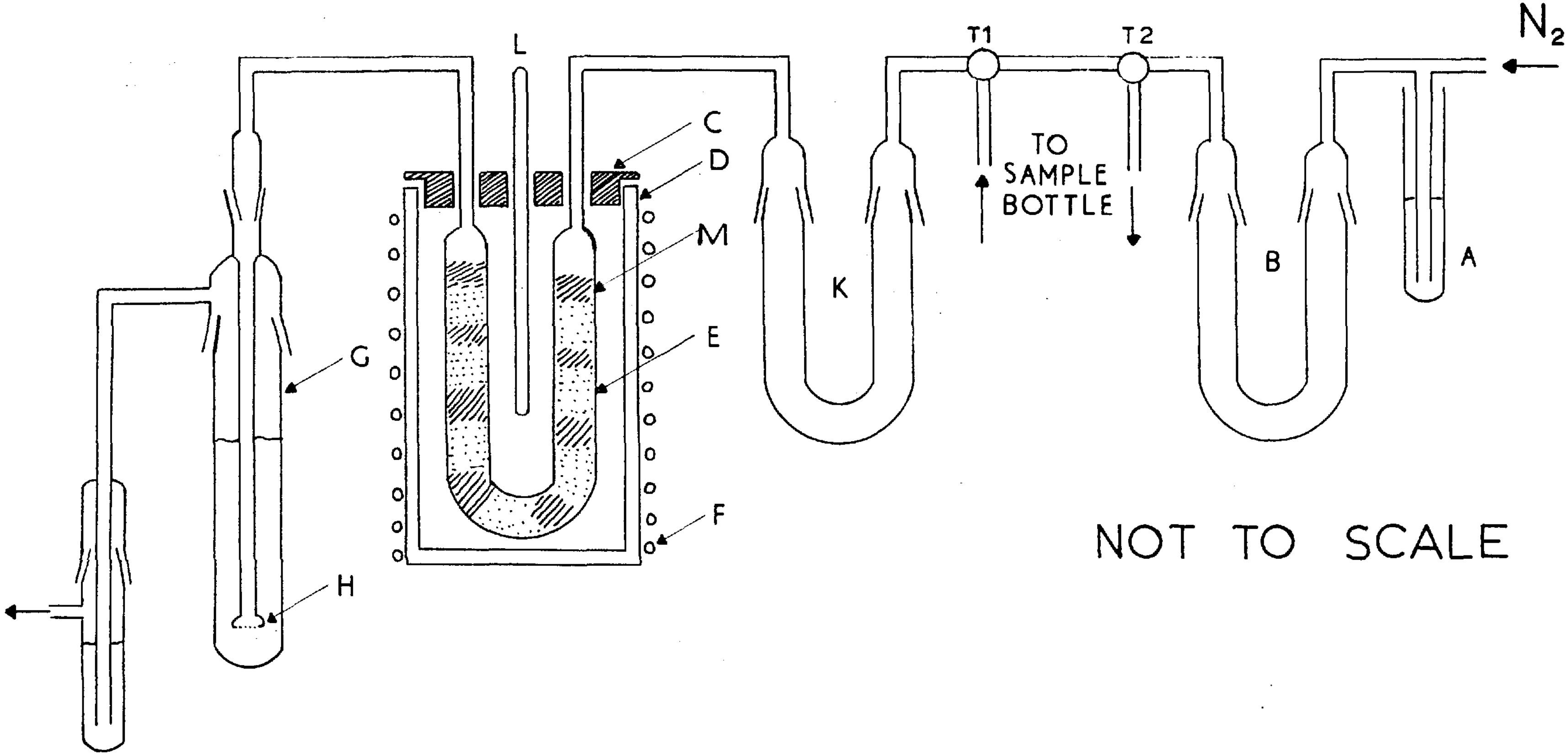


FIG. 4. CARBON MONOXIDE ANALYSIS

LEGEND TO FIGURE 4

A	Blow-off, dibutyl phthalate
B	Drying agent, magnesium perchlorate
C	"Sindanyo" top
D	Copper cylinder
E	Iodine Pentoxide Granules
F	Electrically insulated heating wire
G	Absorption bulb, 25 ml capacity
H	Sintered glass disc
K	Drying agent, phosphorus pentoxide
L	0-300°C mercury in glass thermometer
M	Glass wool

well ground to form a good seal and left ungreased to prevent the loss of iodine from reaction with grease.

In order to obtain low blank readings the iodine pentoxide had to be conditioned before the apparatus could be used for carbon monoxide determinations. This consisted of raising the temperature of the "U" - tube to 220 - 230°C. and flushing nitrogen through the apparatus until the liberated iodine blank was negligibly small. This procedure lasted 48 hours and had to be repeated if the apparatus was left unflushed with nitrogen for more than a day. At the end of the conditioning period the furnace temperature was reduced to 150°C. and a slow flow-rate, 10 ml./minute, of nitrogen was continuously flushed through the apparatus.

At the end of an equilibration experiment the sample bottle was isolated from the circulating system by turning taps T_{16} and T_{17} through 90° and opening tap T_{15}. The temperature of the thermometer suspended against the sample bottle and the laboratory pressure were measured and recorded. A clean absorption bulb was filled with 25 ml. of 5% potassium iodide solution and fitted to the apparatus. The taps T_{17}, T_{16}, T_1, and T_2 were turned so that the nitrogen carrier gas flushed the gas mixture from the sample bottle through the iodine pentoxide apparatus. The carrier gas was passed through the apparatus for one hour at a flowrate of 75 ml./minute. The liberated iodine from the reaction of the carbon monoxide in the gas sample with the iodine pentoxide was absorbed in the 5% potassium iodide solution and determined by one of the two following methods.

The starch end point method for determining iodine was used in the initial experiments. The potassium iodide solution containing the dissolved iodine was transferred from the absorption bulb to a clean 100 ml. beaker. The absorption bulb was carefully washed out and the washings added to the main bulk of solution. The solution was then titrated with 0.002N sodium thiosulphate held in a grade A 10 ml. burette graduated in 0.02 ml. divisions. When the pale yellow of the absorbed iodine had almost disappeared 5 drops of freshly prepared soluble starch were added and the titration continued. The end-point was the disappearance of the blue colour. The sodium thiosulphate was standardised daily against an accurately prepared 0.002N solution of potassium iodate.

The accuracy of the starch endpoint was unsatisfactory for carbon monoxide concentrations below 0.1% and it was decided to search the literature for a more sensitive method of determining iodine. Knowles and Lowden (ref. 33) had carried out a careful investigation of the various methods of determining iodine with sodium thiosulphate. Their conclusion was that an amperometric titration technique was the most accurate method. This could be used to detect as little as 1μ g. of iodine in 40 ml. of solution. The apparatus described in their paper was built and is shown diagramatically in Fig. 5.

The procedure used was as follows. The solution from the absorption bulb was transferred as before to a 100 ml. beaker. A known quantity of 0.002N sodium thiosulphate, slightly in excess of that required to neutralise the iodine, and 3 ml. of 2N sulphuric acid were added to the solution. The electrodes were immersed in the beaker and the stirrer and galvanometer switched on. The steady current reading of the galvanometer was recorded after each addition of 0.002N KIO_3 from the burette to the solution. The first excess drop of 0 0.002N KIO_3 caused a sharp rise in the steady current reading of the galvanometer and further additions caused corresponding rises. A plot of a typical analysis is shown in Fig. 6. At the end of the analysis the beaker was removed and the electrodes washed down with distilled water.

Tests on the potassium iodide used for absorbing the iodine had shown it to obtain a small amount of free iodine and potassium iodate which produced iodine when the solution was acidified. To correct for this and the

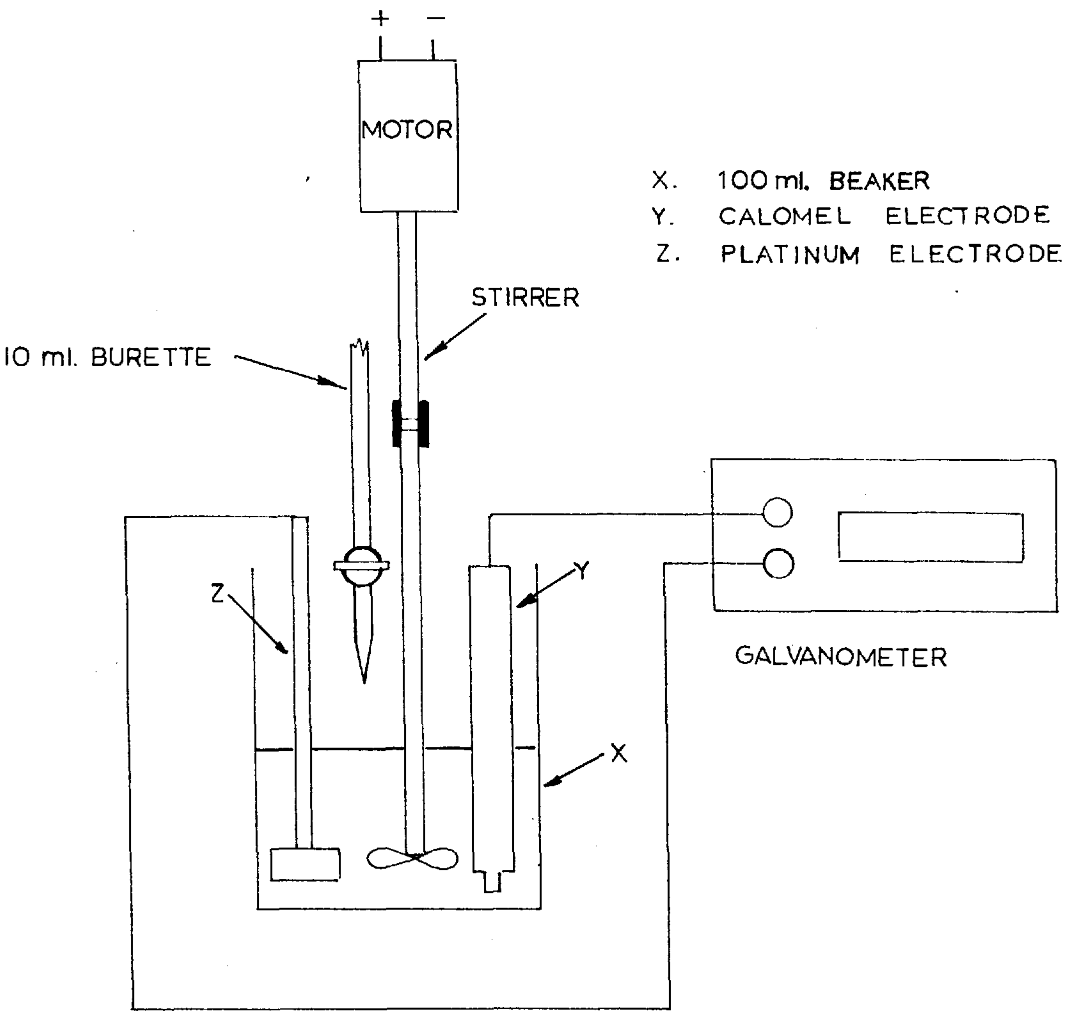


FIG. 5 AMPEROMETRIC TITRATION APPARATUS

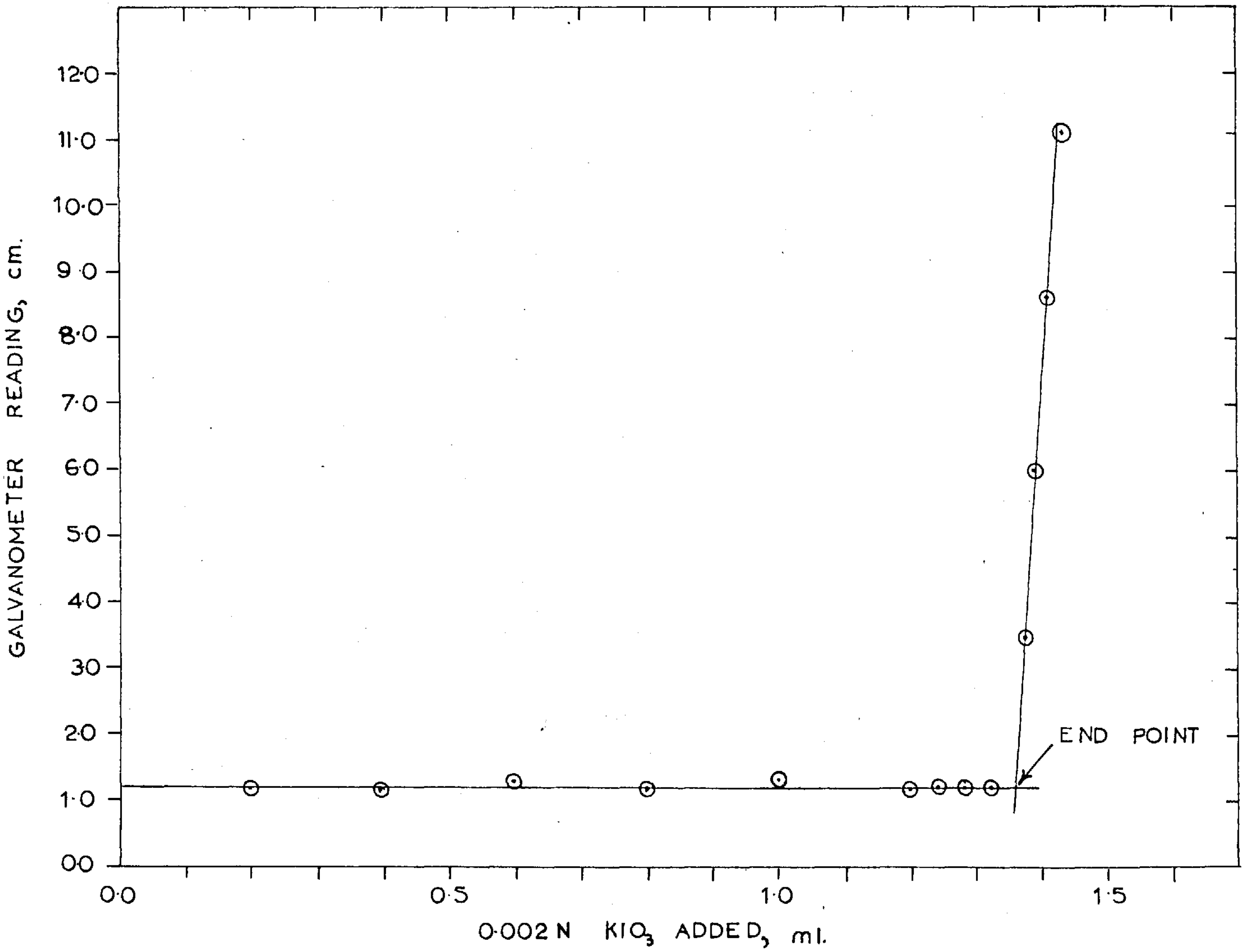


FIG. 6 AMPEROMETRIC TITRATION

blank of the iodine pentoxide apparatus, the absorption bulb was refilled with 25 ml. of 5% potassium iodide solution and replaced on the apparatus. The apparatus was flushed with carrier gas as before and at the end of one hour the absorption bulb removed. The same volume of sodium thiosulphate as used in the previous titration was added to the solution and the titration carried out as before. The volume of 0.002N potassium iodate equivalent to the iodine liberated from the reaction of the carbon monoxide with the iodine pentoxide, was obtained by subtracting the volume of the 0.002 potassium iodate used in the first titration from that in the second. By carrying out this procedure, the analysis result was corrected for any blanks in the iodine pentoxide apparatus or the chemicals used. The accuracy of the result was dependent on the sensitivity of the amperometric titration and the accuracy of the potassium iodate solution.

The following tests were carried out to determine the accuracy of the iodine pentoxide apparatus. The efficiency of the carbon monoxide conversion was checked by attaching a Hopcalite tube to the waste gas outlet of the absorption tube. Hopcalite tubes are used in carbon monoxide gas detectors and indicate the presence of very small carbon monoxide concentrations by a colour change from yellow to brown. At the end of one hour the tube showed no colour change which indicated that all the carbon monoxide in the gas sample was reacted in the iodine pentoxide "U" - tube during this period. The efficiency of the absorption tube was checked by attaching a second tube and testing this for iodine at the end of an analysis. It was found that one absorption tube was sufficient. The final test carried out was to determine a known volume of carbon monoxide from a cylinder. The results are shown below.

Volume of sample	Volume determined by I_2O_5
2.316 ml. at N.T.P.	2.305 ml. at N.T.P.
2.316 ml. at N.T.P.	2.305 ml. at N.T.P.

This corresponds to the sample containing 99.5% carbon monoxide. The average content of the cylinders was guaranteed by the producers I.C.I., to contain between 99.0 to 99.5% CO. From these tests it was deduced that the apparatus behaved satisfactorily.

6. Oxygen Analysis.

a) Hydrogen Reduction Method. The recommended standard method of determining oxygen in copper is Baker's method (ref. 34). In this procedure, the sample is heated in a closed system, in contact with a small excess of pure hydrogen, the water vapour formed is condensed, subsequently vapourised into an evacuated system, then determined by differential pressure measurements. The method is very tedious and the apparatus requires a large amount of attention to obtain satisfactory results.

Previous work in this department by Tomlinson (ref. 35) had indicated that a simple gravimetric method could be used for copper. This method was investigated and found to be satisfactory.

The apparatus is shown diagramatically in Fig. 7. The furnace (V) was an alumina tube wound with 20 gauge Kanthal wire, insulated with asbestos rope, and capable of operating to 1200°C. The reaction tube was a 1½" i.d. x 24" long impervious alumina tube with a B45 socket joined with Araldite to one end and a B45 cone on the other. The joints were cooled by passing water through compo tubing. A rubber bung which formed a tight fit with the B45 socket was used for carrying the impervious alumina gas intake (H) and thermocouple sheath (L) into the reaction tube. The tubes were supported inside the reaction tube by a fired alumina cement block. The rubber bung was firmly held in position by steel springs and coated with "Silastomer" to obtain a gas-tight seal.
The reaction tube was protected from thermal shocks by an alumina "gutter" (M). A B45 socket (P) with a short length of capillary blown on the end fitted into the B45 cone of the reaction tube.

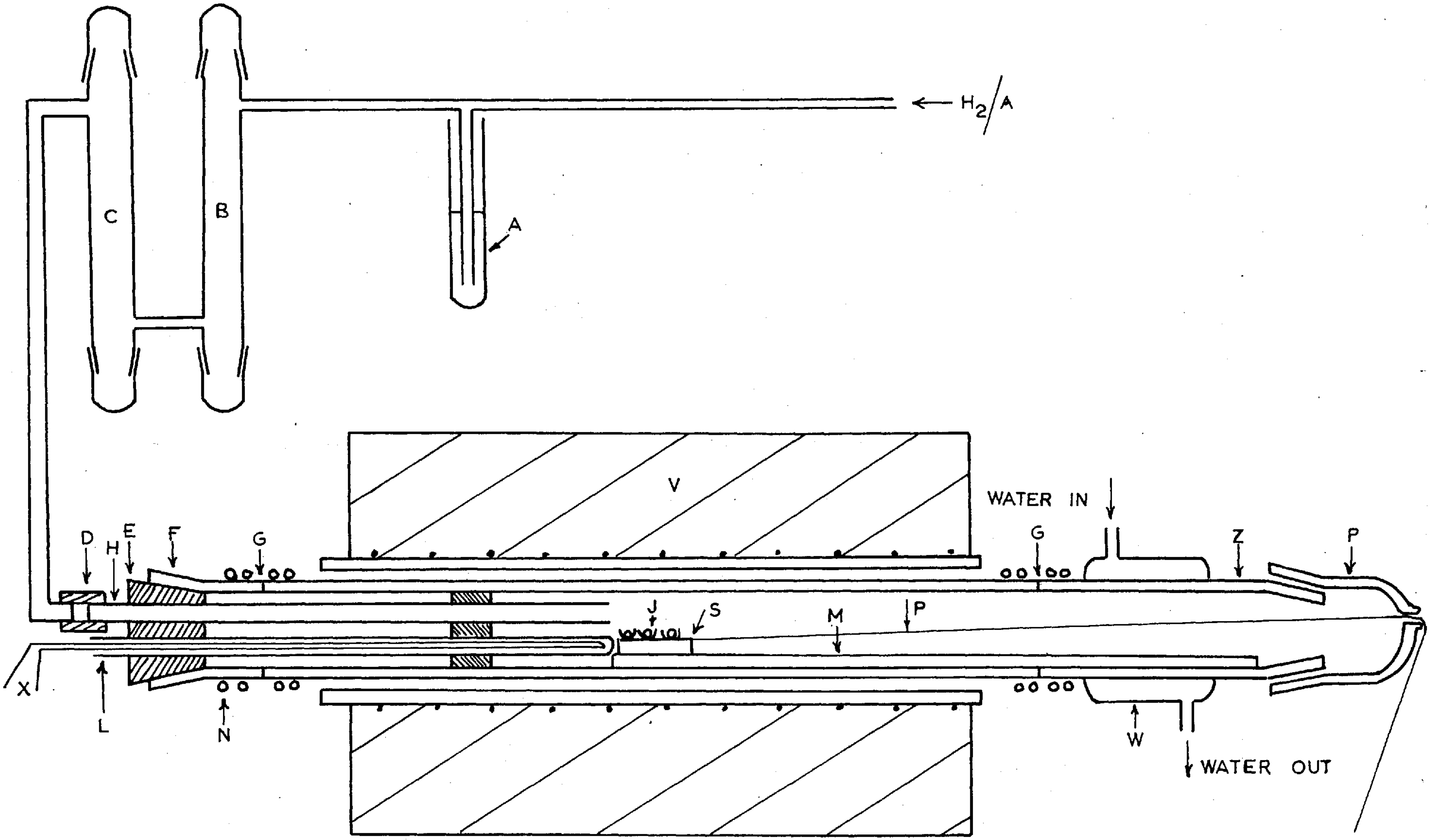


FIG. 7 OXYGEN ANALYSIS APPARATUS

LEGEND TO FIGURE 7

A	Blow-off, dibutyl phtalate
B	Drying agent, silica gel
C	Drying agent, magnesium perchlorate
D	P.V.C. Tubing
E	Rubber bung
F	B45 cone
G	Glass to mullite joint (Araldite)
H	Alumina gas inlet tube
J	Copper specimens
L	Alumina thermocouple sheath
M	Alumina "gutter"
N	Compo water cooling coil
P	B45 socket
R	Platinum wire
S	Alumina boat
V	Furnace
W	Water cooled quenching chamber
X	Pt/Pt+13% Rh thermocouple sheath
Z	B45 cone

In the preliminary experiments forming gas (90% N_2, 10% H_2) was used for reducing the copper. The forming gas was metered, dried with silica gel and magnesium perchlorate, and passed into the reaction tube. For the transitional metal alloy determinations where nitrogen is soluble forming gas is unsuitable and after the preliminary experiment it was decided to use a metered gas mixture consisting of 70% argon and 30% hydrogen. The purification of these gases consisted of drying with silica gel and magnesium perchlorate, and removing any oxygen from the argon by passing over titanium held at 900°C. The gases were then metered with conventional capillary flowmeters, mixed, and passed into the reaction tube.

Small ½" diameter x ¼" deep platinum cups were used for holding the copper beads. These cups were made with a punch and die from 5/1000" platinum sheet. The cups were cleaned by boiling in dilute hydrochloric acid, followed by washing in distilled water, drying, and finally reducing in the apparatus.

The procedure used was as follows. The B45 socket was removed from the reaction tube and the alumina boat containing the cups was pushed along the "gutter" into the uniform temperature zone of the furnace by means of an alumina rod. The platinum wire attached to the boat was threaded through the capillary of the B45 socket which was then replaced on the reaction tube. The reducing gas mixture was flushed through the reaction tube at 150 ml/min. and the furnace temperature adjusted to 1050°C. After 30 minutes the boat was withdrawn to the cool end of the reaction tube by means of the platinum wire. The boat was allowed to cool for 10 minutes before removing the B45 socket and opening the apparatus to the atmosphere. The platinum cups were removed from the boat with clean jewellers tweezers and placed on a copper block held inside a desiccator. The cups were then weighed on a semi-microbalance which had been calibrated against an N.P.L. standardised 1 mg. weight. The calibration had shown that the balance was precise to $\pm 7 \mu g$. The weighed platinum cups were replaced in the alumina boat and the same procedure of reducing and weighing carried out. When the platinum cups showed no weight change the metal beads for analysis were placed in them and weighed. The cups were then placed in the alumina boat and reduced for two hours. The same procedure as used for the platinum cups, of removing, cooling and weighing, was then carried our. A series of experiments had shown that the copper beads were fully reduced in 2 hours. A second reduction of thirty minutes was carried out however, to ensure there was no further loss in weight.

The oxygen content of the copper was determined from the difference in weight of the platinum cup and copper bead before and after reduction and the weight of the copper bead.

The blank from the loss in weight of the copper due to its vapour pressure and the gain in weight due to the solubility of hydrogen are too small to be determined experimentally. The expected size of the blank was calculated as follows. At 1050°C the vapour pressure of copper is 1.49×10^{-4} mm Hg (ref. 36). If the carrier gas is assumed to be saturated with copper vapour the weight loss in one hour is:-

$$\frac{1.49 \times 10^{-4} \times 150 \times 60 \times 63.5}{760 \times 22.400} \text{ gms.}$$

$$= 5 \times 10^{-7} \text{ gms.}$$

The solubility of hydrogen at 1050°C is approximately 2 ml. per 100 gm. (ref. 37). The weight gain due to hydrogen for a 1 gm. copper bead is

$$\frac{2 \times 0.3^{\frac{1}{2}} \text{ gms.}}{22{,}400 \times 100}$$

$$= 4.9 \times 10^{-7} \text{ gms.}$$

It may be recognised from these calculationsthat the size of the blank is very small and can be neglected.

The results obtained by this method were compared with Baker's method by analysing a standard oxygen copper sample obtained from the B.N.F.R.A. The results are shown below.

Baker's method (B.N.F.M.R.A.)	Gravimetric method
	0.0299%
0.0292%	0.0296%
	0.0292%
Average	0.0296

The difference of 0.0004% oxygen for the two methods was inside the limits of the expected experimental accuracies. From the above results it was decided that the gravimetric method could be satisfactorily used for this experimental programme.

b) <u>Carbon Reduction Method</u>. After many attempts to determine the oxygen concentration in nickel-copper alloys by the gravimetric hydrogen reduction method it was decided that the method was unsuitable. In order to reduce the nickel-rich alloys in a reasonable time period it was found necessary to raise the temperature to 1200°C. At this temperature the blank values were erratic and too high for accurate results. To overcome this problem it was decided to build a new apparatus. To compare the results obtained with this apparatus and other laboratory methods the nickel-copper beads were sealed in glass ampoules and sent to I.R.S.I.D. *

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* Institut de Recherches de la Siderurgie

and B.N.F.M.R.A. for oxygen analysis. I.R.S.I.D. determined the oxygen concentration by an inert gas fusion method and B.N.F.M.R.A. by a conventional vacuum fusion analysis apparatus.

Elwell (ref. 38) gives an excellent review of the different methods of determining oxygen in metals and from this it was decided that the most suitable method for this investigation was an inert gas fusion apparatus. The principle of this method is to reduce the metal sample in a carbon crucible heated to a temperature above the melting point of the metal and surrounded by an inert gas. The carbon monoxide formed from the reduction is flushed by the inert gas from the reaction chamber into a gas analytical train where it is determined by one of several methods. The oxygen concentration of the metal is calculated from the amount of carbon monoxide formed. The problems of designing and building this apparatus were simplified by the experience gained in determining small quantities of carbon monoxide by the Iodine Pentoxide method. The remainder of the apparatus was designed and adapted from the previous work in this field by Shanahan and Cook, (ref. 39), Smiley, (ref. 40), Singer, (ref. 41) and Peterson, Melnick and Steers (ref. 42).

The apparatus is shown diagramatically in Fig. 8. The argon flowrate was controlled by the dibutyl phthalate

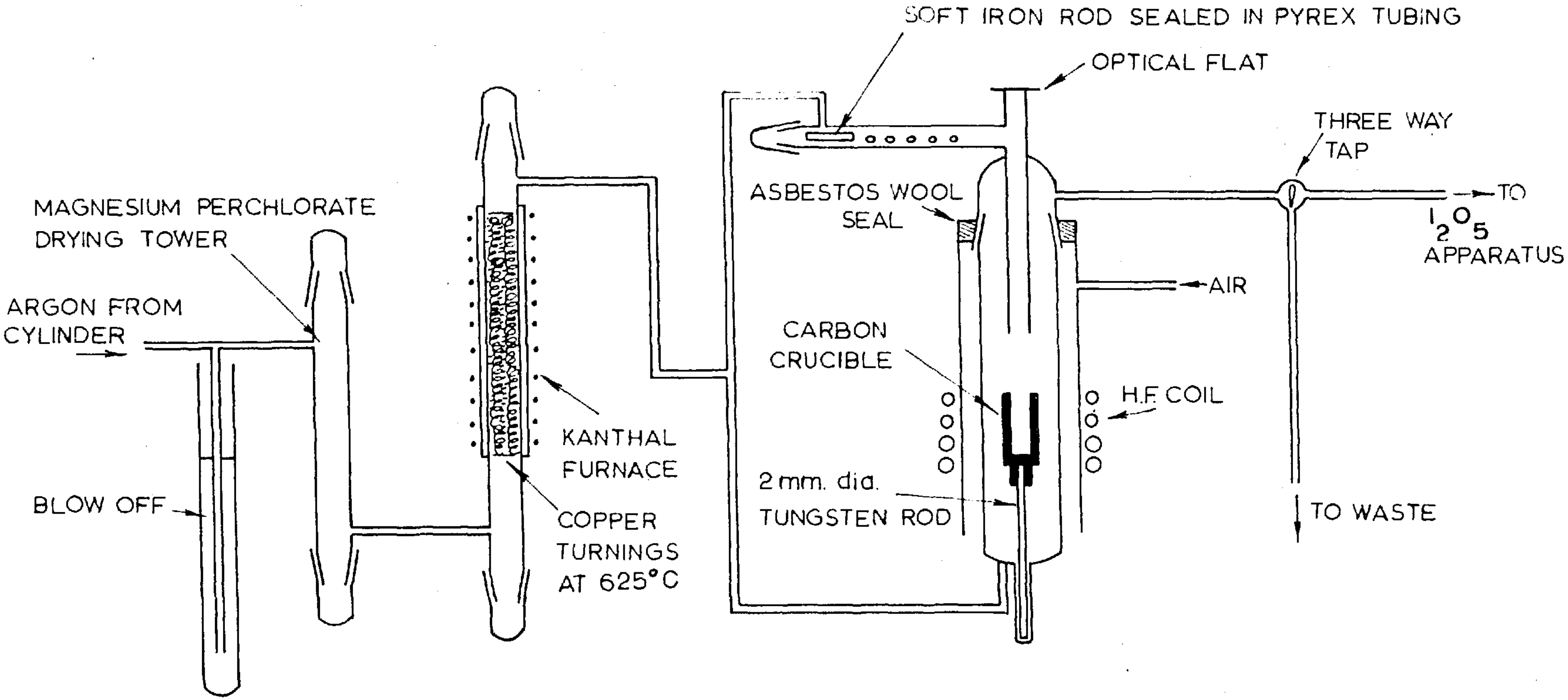


FIG. 8. INERT FUSION OXYGEN ANALYSIS APPARATUS

blowoff and the gas purified by passing through a drying tower containing magnesium perchlorate and a mullite tube containing copper gauze heated to 600°C. to remove oxygen. The mullite tube was heated by a Kanthal wound furnace whose power was controlled by a Sunvic bi-metallic strip regulator. The argon flow was divided into two and entered the reaction chamber at the top and bottom.

The reaction chamber was a 7" long pyrex cylinder made by extending a standard B45 cone with similar diameter pyrex tubing. The bottom of the cylinder was sealed off and a short length of pyrex capillary blown into the centre and a pyrex tube just off centre. The pyrex tubing was joined to the argon line. A B45 socket with a central internally sealed ½" i.d. pyrex tube fitted on the socket of the cylinder. The top of the½" i.d. pyrex tubing was sealed with Araldite to an optical flat. A 7" long x ½" i.d. pyrex sidearm with a B14 cone at the end was blown onto the pyrex tubing. This sidearm was used for holding the metal specimens and was slightly inclined to prevent them slipping into the reaction chamber. The sidearm was joined to the argon flow by a short length of pyrex tubing. The specimens were introduced into the sidearm through the opening of the B14 cone. A glass covered soft iron rod which could be pushed along the inside of the sidearm by means of an external magnet was used for introducing the specimens into the reaction chamber.

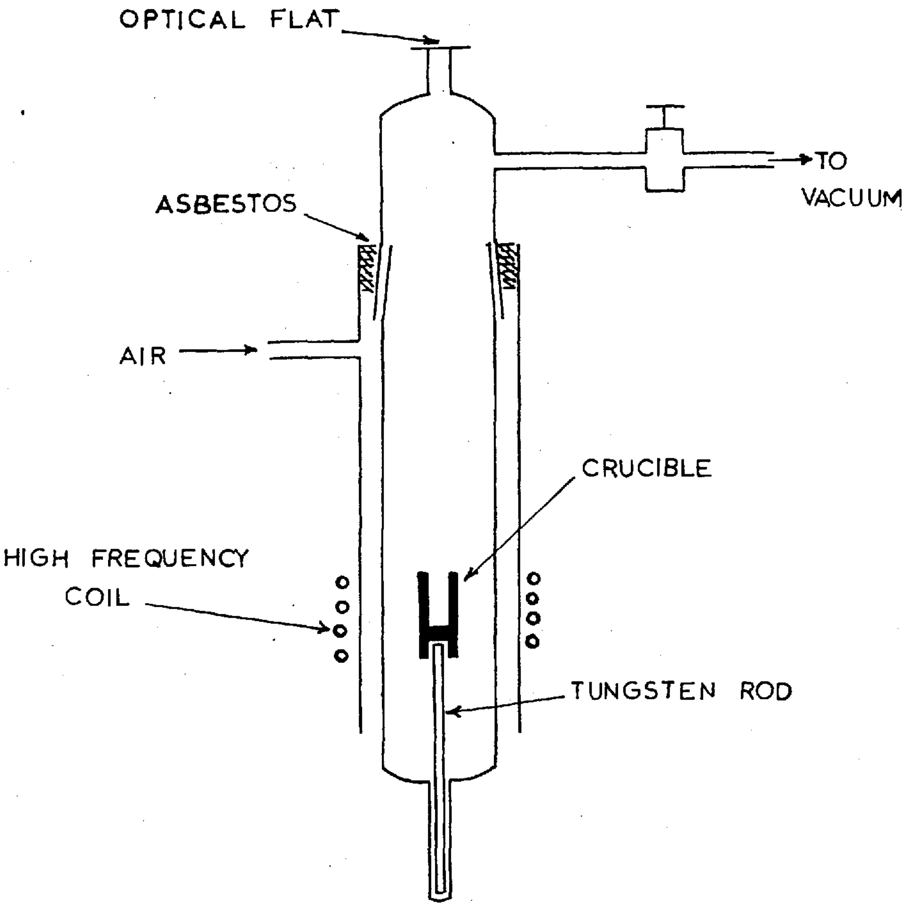
The graphite crucible was turned from a solid graphite rod in a lathe. The crucible was mounted centrally in the pyrex reaction chamber by means of a 2 mm diameter tungsten rod which fitted into the glass capillary.

The gases left the reaction chamber through a pyrex sidearm blown onto the side of the B45 socket. The sidearm was joined to a three-way tap which connected with the iodine pentoxide apparatus or the atmosphere.

A second pyrex cylinder with a sidearm joined to a compressed air supply was placed round the reaction chamber and the annulus at the top packed with asbestos wool. The reaction tube was cooled by passing an air blast down the annulus between the two cylinders. The graphite crucible was heated by a high frequency coil, mounted on the outer cylinder.

The apparatus had to be carefully blanked before the oxygen contents of the metal beads could be determined. The graphite crucible was degassed in the apparatus represented diagramatically in Fig. 9. This apparatus was evacuated by a two-stage rotary vacuum pump which was capable of reducing the pressure in the system to 0.005 mm. Hg. When a satisfactory vacuum had been obtained as indicated by a Pirani gauge, the high frequency coil was turned on, and the crucible slowly heated. The crucible

FIG. 9 CRUCIBLE DEGASSING



was heated at 1500°C. for one hour followed by half an hour at 1800°C. The latter temperature was the maximum which could be used without the pyrex chamber becoming soft and collapsing. This procedure removed most of the volatite impurities which otherwise would have contaminated the main apparatus. The graphite crucible was cooled to room temperature and the vacuum line disconnected. The crucible was then mounted in the main apparatus and the metal specimens placed in the holding sidearm. The argon flow was turned on and 100 ml./min. passed through the apparatus and exhausted to the atmosphere. After ten minutes the high frequency coil was turned on and the graphite crucible heated to 1550°C. The temperature was measured by an optical pyrometer which was mounted above the optical flat and sighted onto the bottom of the crucible. The three-way tap was turned to pass the gases through the iodine pentoxide apparatus and after one hour the absorption bulb was removed and washed with distilled water. The bulb was refilled with fresh 5% potassium iodide solution and replaced on the apparatus. After 15 minutes the bulb was removed and the liberated iodine blank determined by the procedure described in the Amperometric Titration section. The blank rate was determined three times to check that it remained small and constant.

In order to test the apparatus, a standard oxygen bearing steel provided by the B.N.F.M.R.A. was used. This was carefully sawn and filed to obtain approximately one gram beads which were placed in the apparatus. When the blank rate was found to be satisfactory the absorption bulb was refilled with fresh 5% potassium iodide solution and the steel sample introduced into the carbon crucible by moving the pusher rod along the holding sidearm with a magnet. The temperature was measured with the optical pyrometer and adjusted to 1550°C. by altering the power setting of the high frequency set. After 15 minutes the absorption bulb was removed and replaced by a similar one containing fresh potassium iodate solution. The solution from the first bulb was transferred to a 100 ml. beaker and the amount of iodine determined by the amperometric method. The second absorption bulb which was used as a check on the blank rate was removed after fifteen minutes and the iodine determined. The amount of carbon monoxide formed by the reaction of the oxygen in the metal and the graphite crucible was calculated from the amounts of potassium iodate used in the two titrations. This procedure corrects for any blank caused by the apparatus or chemicals.

Three standard steel samples were determined and the average value of 0.058% O ± 0.001 was in good agreement with the recommended value of 0.056% O + 0.004 quoted by the B.N.F.M.R.A.

The oxygen in the metal specimens was determined by the same procedure and in the order of the melting point of the alloys; the highest first. The temperature of the bath was maintained approximately 20°C. over the liquidus temperature by noting the additions made to the crucible and adjusting the power.

This apparatus was used to determine the oxygen content of a few of the Ni-Cu alloys and all the Co-Cu alloys.

7. Chemical Analysis of Alloys

The compositions of the nickel-copper and cobalt-copper alloys equilibrated at 1500°C. were checked by chemically analysing one of the three metal beads from every experiment. The copper in the alloy was determined by the "Electrolytic Method" (ref. 43) and the nickel or cobalt by weight difference. The analyses were used to correct the compositions of the two other similar metal beads.

CHAPTER 3

NICKEL - NICKEL OXIDE SYSTEM

1. Introduction

In the experiments carried out with the circulating apparatus using the regenerator, the oxygen pressure of the gas phase was fixed by circulating the carbon dioxide + carbon monoxide gas mixture over nickel and nickel oxide held at a constant known temperature. The equilibrium P_{CO_2}/P_{CO} ratio was measured during the experiment and hence data were obtained on the thermodynamics of the nickel + nickel oxide system over the temperature range 550°C. to 850°C.

The reaction which takes place in the regenerator can be represented by the equation,

9 $$NiO\ (s) + CO\ (g) = Ni\ (s) + CO_2\ (g) \qquad (3.1)$$

for which $$K_p = \frac{a_{Ni} \cdot P_{CO_2}}{a_{NiO} \cdot P_{CO}} \qquad (3.2)$$

Since nickel and nickel oxide are present in their standard states their activities are equal to one and

$$K_p = P_{CO_2}/P_{CO} \qquad (3.3)$$

The approach to equilibrium of the system was followed by recording the Infra Red Gas Analyser readings at regular time intervals. Fig. 10 is a typical plot of the percentage carbon monoxide in the gas phase versus time. All experiments were at least four hours duration.

2. Results

The results are summarised in Table 2. Experiments 1T to 5P were carried out by Tomlinson, Nicholls and the author in a series of preliminary investigations. The Infra Red Gas Analyser was replaced by the Iodine Pentoxide Apparatus for determining the equilibrium P_{CO_2}/P_{CO} ratio in all experiments after No. 38. The reasons for this are explained in the Gas Analysis Section of the Experimental Methods Chapter.

From a plot of $\log K_p$ versus $1/T\,^\circ K$, Fig. 11, it can be seen that the results are best fitted by a straight line which by the method of least squares was found to be represented by the equation;

$$\log K_p = \frac{2{,}430}{T} + 0.0219 \qquad (3.4)$$

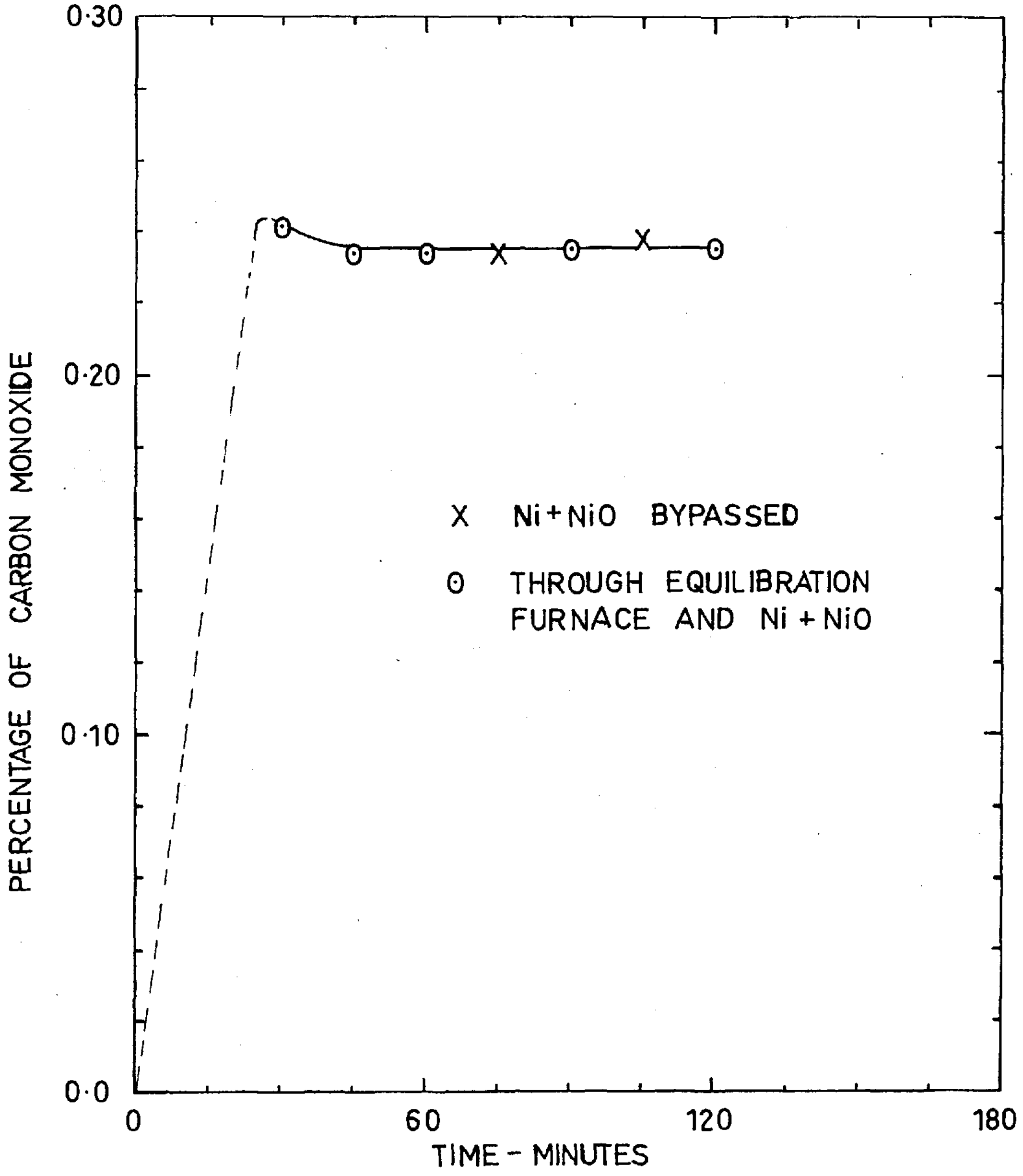
Noting that $\Delta G^o = -RT \ln K_p$

then, $\Delta G^o{}_{550^oC \text{ to } 850^oC} = -11{,}100 - 0.1T$ (3.5)

for the reaction represented by equation (3.1). In order to avoid confusion only the results obtained by the author are shown in Fig. 11. This was necessitated by the large number of results and the small size of Fig. 11. When all

FIG. 10

TIME OF APPROACH TO EQUILIBRIUM



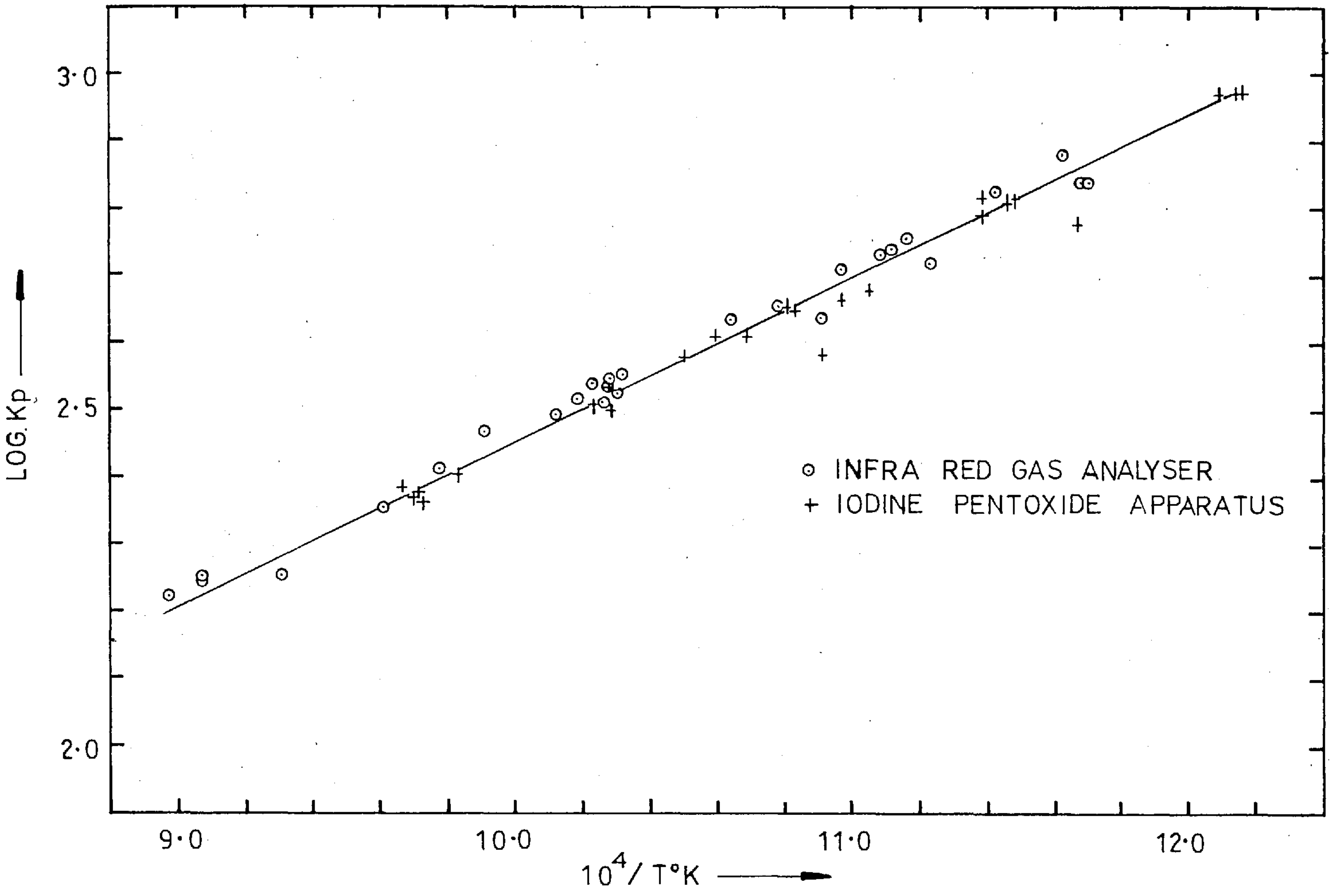


FIG. 11

THERMODYNAMICS OF THE Ni, NiO, CO AND CO_2 SYSTEM

TABLE 2

Summarized Equilibrium Data for,

$NiO(s) + CO(g) = Ni(s) + CO_2(g)$

Run No.	Temp °C	CO Pct.	P_{CO_2}/P_{CO}	Log K_p
1T	634	0.170	587	2.769
2T	607	0.160	624	2.795
3T	563	0.085	1175	3.070
4T	512	0.064	1562	3.194
5T	701	0.320	312	2.494
6T	814	0.600	166	2.220
7T	990	1.15	86	1.934
8T	660	0.210	475	2.677
9T	659	0.265	376	2.575
10T	648	0.230	434	2.637
11T	560	0.140	713	2.853
12T	534	0.108	926	2.967
13T	754	0.410	243	2.386
14T	656	0.210	475	2.677
15T	625	0.145	689	2.838
16T	692	0.325	307	2.487
17T	666	0.270	369	2.567
18T	603	0.185	540	2.732
19T	591	0.153	653	2.815
20T	565	0.133	751	2.876

Run No.	Temp °C	CO Pct.	P_{CO_2}/P_{CO}	Log K_p
21T	538	0.110	908	2.958
22T	489	0.073	1378	3.139
1N	737	0.345	289	2.461
2N	732	0.293	340	2.531
3N	665	0.205	487	2.687
4N	789	0.450	221	2.344
5N	984	1.05	94	1.974
6N	618	0.202	494	2.694
7N	639	0.149	670	2.826
8N	732	0.330	302	2.480
1P	679	0.262	381	2.581
2P	629	0.215	464	2.666
3P	576	0.132	757	2.879
4P	728	0.420	237	2.375
5P	666	0.252	396	2.598
2	617	0.190	525	2.720
3	583	0.145	689	2.838
4	533	0.102	976	2.989
5	801	0.555	179	2.253
6	532	0.110	908	2.958
9	602	0.149	670	2.826
10	654	0.220	454	2.657
11	704	0.288	346	2.539
12	667	0.232	430	2.633

Run No.	Temp °C	CO Pct.	P_{CO_2}/P_{CO}	Log K_p
13	736	0.342	291	2.464
14	715	0.322	310	2.491
15	768	0.430	232	2.365
16	587	0.132	757	2.879
17	622	0.175	570	2.756
19	629	0.185	540	2.732
20	700	0.292	341	2.533
21	696	0.280	356	2.551
22	697	0.299	333	2.522
23	700	0.283	352	2.546
24	708	0.305	327	2.514
25	701	0.310	322	2.508
26	699	0.292	341	2.533
28	702	0.292	341	2.533
29	626	0.182	548	2.739
30	582	0.145	689	2.838
31	750	0.385	259	2.413
32	830	0.565	176	2.245
33	829	0.560	178	2.250
34	842	0.590	168	2.225
36	643	0.231	432	2.635
37	639	0.195	512	2.709
38	703	0.292	341	2.533

Run No.	Temp °C	CO Pct.	P_{CO_2}/P_{CO}	Log K_p
60	649	0.215	464	2.666
61	598	0.153	653	2.815
62	551	0.107	934	2.970
63	554	0.107	934	2.970
64	600	0.155	644	2.809
65	606	0.162	616	2.790
66	550	0.107	934	2.970
67	653	0.222	449	2.652
68	652	0.224	445	2.648
69	698	0.299	333	2.522
70	756	0.435	229	2.360
71	744	0.394	253	2.403
72	606	0.152	657	2.818
74	663	0.245	407	2.610
75	705	0.310	322	2.508
76	757	0.416	239	2.378
77	758	0.423	235	2.371
78	584	0.167	598	2.777
79	644	0.261	382	2.582
80	632	0.209	477	2.678
81	700	0.316	315	2.498
82	699	0.297	336	2.526
83	762	0.412	242	2.384
85	671	0.246	496	2.610
86	679	0.262	381	2.581

the results are plotted on a larger scale diagram it can be seen that the results of Tomlinson, Nicholls and the author are randomly scattered about the calculated line of best fit. The equation for log K_p was obtained by considering all the results in the least squares calculation.

3. Errors

The standard error of log K_p derived from equation (3.4) is ± 0.044. The standard error in the temperature measurements was estimated to be ± 3°C. Noting that,

$$\Delta G^o = -RT \ln K_p$$

then

$$\alpha_{\Delta G^\circ} = \pm\sqrt{\left(\frac{\partial \Delta G^\circ}{\partial T}\right)\alpha_T^2 + \left(\frac{\partial \Delta G^\circ}{\partial K_p}\right)\alpha_{K_p}^2}$$

where $\alpha_{\Delta G^o}$, α_T and α_{K_p} are the standard errors in ΔG^o, temperature and K_p respectively. At 700°C the mean of the temperature range investigated $\alpha_{\Delta G^o}$ was found to be ± 200 cals.

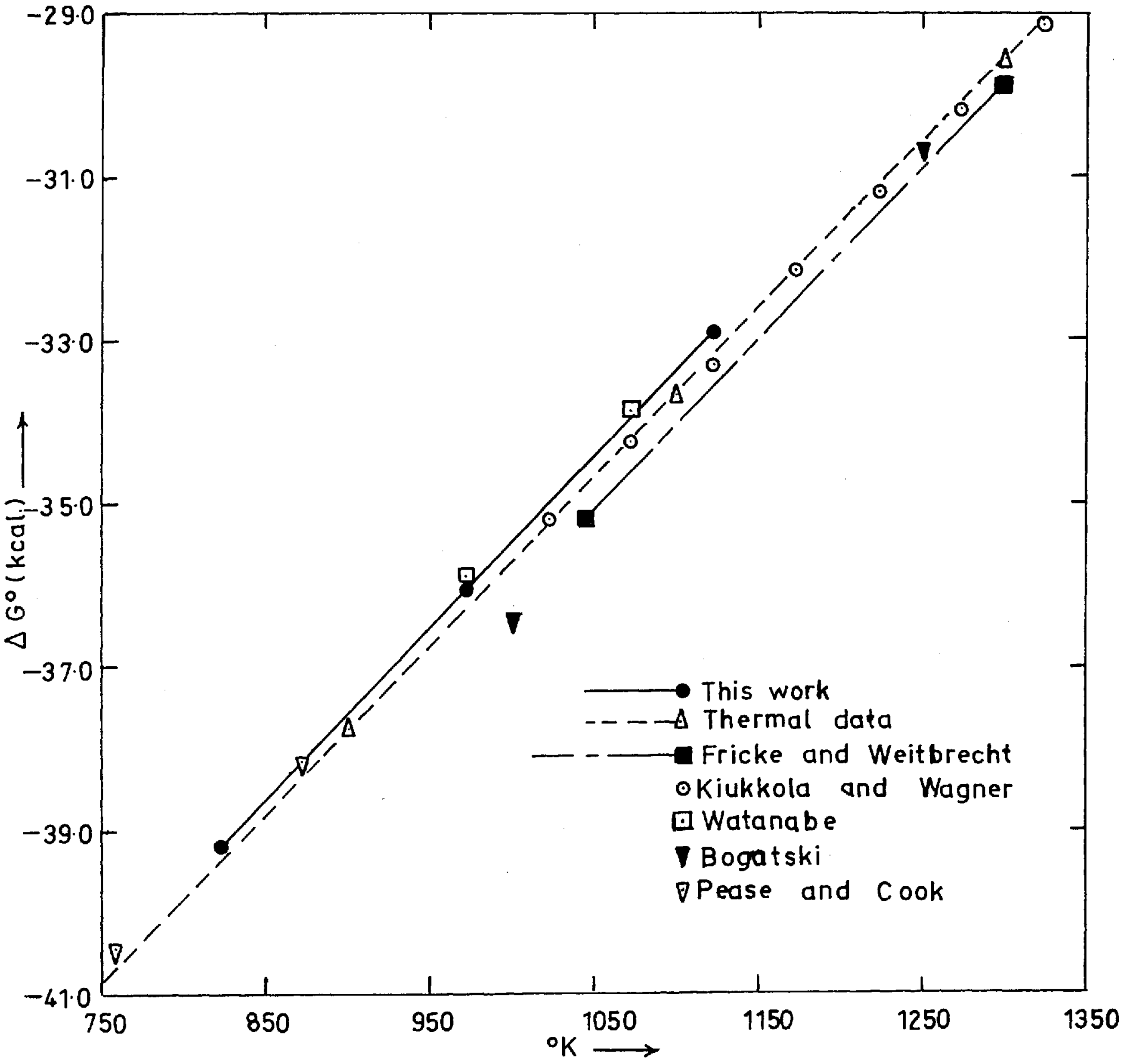
4. Discussion

The results of the previous investigations on the thermodynamics of the nickel + nickel oxide system are summarized in Fig. 12 by a plot of the standard molar free energy change versus absolute temperature for the reaction,

$$\mathrm{Ni\ (s)} + \tfrac{1}{2}\,\mathrm{O_2\ (g)} = \mathrm{NiO\ (s)} \qquad (3.6)$$

FIG. 12 Standard Free Energy Change ΔG° of the Reaction

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



The P_{CO_2}/P_{CO} ratio in equilibrium with nickel + nickel oxide has been measured by Fricke and Weitbrecht (ref. 44) (1044° - 1298°K), Watanabe (ref. 45) (980° - 1110°K) and Bogatski (ref. 46) (673° - 1273°K). Pease and Cook (ref. 47) have measured the P_{H_2O}/P_{H_2} ratio in equilibrium with nickel + nickel oxide at 758° and 873°K. These data were converted to the reaction represented by equation (3.6) by means of the tabulated thermodynamic data of Elliot and Gleiser (ref. 48) for CO_2/CO and H_2O/H_2 gas mixtures.

Kiukkola and Wagner (ref. 49) have used the following galvanic cell,

$$\text{Fe, wüstite} \;\Big|\; 0.85\, ZrO_2 + 0.15\, CaO \;\Big|\; \text{Ni, NiO}$$

to determine the standard molar free energy of formation of nickel oxide over the temperature range 750°C to 1140°C.

The thermal data for nickel oxide has been the subject of a number of recent investigations. Boyle, King and Conway (ref. 50) have determined the heat of formation of nickel oxide at 298°K and King (ref. 51) the entropy of the oxide at 298°K. The values are -57,300 cal/gm. mole. and 9.08 cal/gm. mole./°K respectively. The heat capacity of nickel oxide has been measured over the temperature range 298° to 1810°K by King and Christensen (ref. 52) and from 273° to 1108°K by Tomlinson, Domash, Hay and Montgomery (ref. 53). From this data and the tabulated thermal data of oxygen and nickel listed by Elliot and Gleiser (ref. 48) the standard molar free energy of formation of nickel oxide was calculated for 700°, 900°, 1100° and 1300°K.

From Fig. 12 it can be seen that the results of the latest thermal data and Kiukkola and Wagner's measurements are in good agreement and lie between the results of the different gas equilibrium studies. The most probable reason for the discrepancies between the gas equilibrium studies using CO_2/CO gas mixtures is the low accuracy of the early analytical methods for the determination of fairly large CO_2/CO ratios (912/1 at 823°K to 77/1 at 1300°K). For this reason it maybe expected that the results of Bogatski, Fricke and Weitbrecht, and Watanabe are more reliable at the higher temperatures. The accuracy of the analytical methods used in this investigation does not significantly change for the range of CO_2/CO ratios investigated.

Pease and Cook passed known H_2O/H_2 gas mixtures over nickel + nickel oxide held at a constant known temperature and analysed the exit gases from the reaction tube. The equilibrium H_2O/H_2 ratio was found by determining the incoming H_2O/H_2 ratio which resulted in the same outgoing ratio from the reaction tube. From the data in their paper it would appear that the stated accuracy of ± 100 cals is optimistic and ± 250 cals would be a more realistic value.

The results of the present investigation are in good agreement with Pease and Cook, and Watanabe, and are approximately 250 cals more positive than the results of Kuikkola and Wagner and the thermal data.

The discrepancy of 250 cal is outside the expected accuracy limits of this investigation and it was concluded that the standard molar free energy charge of the reaction represented by equation (3.6) is best represented by the relationship,

$$\Delta G^{o}_{(500^{o}\text{ to }1140^{o}C)} = -56{,}370 + 20.8T \pm 200 \text{ cal.}$$

which is the mean of the data of this research, Kuikkola and Wagner's results and the thermal data.

CHAPTER 4

COPPER - CUPROUS OXIDE SYSTEM

1. Introduction

The P_{CO_2}/P_{CO} ratio in equilibrium with copper and cuprous oxide was measured over the temperature range 993°C to 1188°C in the circulating apparatus. For the temperature range 993°C to 1065°C 10 sq.cm. spectrographically pure copper sheet was wound in a spiral and placed in an alumina boat. A small amount of cuprous oxide was formed on the surface of the copper by placing the boat in the uniform zone of the furnace and flushing carbon dioxide over it for ten minutes at 1050°C. At the end of this time the carbon dioxide flow was stopped, the gas pump started, and the furnace temperature adjusted to the required value. After four hours the pump was stopped and gas analysis carried out. These experiments were then repeated with a 50 sq.cm. copper spiral to determine if the equilibrium P_{CO_2}/P_{CO} ratio was independent of the surface area.

The Infra Red Gas Analyser was found to be unsatisfactory for quantitative results at the low carbon monoxide concentrations involved in these experiments and was only used as an indicator to determine when the P_{CO_2}/P_{CO} ratio became constant. The instrument showed that the P_{CO_2}/P_{CO} ratio became constant after one hour at 1000°C.

For experiments above the eutectic temperature, 1065°C, of the copper + oxygen system, Fig. 13, (ref. 54), the above procedure was modified. Five gm. of spectrographically pure copper were placed in an alumina boat and oxidised for one hour at 1050°C in a muffle furnace. The boat was then placed in the apparatus and carbon dioxide flushed over it for one hour at 1180°C. At the end of this time the same equilibration procedure as used before was adopted.

2. Results

The partial pressures of oxygen equivalent to the experimentally determined CO_2/CO ratios were calculated from the tabulated thermodynamic data of Elliot and Gleiser (ref. 48). For the reaction,

$$CO\ (g) + \tfrac{1}{2}\ O_2\ (g) = CO_2\ (g) \qquad (4.1)$$

$$\log \frac{P_{CO_2}}{P_{CO} \cdot P_{O_2}^{\frac{1}{2}}} = \frac{14,670}{T} - 4.490$$

The results are summarized in Table 3.

From the copper + oxygen phase diagram shown in Fig. 13 (ref. 54) it may be recognised that the results obtained in this investigation are for the equilibrium between copper saturated with oxygen and pure solid cuprous oxide. Therefore in order to calculate the standard molar

FIG. 13

COPPER–OXYGEN PHASE DIAGRAM

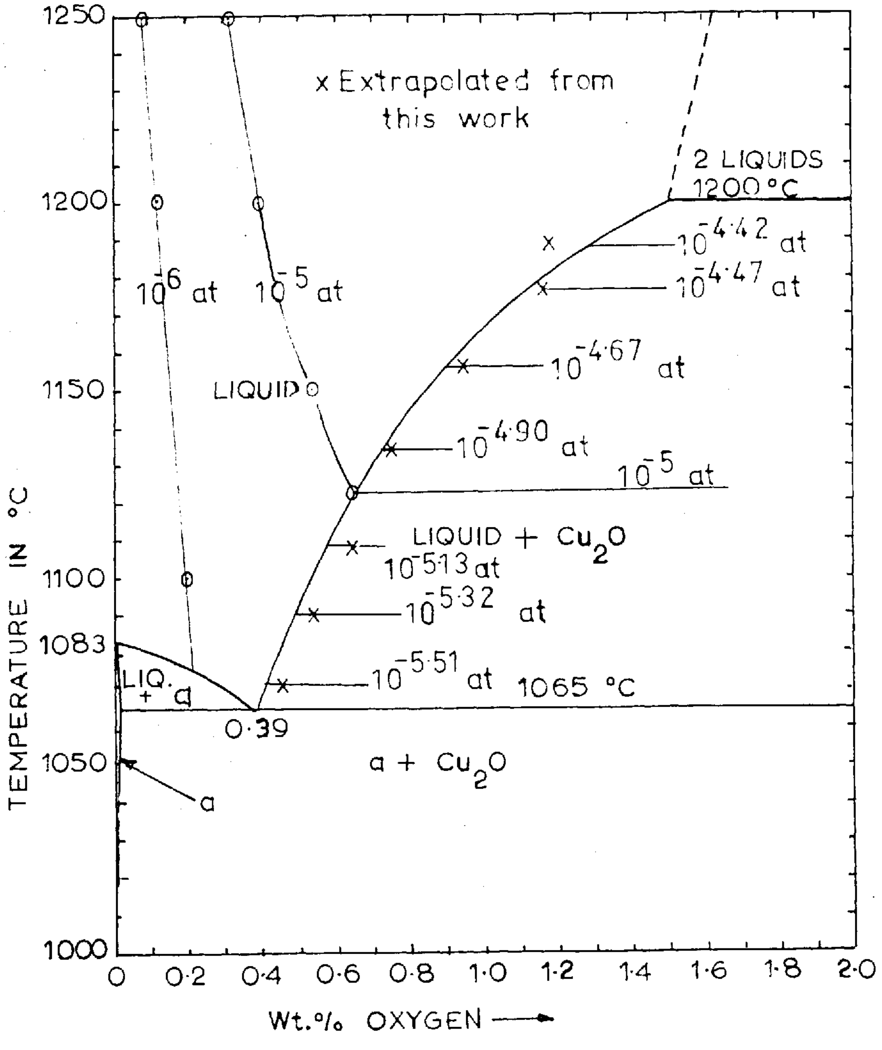


TABLE 3

Results for the equilibrium between cuprous oxide, copper saturated with oxygen and carbon monoxide, carbon dioxide gas mixtures.

Run No.	Temp °C	P_{CO_2}/P_{CO}	$\text{Log}P_{O_2}^{\frac{1}{2}}$	$2\text{Log}\, a_{Cu}$	$\text{Log}\frac{1}{P_{O_2}\cdot a^2_{Cu}}$
6	1036	6060	-2.939	0	2.939
7	1017	7870	-2.990	0	2.990
9	995	11000	-3.041	0	3.041
10	1013	8000	-3.015	0	3.015
11	1031	6900	-2.923	0	2.923
12	1046	5950	-2.860	0	2.860
13	1047	5380	-2.896	0	2.896
15	993	8770	-3.155	0	3.155
16	1006	7520	-3.108	0	3.108
17	1028	6140	-2.998	0	2.998
18	1048	5850	-2.852	0	2.852
19	1052	4390	-2.944	0	2.944
20	1050	5880	-2.831	0	2.831
21	1030	7690	-2.885	0	2.885
22	1029	5460	-3.044	0	3.044
23	1072	4430	-2.774	-0.013	2.787
24	1071	4830	-2.742	-0.013	2.755
25	1089	4070	-2.674	-0.015	2.689
26	1090	4270	-2.646	-0.015	2.661
27	1108	3680	-2.570	-0.017	2.587

Table 3 Cont.

Run	Temp	P_{CO_2}/P_{CO}	$\text{Log}P_{O_2}^{\frac{1}{2}}$	$2\text{Log } a_{Cu}$	$\text{Log}\frac{1}{P_{O_2} \cdot a^2_{Cu}}$
28	1107	3830	-2.557	-0.017	2.574
29	1133	3190	-2.440	-0.020	2.460
30	1133	3070	-2.460	-0.020	2.480
31	1156	2860	-2.323	-0.025	2.348
32	1156	2710	-2.343	-0.025	2.368
33	1178	2510	-2.223	-0.030	2.253
34	1178	2400	-2.243	-0.030	2.273
35	1188	2210	-2.209	-0.033	2.242

TABLE 4

Activities of copper in copper saturated with oxygen solutions.

Temp °C	N_O	Log a_{Cu}
1090	0.0188	-0.008
1100	0.0205	-0.008
1130	0.0272	-0.010
1150	0.0322	-0.012
1180	0.0445	-0.015
1200	0.0570	-0.018

free energy change for the reaction,

$$2\ Cu\ (l) + \tfrac{1}{2}\ O_2\ (g) = Cu_2O\ (s) \qquad (4.2)$$

for which the thermodynamic equilibrium constant may be represented as,

$$K_p = \frac{a_{Cu_2O}}{a_{Cu}{}^2 \cdot P_{O_2}{}^{\frac{1}{2}}} \qquad (4.3)$$

it is also necessary to know the activity of copper in the copper saturated with oxygen solution. These data may be obtained by applying the Gibbs - Duhem relationship to the equilibrium results involving solutions of oxygen in molten copper and CO_2/CO gas mixtures which also forms part of this investigation and is discussed in Chapter 5. From the solution studies it was found that the activity coefficient of oxygen could be represented by the relationship,

$$\log f_O = -0.041 \text{ atom \% } O \qquad (4.4)$$

This may be rewritten as,

$$\log f_O = -4.1\ N_O$$

and integrated by the Gibbs - Duhem relationship suggested by Wagner (ref. 55):

$$\log \gamma_1 = \int_0^{N_2} \frac{\log \gamma_2}{(1-N_2)^2}\, dN_2 - \frac{N_2}{(1-N_2)} \log \gamma_2 \qquad (4.5)$$

On substituting the relationship for the activity coefficient of oxygen and integrating between the limits of pure liquid copper and copper saturated with oxygen the following equation is obtained,

$$\log \gamma_{Cu} = -9.44 \log N_{Cu} - 4.1 N_O$$

and hence

$$\log a_{Cu} = -8.44 \log N_{Cu} - 4.1 N_O \qquad (4.6)$$

The activities of copper relative to pure liquid copper can be calculated for the saturated copper oxygen solutions by substituting the values of N_{Cu} and N_O for these solutions. The values of N_{Cu} and N_O were obtained from the phase diagram Fig. 13. The results are summarized in Table 4 and Fig. 14 where a plot of log a_{Cu} versus temperature is shown. The activities of copper were calculated for the temperatures at which the partial pressures of oxygen had been determined by interpolation from Fig. 15. From the partial pressures of oxygen and the activities of copper the values of K_p were calculated. The results are summarized in Table 3.

A plot of log K_p versus $1/T^oK$ is shown in Fig. 15. For the temperature range 1188°C to 1083°C, the melting point of copper, the results are best fitted by a straight line which may be represented by the equation,

$$\log K_p = \frac{9490}{T} - 4.282 \qquad (4.7)$$

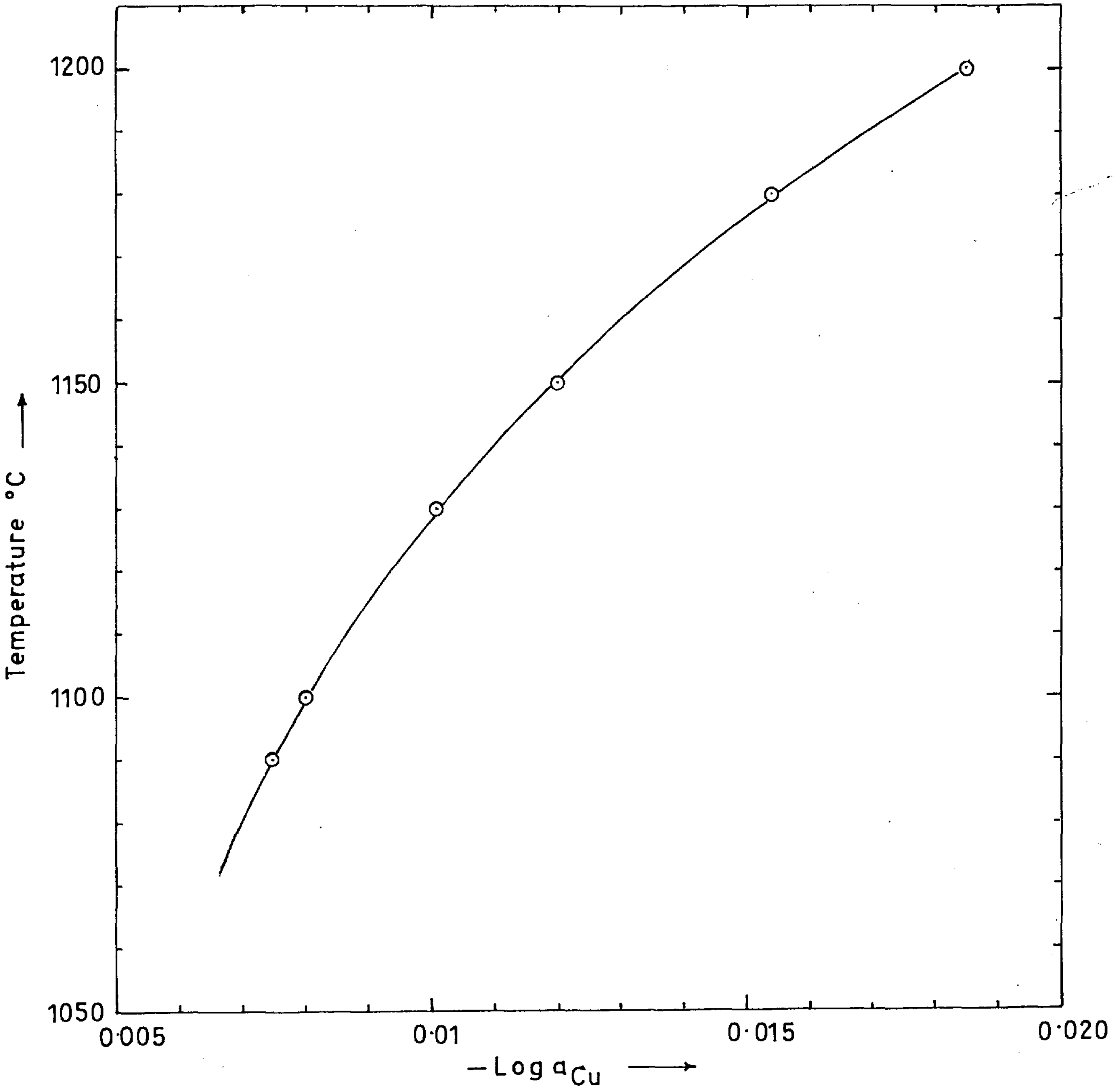
and hence

$$\Delta G^o_{1188^oC \text{ to } 1083^oC} = -43{,}410 + 19.59T \qquad (4.8)$$

In the temperature range where solid copper is in equilibrium with solid cuprous oxide the solubility of

FIG. 14

Activity of Copper in Saturated Copper + Oxygen Solutions



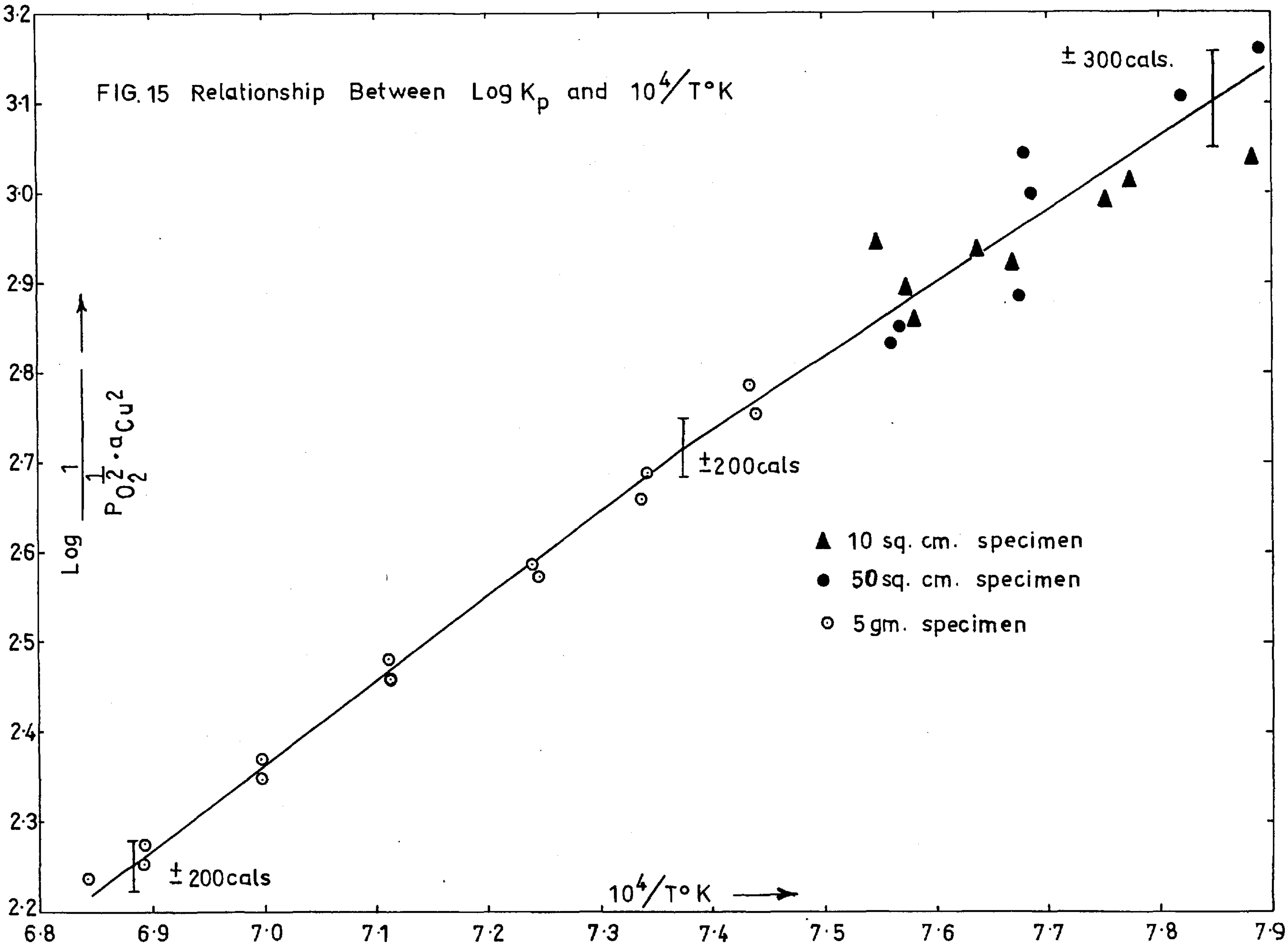


FIG. 15 Relationship Between Log K_p and $10^4/T°K$

oxygen is less than 0.008 wt.% and the activity of copper may be regarded as equal to one. The equilibrium constant for the reaction,

$$2\ Cu\ (s) + \tfrac{1}{2}\ O_2\ (g) = Cu_2O\ (s) \qquad (4.9)$$

may therefore be written as,

$$K_p = \frac{1}{P_{O_2}{}^{\frac{1}{2}}} \qquad (4.10)$$

From Fig. 15 it can be seen that there is no significant difference in the results obtained with the 10 and 50 sq.cm. copper spirals and hence it may be assumed that the reaction was at equilibrium rather than a steady state process dependent on the surface area of the copper. The scatter of the results is too great to accurately determine the relationship between log K_p and temperature. The expected behaviour of K_p in this region however may be calculated from the free energy relationship for the liquid copper region and the data for the heat of fusion of copper. Kelley (ref. 56) gives a value of 3120 cals/gm. atom for the heat of fusion of copper. Therefore for the transformation,

$$2\ Cu\ (s) = 2\ Cu\ (l) \qquad (4.11)$$

$$\Delta G^o{}_F = 6{,}240 - 4.60T \qquad (4.12)$$

Combining this with $\Delta G^o{}_T$ for equation (4.2) gives for the reaction,

$$2\ Cu\ (s) + \tfrac{1}{2}\ O_2\ (g) = Cu_2O\ (s) \qquad (4.13)$$

that

$$\Delta G^{o}_{10830C \text{ to } 1000^{o}C} = -37,170 + 14.99T \qquad (4.14)$$

and hence

$$\log K_p = \frac{8125}{T} - 3.277$$

From Fig. 15 it can be seen that the results are reasonably well fitted by this relationship.

The data for the solubility of oxygen in molten copper and the P_{CO_2}/P_{CO} ratios in equilibrium with copper saturated with oxygen may be combined to calculate the oxygen content of liquid copper in equilibrium with solid cuprous oxide. These values and the partial pressures corresponding to these points are shown in Fig. 13. The excellent agreement between the extrapolated solubility points and Hansen's phase boundary, within the experimental errors, shows the reliability of this part of the phase diagram.

3. Errors

The major source of error in these experiments was the determination of the equilibrium P_{CO_2}/P_{CO} ratios. The Iodine Pentoxide Apparatus was accurate to ± 0.011 ml. of carbon monoxide and the volume of the gas sample bottle used was 1000 ml. From these values the accuracy of the P_{CO_2}/P_{CO} ratio was calculated to be ± 2.5% at 1188°C, ± 4.7% at 1083°C and ± 10% at 1000°C. In the temperature range where solid copper is present other sources of error such as temperature measurement, and neglect of ΔC_p, are small compared with the gas analysis error and may be neglected. With increase in temperature however the errors from temperature measurement, ± 3°C, and the activity of copper, log $a_{Cu} \pm 0.005$, cannot be neglected. It may be concluded that the free energy equations for the temperature ranges 1188°C to 1083°C and 1083°C to 1000°C are accurate to ± 200 cals and ± 300 cals respectively. These limits are shown in Fig. 15.

4. Discussion

The previous studies on the determination of the partial pressure of oxygen in equilibrium with copper saturated with oxygen and cuprous oxide are summarized in Fig. 16 where the earlier work is compared with the results of this study.

Roberts and Smyth (ref. 57) have determined oxygen partial pressures over liquid copper and solid Cu_2O in the temperature range 1119°C to 1185°C. From Fig. 16 it can be seen that their values are more positive than the present investigation. In view of inherent difficulties discussed in the paper by Roberts and Smyth, it seems probable that the effect of side reactions has not been sufficiently eliminated in their measurements of oxygen partial pressures.

The equilibrium involving solutions of oxygen in liquid copper and CO_2/CO gas mixtures has been investigated by Girardi and Siebert (ref. 58), 1090°C to 1300°C, Sano and Sakao (ref. 59), 1155°C to 1256°C, and the author (chapter 5) 1085°C to 1500°C. Allen and

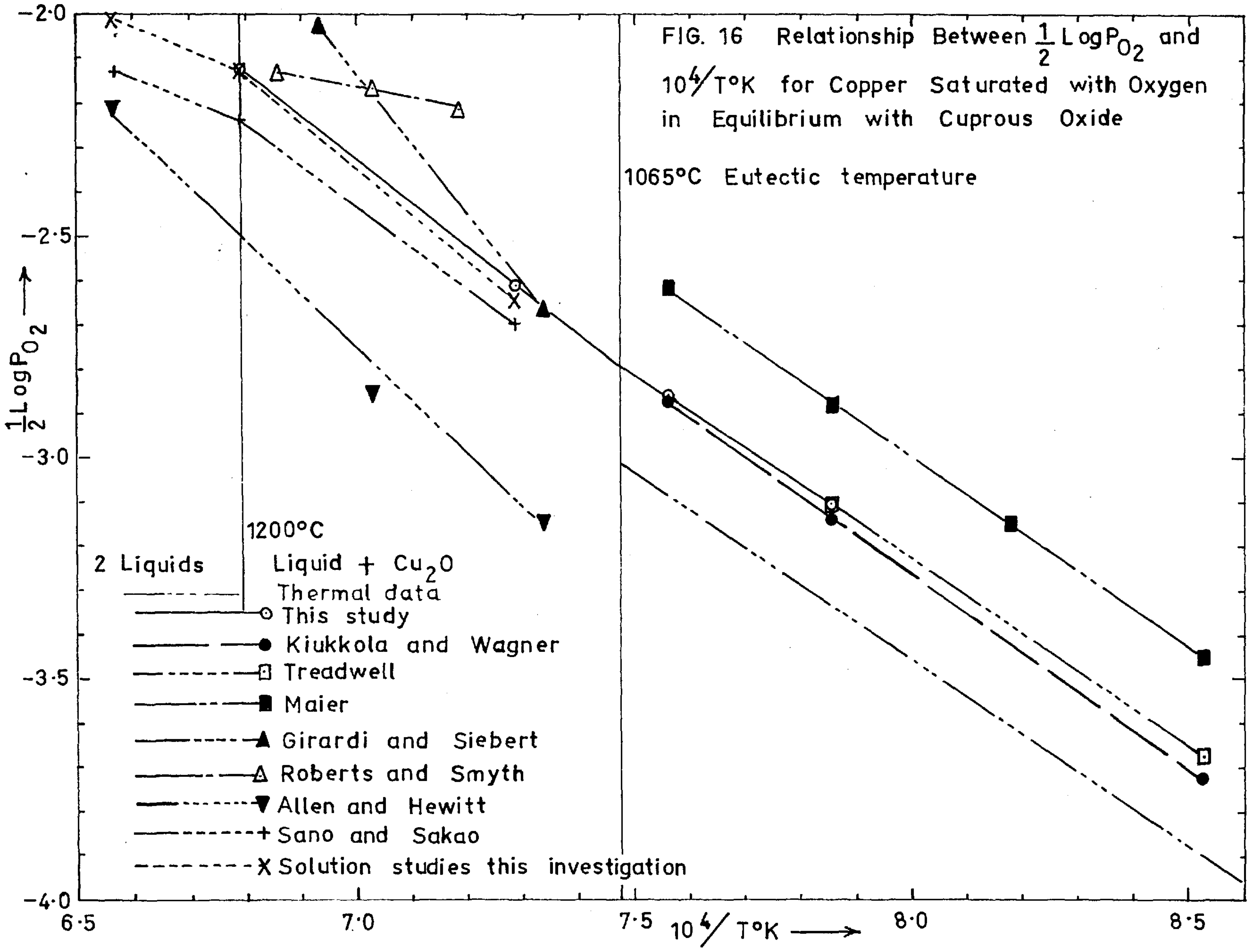


FIG. 16 Relationship Between $\frac{1}{2}\,\mathrm{Log}\,P_{O_2}$ and $10^4/T$°K for Copper Saturated with Oxygen in Equilibrium with Cuprous Oxide

Hewitt (ref. 60) have investigated the equilibrium between solutions of oxygen and H_2O/H_2 gas mixtures between 1090°C and 1350°C. These data were extrapolated to the solubility limits of oxygen in molten copper obtained from the phase diagram Fig. 13, and converted to partial pressures of oxygen by means of the tabulated thermodynamic data of Elliot and Gleiser (ref. 48) for CO_2/CO and H_2O/H_2 gas mixtures. The values obtained from Allen and Hewitt's work are considerably more negative than any of the other investigations. The most probable reason for this discrepancy was the method used by Allen and Hewitt to measure the pressure of hydrogen in the equilibrium H_2O/H_2 gas mixture. The apparatus for this purpose consisted of an evacuated platinum tube suspended in the hot zone of the reaction tube and joined to a manometer mounted on the outside of the enclosed furnace assembly. It is doubtful if accurate pressure measurements can be obtained by this method at high temperatures and furthermore the platinum may also produce side reactions to effect the equilibrium.

Girardi and Siebert only studied a small range of low oxygen concentrations, less than 0.4 atom %, and hence were unable to detect the negative departure from Henry's law which was observed in the investigations of

Sano and Sakao, and the author. If Girardi and Siebert's results are corrected by using the author's value for the activity coefficient of oxygen,

$$\log f_O' = -4.1 N_O$$

the discrepancy from the present investigation is considerably decreased. The discrepancies in the values of Girardi and Siebert, Sano and Sakao, and the author are probably due to small non-random errors in the different experimental procedures and an attempt has been made in the following chapter to analyse the different methods to find such possible sources of error.

From Fig. 16 it can be seen that the values obtained in this investigation by direct measurement and by extrapolating to the solubility limits of oxygen are in good agreement.

The CO_2/CO and H_2O/H_2 ratios in equilibrium with solid copper and cuprous oxide are too high for accurate determination by the early gas analytical methods. For this reason the equilibrium H_2O/H_2 ratios determined by Maier (ref. 61) and Wohler and Balz (ref. 62) are very doubtful and may be disregarded.

In order to overcome the problem of measuring the unconveniently high CO_2/CO or H_2O/H_2 ratios Treadwell (ref. 63) used the following galvanic cell, Cu(s) Cu_2O(s), borate melt porcelain Ag(l), O_2(g) to determine the standard molar free energy of formation of cuprous oxide. The measurements of Treadwell have been subsequently corrected for thermoelectric effects by Gundermann, Hauffe and Wagner (ref. 64). Kuikkola and Wagner (ref. 49) used the galvanic cell,

$$\text{Fe, wustite} \,\Big|\, 0.85ZrO_2 + 0.15CaO \,\Big|\, \text{Cu, } Cu_2O$$

to determine the standard molar free energy of formation of cuprous oxide over the temperature range 800°C to 1050°C. The reproducibility of the e.m.f. values was ± 0.002 mv or better which corresponds to an uncertainty in ΔG^o of ± 0.1 kcal.

An excellent review of the work until 1931 on the thermochemistry of cuprous oxide is given by Randall, Nielsen and West (ref. 65). Since this review Wohler and Jochum (ref. 66) have measured the specific heat of cuprous oxide between 290° and 1223°K and Hu and Johnston (ref. 67) the molar heat of cuprous oxide between 14° and 300°K. The standard entropies of oxygen and copper listed by Elliot and Gleiser (ref. 48) are 49.0 and 7.97 cal/deg/mole respectively. On combining these values with Hu and Johnston's value of 22.44 cal/deg/mole for the standard entropy of cuprous oxide the standard entropy of formation of cuprous oxide, ΔS^o_{298}, is found to be -18.0 cal/deg/mole. From e.m.f. measurements at 25°C and $\Delta S^o_{298} = -18.0$ cal/deg/mole the following heats of formation may be obtained:

-39,900 Makolkin (ref.68), -40,000 Maier (ref. 69), -40,450 Allmand (ref. 70) and -40,600 Ishikawa and Kimura (ref. 71).

The calorimatric value determined by Thomsen (ref. 72) is -40,800 cals/mole. If Thomsen's value for ΔH^o_{298} and Hu and Johnston's value for ΔS^o_{298} are selected as the best values and combined with the specific heat data for cuprous oxide, copper and oxygen which have been analysed and tabulated by Kelley (ref. 56), the following equation for the free energy of formation of cuprous oxide up to the melting point of copper may be obtained,

$$\Delta G^o_T = -40{,}980 + 21.9T - 1.1\times10^{-3}T^2 - 0.10\times10^5T^{-1} - 1.15T\log T$$

From Fig. 16 it can be seen that the results of Kuikkola and Wagner, Treadwell and this investigation are in good agreement, between 1000°C and the eutectic temperature of the copper + oxygen system. Kuikkola and Wagner's results however show that the equilibrium partial pressure of oxygen decreases more rapidly with decrease in temperature than that found in Treadwell's study or the present investigation extrapolated to lower temperatures. The experimental method used by Kuikkola and Wagner appears to be the most accurate of the three investigations and in view of the scatter of the results obtained in the present investigation and the small temperature range covered 1000° to 1065°C it is not justifiable to extrapolate the results to lower temperatures. For these reasons the data of Kuikkola and Wagner are selected as best representing the standard molar free energy of formation of cuprous oxide in the temperature range 800°C to 1065°C.

The discrepancy between the results of Kuikkola and Wagner and the thermal data extrapolated to high temperatures may be explained by assuming that the selected value for ΔH^o_{298} is too negative and the specific heat data for cuprous oxide increases too rapidly with temperature. The first assumption is substantiated by the ΔH^o_{298} values deduced from the e.m.f. measurements at room temperature but the second must remain doubtful until the specific heat of cuprous oxide is redetermined.

It may be concluded that the standard molar free energy of formation of cuprous oxide is adequately represented by the relationships expressed by equations, (4.8) and (4.14) for the temperature range 1200°C to 1000°C.

CHAPTER 5

DILUTE SOLUTIONS OF OXYGEN IN MOLTEN COPPER

1. Introduction

The equilibrium between liquid copper and carbon monoxide, carbon dioxide gas mixtures was studied over the temperature range 1085°C to 1500°C.

The reaction studied was;

$$[O] + CO\ (g) = CO_2\ (g) \qquad (5.1)$$

for which

$$K = \frac{P_{CO_2}}{P_{CO} \cdot \text{atom\%O}\ f'_O} \qquad (5.2)$$

The activity coefficient of oxygen, f'_O, is based on the reference state,

$$a_O = \text{atom \% O as atom \% O} \longrightarrow 0$$

If oxygen in copper obeys Henry's law f'_O becomes 1 for pure copper. Thus,

$$K' = \frac{P_{CO_2}}{P_{CO} \cdot \text{atom \%O}} \qquad (5.3)$$

The circulating apparatus was used for experiments over the temperature range 1085°C to 1300°C. Above 1350°C it was found that the reaction tube of the circulating apparatus became sufficiently porous to allow a significant leak of oxygen into the system. This was indicated by the experimental observation that the P_{CO_2}/P_{CO} ratio slowly increased with time and was always greater than the reading recorded on by-passing the furnace. To overcome this problem and also the difficulty in obtaining low P_{CO_2}/P_{CO} ratios with the circulating apparatus the flowmeter apparatus was used in the temperature range 1300°C to 1500°C.

The effect of the rate of quenching on the equilibrium oxygen concentration was also investigated in the circulating apparatus. The procedure for this consisted of recirculating the equilibrium gas mixture after quenching and observing any change in the Infra Red Gas Analyser reading. From an estimate of the volume of the apparatus, 1200 ml, and the change in P_{CO_2}/P_{CO} ratio the gain or loss in weight of oxygen could be calculated. It was found at 1200°C that by slowly removing the boat containing 3 gm of copper from the hot zone to the cold end of the furnace the percentage of carbon monoxide in the equilibrium gas mixture decreased from 0.225% to 0.210%. This corresponds to a loss in weight of 100 ugm of oxygen from the copper. By containing the copper in the minimum amount of refractory and using a fast rate of withdrawal from the hot zone of the furnace it was found that no change in the P_{CO_2}/P_{CO} ratio could be detected after quenching.

The attainment of equilibrium was measured at

1100°C by run numbers 21 to 28. A plot of log K' versus time is shown in Fig. 17. It was concluded from these results that equilibrium is reached in less than 2 hrs. and all subsequent experimental runs were equilibrated for 3 to 4 hrs.

2. Results

The results are summarized in Table 5. The Iodine Pentoxide Apparatus was used for determining the final P_{CO_2}/P_{CO} ratios for all experiments after No. 42. Detailed studies were made at 1100°C in order to determine the effect of oxygen concentration on the equilibrium constant. Fig. 18 shows the relation between the P_{CO_2}/P_{CO} ratio and oxygen content at 1100°C. It can be seen that the results are best fitted by a curve and that the equilibrium ratio;

$$K' = \frac{P_{CO_2}}{P_{CO} \cdot \text{atom\%O}} \tag{5.4}$$

is not a true constant but decreases with increasing oxygen content. In the introduction it was stated that interactions between solute atoms in dilute solutions may be approximately taken into account by the relationship;

$$\log f_O' = k \text{ atom\%O} \tag{5.5}$$

hence

$$\log K' = \log K + k \text{ atom\%O} \tag{5.6}$$

From this it is evident that a plot of log K' versus atom%O should be a straight line whose slope is equal to

FIG. 17

TIME TO EQUILIBRIUM AT 1100°C

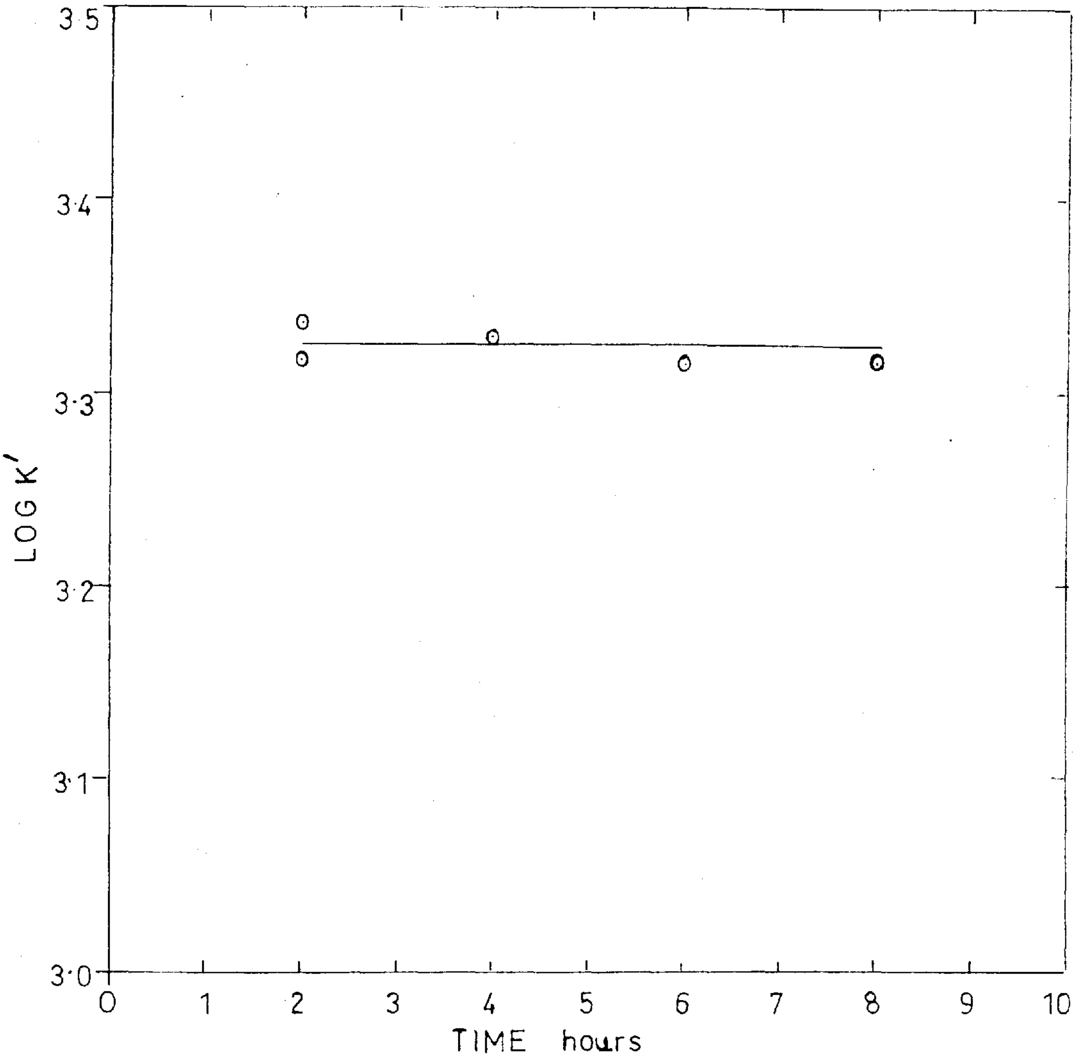
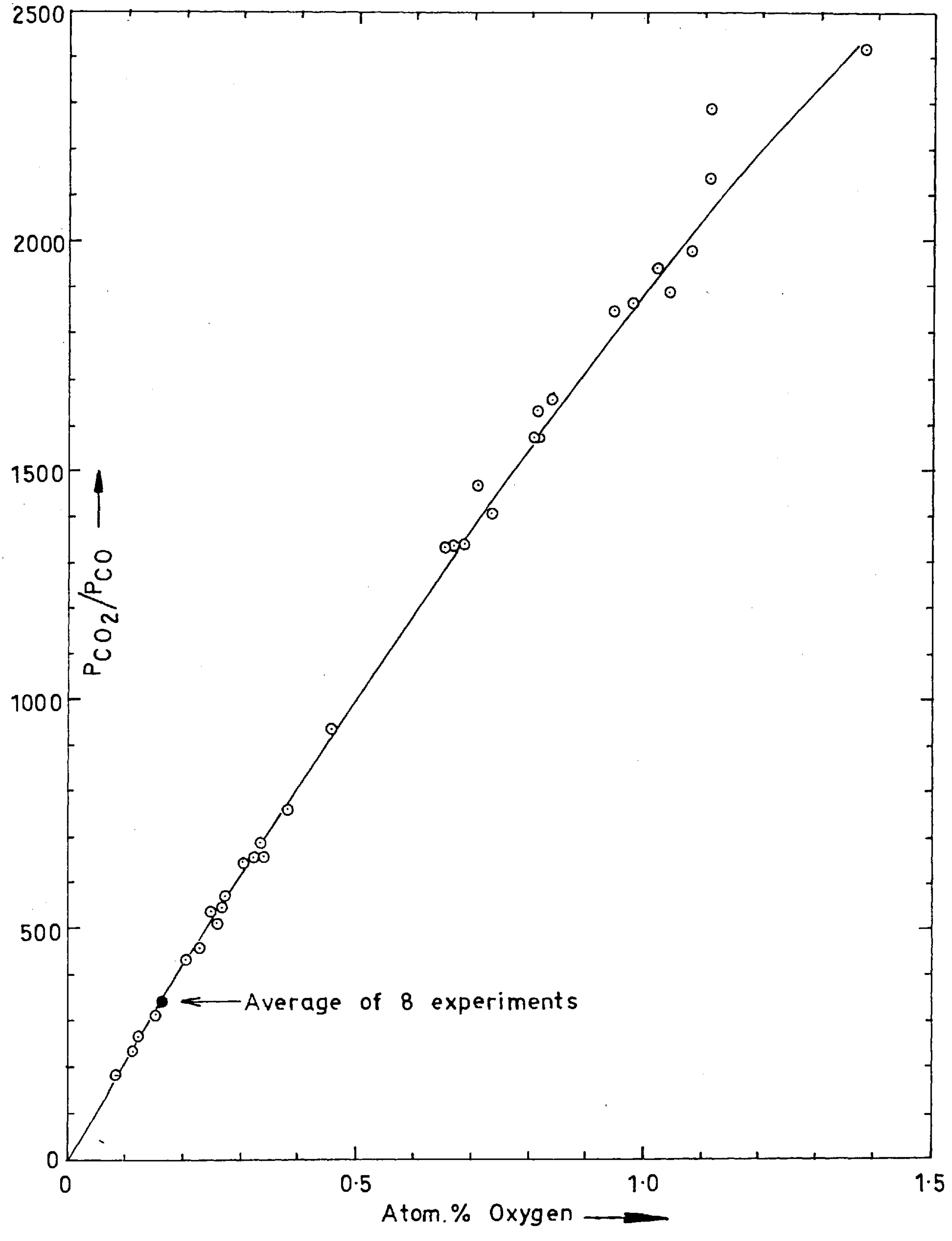


FIG. 18.

Relationship Between Oxygen Content and P_{CO_2}/P_{CO} Ratio at 1100°C



k and intercept at zero percentage oxygen log K. The results would appear to be well fitted by this relationship, Fig. 19. The method of least squares was used to determine the lines of best fit at 1100°C and 1300°C;

$1100^{\circ}C \; \log K' = 3.326(\pm 0.004) - 0.041(\pm 0.005) \text{ atom\%O} \quad (5.7)$

$1300^{\circ}C \; \log K' = 2.401(\pm 0.011) - 0.041(\pm 0.007) \text{ atom\%O} \quad (5.8)$

In general, the activity coefficient should be a function of temperature as well as composition for non-ideal solutions. The above results would appear to show that the activity coefficient of oxygen is constant over the temperature range 1100°C to 1300°C. If it is assumed that $\log f'_O$ is proportioned to the reciprocal of the absolute temperature the following relationship is obtained;

$$\log f'_O = \frac{\phi}{T} \text{ atom\%O} \qquad (5.9)$$

where ϕ is a constant. On substituting the experimental values for $\log f'_O$ at 1100°C and 1300°C ϕ is found to be -56.3 and -64.5 respectively. From the average value of ϕ;

$$\log f'_O = \frac{-60.4}{T} \text{ atom\%O} \qquad (5.10)$$

and the following values of $\log f'_O$ may be calculated for 1100°C and 1300°C respectively;

$1100^{\circ}C \; \log f'_O = -0.044 \text{ atom \% O} \qquad (5.11)$

$1300^{\circ}C \; \log f'_O = -0.038 \text{ atom \% O} \qquad (5.12)$

It may be concluded from this calculation that the

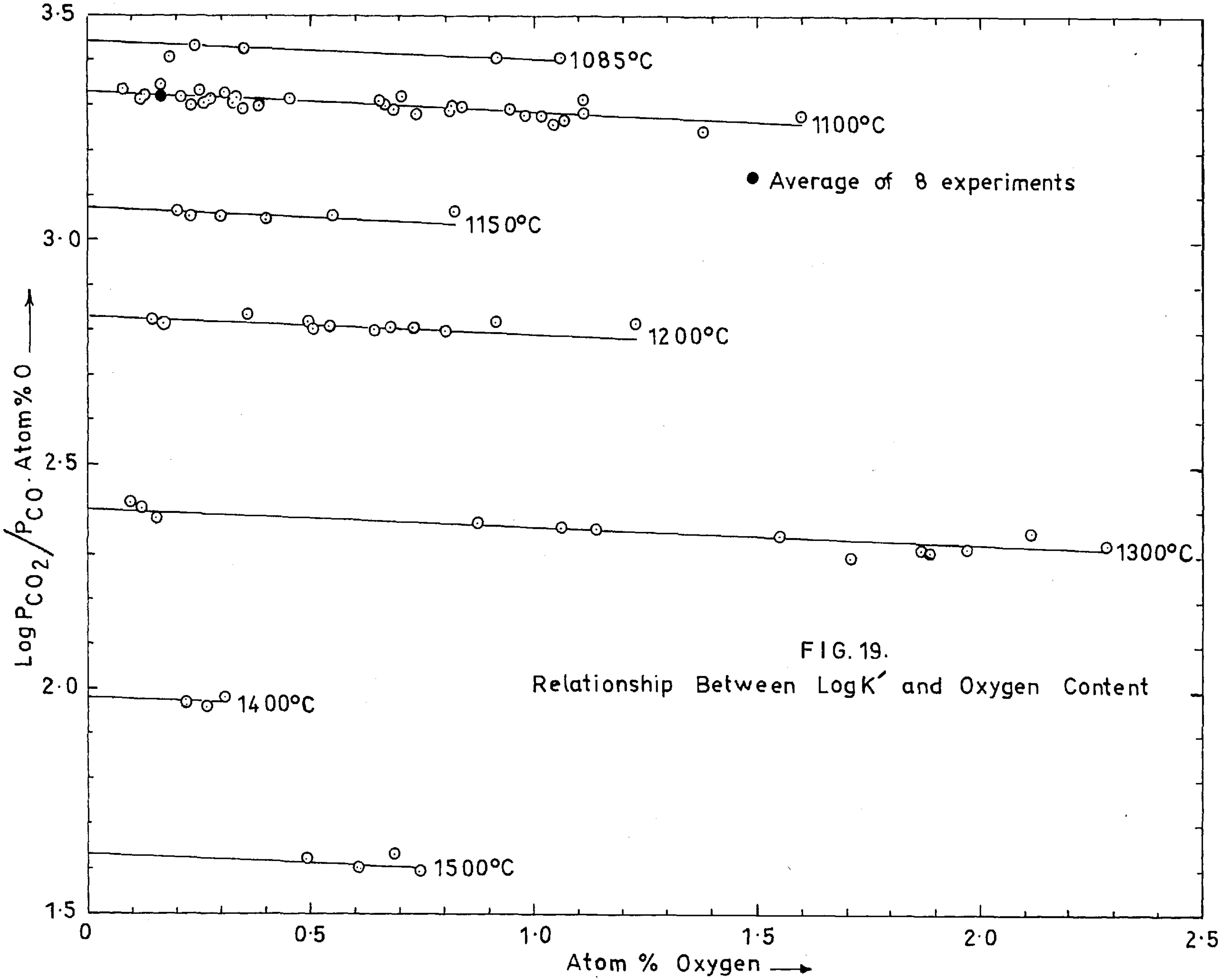


FIG. 19.

Relationship Between Log K′ and Oxygen Content

TABLE 5

Experimental results for the equilibrium:

$$[O]_{Cu} + CO\ (g) \rightleftharpoons CO_2\ (g); \quad K' = \frac{P_{CO_2}}{P_{CO} \cdot \text{Atom\%O}_{Cu}}$$

Temperature 1085°C

Run No.	P_{CO_2}/P_{CO}	Wt%O	Mean Atom%O	K'	LogK'
60	465	0.0460 0.0467 0.0460	0.183	2540	3.405
61	656	0.0606 0.0606	0.240	2730	3.435
62	931	0.0872 0.0882	0.348	2670	3.427
P	2687	0.265 0.273 0.264	1.06	2540	3.405
Q	2330	0.228 0.233 0.235	0.915	2550	3.407

Temperature 1100°C

Run No.	P_{CO_2}/P_{CO}	Wt%O	Mean Atom%O	K'	LogK'
9	671	0.0853 0.0852 0.0872	0.340	1970	3.294
10	455	0.0560 0.0560 0.0583	0.229	1990	3.299

TABLE 5 (Continued)

Run No.	P_{CO_2}/P_{CO}	Wt%O	Mean Atom%O	K'	LogK'
11	347	0.0416	0.170	2040	3.310
		0.0446			
		0.0427			
12	431	0.0521	0.206	2090	3.320
		0.0517			
		0.0521			
14	311	0.0388	0.152	2050	3.312
		0.0373			
		0.0387			
15	233	0.0300	0.114	2040	3.310
		0.0279			
		0.0286			
16	756	0.0946	0.381	1990	3.299
		0.0996			
		0.0943			
17	571	0.0677	0.273	2090	3.320
		0.0707			
		0.0684			
19	538	0.0638	0.249	2160	3.334
		0.0616			
		0.0629			
20	542	0.0409	0.159	2150	3.332
		0.0390			
21	356	0.0413	0.163	2180	3.338
		0.0409			
23	352	0.0429	0.169	2080	3.318
		0.0415			
		0.0437			

TABLE 5 (Continued)

Run No.	P_{CO_2}/P_{CO}	Wt%O	Mean Atom%O	K'	LogK'
24	327	0.0393	0.153	2140	3.330
		0.0386			
		0.0384			
26	342	0.0425	0.164	2080	3.318
		0.0406			
28	342	0.0446	0.167	2070	3.316
		0.0407			
		0.0414			
29	548	0.0675	0.268	2040	3.310
		0.0674			
		0.0679			
30	689	0.0836	0.332	2070	3.316
		0.0840			
31	259	0.0322	0.123	2100	3.322
		0.0309			
		0.0300			
33	178	0.0205	0.082	2170	3.336
		0.0210			
		0.0199			
37	512	0.0646	0.260	1970	3.294
		0.0665			
		0.0658			
38	341	0.0400	0.161	2120	3.326
		0.0408			
		0.0412			
40	1332	0.166	0.651	2040	3.310
		0.166			
		0.165			

TABLE 5 (Continued)

Run No.	P_{CO_2}/P_{CO}	Wt%O	Mean Atom%O	K'	LogK'
42	1470	0.177 0.180	0.707	2080	3.318
43	1339	0.167 0.175 0.180	0.687	1950	3.290
45	1575	0.206 0.188 0.222	0.808	1950	3.290
46	654	0.0802 0.0834 0.0816	0.324	2020	3.305
47	1630	0.200 0.211	0.812	2000	3.301
48	1885	0.248 0.273 0.273	1.04	1810	3.258
49	1980	0.271 0.275 0.274	1.07	1850	3.267
51	2420	0.351 0.352 0.351	1.38	1750	3.243
53	1850	0.240 0.241 0.240	0.946	1960	3.292
56	2295	0.274 0.282 0.288	1.11	2060	3.314

TABLE 5 (Continued)

Run No.	P_{CO_2}/P_{CO}	Wt%O	Mean Atom%O	K'	LogK'
57	2140	0.276 0.282 0.289	1.11	1930	3.286
58	1940	0.253 0.250 0.266	1.02	1900	3.279
59	1865	0.251 0.246 0.248	0.977	1910	3.281
w	3038	0.394 0.405	1.60	1900	3.279
x	1338	0.167 0.171 0.170	0.667	2000	3.301
y	1406	0.185 0.186	0.732	1920	3.283
z	1654	0.211 0.214	0.838	1980	3.297
63	934	0.115 0.114	0.453	2060	3.314
64	646	0.0771 0.0761	0.303	2130	3.328
Temperature 1150°C					
65	616	0.139 0.138	0.546	1130	3.053
66	935	0.204 0.207	0.807	1160	3.064

TABLE 5 (Continued)

Run No.	P_{CO_2}/P_{CO}	Wt%O	Mean Atom%O	K'	LogK'
67	450	0.100 0.103	0.401	1120	3.049
68	447	0.102 0.102	0.403	1110	3.045
69	334	0.0743 0.0754	0.297	1130	3.053
70	229	0.0481 0.0481	0.196	1170	3.068
71	254	0.0572 0.0562	0.225	1130	3.053
		Temperature 1200°C			
73	805	0.307 0.321	1.23	654	2.816
74	407	0.162 0.165	0.643	633	2.801
75	322	0.126 0.126	0.494	652	2.814
76	236	0.0892 0.0894	0.354	667	2.824
77	236	0.0898 0.0899	0.356	663	2.822
78	598	0.232 0.231	0.911	656	2.817
4Au	465	0.185	0.730	637	2.804
5Au	436	0.173	0.683	639	2.806
6Au	505	0.203	0.801	630	2.799

TABLE 5 (Continued)

Run No.	P_{CO_2}/P_{CO}	Wt%O	Mean Atom%O	K'	LogK'
2Ag	322	0.128	0.506	636	2.803
3Ag	346	0.137	0.541	639	2.806
1Ni	107	0.0410	0.163	656	2.817
2Ni	109	0.0421	0.167	652	2.814
3Ni	94.2	0.0359	0.143	659	2.819
		Temperature 1300°C			
79	383	0.482 0.474	1.87	204	2.310
80	478	0.527 0.560	2.12	225	2.352
81	343	0.395	1.55	221	2.344
82	336	0.440 0.433	1.71	197	2.294
83	243	0.265 0.269	1.06	229	2.360
84	205	0.220 0.222	0.871	235	2.371
85	406	0.505 0.504	1.97	206	2.314
86	382	0.484 0.484	1.89	202	2.305
8A	24.3	0.0236	0.094	258	2.412
20A	29.4	0.0296	0.117	251	2.400
21A	35.8	0.0378	0.150	239	2.378
R	261	0.294 0.291 0.288	1.14	229	2.360

TABLE 5 (Continued)

Run No.	P_{CO_2}/P_{CO}	Wt%O	Mean Atom%O	K'	LogK'
S	480	0.586	2.29	209	2.320
		Temperature 1400°C			
9A	24.3	0.0672	0.266	91.0	1.959
10A	20.4	0.0560	0.222	92.0	1.964
11A	20.4	0.0550	0.218	94.0	1.973
12A	29.4	0.0776	0.307	96.0	1.982
14A	20.5	0.0560	0.222	92.0	1.964
		Temperature 1500°C			
13A	24.3	0.154	0.608	40.0	1.602
15A	20.5	0.125	0.494	41.5	1.618
16A	24.3	0.155	0.611	39.8	1.600
18A	29.3	0.175	0.690	42.7	1.630
19A	29.4	0.189	0.746	39.3	1.594

expected change in $\log f'_O$ in going from 1100°C to 1300°C is too small to be accurately determined by this experimental method and the relationship;

$$\log f'_O = -0.041 \text{ atom\%O} \qquad (5.10)$$

may be regarded as satisfactorily representing the activity coefficient of oxygen. The values of logK at 1085°C, 1150°C, 1300°C, 1400°C and 1500°C were obtained by extrapolating logK' to zero percentage oxygen by means of equation (5.10).

A plot of logK against the reciprocal of the absolute temperature is shown in Fig. 20. From this plot logK was found to be represented by the following relationship;

$$\log K = \frac{10,150}{T} - 4.07 \qquad (5.13)$$

and hence for the reaction

$$[O] + CO\ (g) = CO_2\ (g) \qquad (5.1)$$

$$\Delta G^o = -46,440 + 18.6T \qquad (5.14)$$

3. Errors

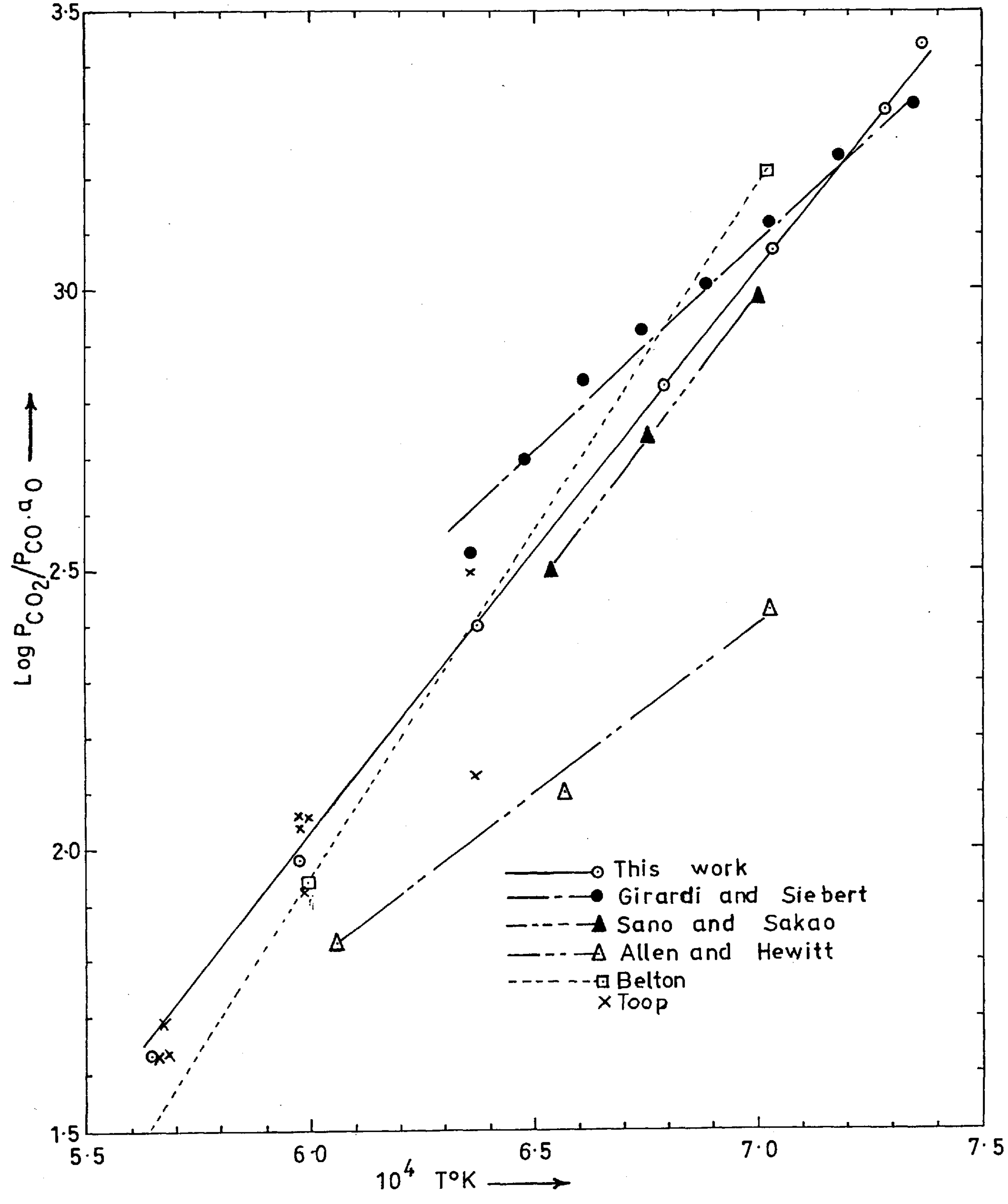
The major sources of error in this investigation are tabulated below:

	1085°C	1500°C
Temperature	± 3°C	± 6°C
P_{CO_2}/P_{CO}	± 2%	± 2%
atom%O	± 2%	± 2%

From these values it was estimated that the values of

FIG. 20.

Relationship Between Log K and Reciprocal of Absolute Temperature



logK should be accurate to ±0.015 and for the reaction

$$[O] + CO\ (g) = CO_2\ (g)$$

$$\Delta G^o = -46{,}440 + 18.6T \pm 150 \text{ cals}$$

4. Discussion

The previous work on the solubility of oxygen in liquid pure copper is summarized in Fig. 20 where the earlier work is compared with the results of this study. Sano and Sakao (ref. 59) bubbled CO/CO_2 gas mixtures through 45 gm charges of liquid copper in a circulating apparatus. They carried out detailed studies at 1206°C to determine the effect of oxygen concentration on the equilibrium constant. At this temperature they found the following relationship between the activity coefficient and concentration of oxygen;

$$\log f'_O = -0.053 \text{ atom\%O}$$

No attempt was made to find the relationship between f'_O and temperature. Although their results are in reasonable agreement with this study the smaller values of logK and the increased deviation from ideality may be significant. Both of these differences could be explained by a non-random error in their carbon monoxide analysis such that the reported values are too high by a small constant amount. Such an error could possibly occur by some of the carbon dioxide in the equilibrium gas mixture reacting with copper lost by vaporization from the melt and depositing on the colder parts of the reaction tube. If this takes place it would be expected that at constant temperature and flowrate the measured carbon monoxide concentration would be too high by a small constant amount. Although the above phenomena could not be detected in the author's study where the CO/CO_2 gas mixture was circulated over 3 gm of copper it may have been present in Sano and Sakao's work where the gas mixture was bubbled through 45 gm of copper.

Girardi and Siebert (ref. 58) equilibrated 30 gm samples of copper with CO/CO_2 gas mixtures over the temperature range 1090°C to 1300°C. Their apparatus was of the flowmeter type and the CO/CO_2 gas mixture was passed over the surface of the melt. The design of their apparatus was such that only a very small range of low oxygen concentrations could be investigated and hence no information on the effect of oxygen concentration on the equilibrium constant could be obtained. One possible source of error in this work was the method of quenching the melt. The procedure used was to remove the alumina boat containing 30 gm of copper to the air cooled section of the furnace tube, where it was allowed to remain in contact with the furnace gases until it reached a convenient handling temperature and then quenched into water. From the author's experience of trying to retain all the oxygen in a 3 gm sample by this method of quenching it is thought that a significant loss of oxygen could have occurred. It may be expected that the magnitude of this error would increase as the reaction temperature increased. From Fig. 20 it can be seen that the discrepancy between Girardi and Siebert's results and the present investigation could be accounted for if this error occurred.

Allen and Hewitt (ref. 60) equilibrated samples of cathode copper with H_2/H_2O gas mixtures over the temperature range 1090°C to 1350°C. From the tabulated thermodynamic data of Elliot and Gleiser (ref. 48) the equivalent equilibria under CO/CO_2 gas mixtures can be calculated. The scatter of their data was too great for them to obtain any information on the effect of oxygen concentration on the equilibrium constant. It is apparent from Fig. 20 that at a given temperature they obtained a much higher oxygen solubility in copper for a given oxygen potential than any of the other studies.

The experimental method used by Allen and Hewitt is not very satisfactory for reasons discussed in Chapter 4 and it may be assumed that their results are unreliable.

Belton (ref. 73) has recently studied the equilibrium between H_2/H_2O gas mixtures and liquid copper from 1150°C to 1605°C. Belton expresses the equilibria as;

$$\log P_{H_2O}/P_{H_2} \;\; \mathrm{Wt}\ \%\ O = \frac{10,890}{T} - 3.462$$

From the tabulated thermodynamic data of Elliot and Gleiser (ref. 48) the equilibria under CO/CO_2 gas mixtures may be calculated to be;

$$\log P_{CO_2}/P_{CO} \;\; \mathrm{atom}\%O = \frac{12,390}{T} - 5.49$$

From Fig. 20 it can be seen that Belton's results are in good agreement with the present study at 1300°C but at lower temperatures contain less oxygen than that found for any of the previous investigations and at higher temperatures much more than this investigation. If Belton's results are reliable, it must be considered that the discrepancy between the CO/CO_2 and H_2/H_2O results may be due to the difference between the effects of hydrogen and carbon on the activity of oxygen in liquid copper.

Toop~~s~~ (ref. 74) has recently determined the equilibria between CO/CO_2 gas mixtures and liquid copper by means of the levitation technique. The results of his investigation are shown in Fig. 20. At the lower temperature 1300°C he found the kinetics of the reaction slow and the mean of his experiments for oxidation and deoxidation is in reasonable agreement with this work. At higher temperatures his results are in excellent agreement with this work.

It may be concluded that the results obtained in this investigation are reliable within the stated accuracy limits over the temperature range 1085°C to 1500°C and resolve the discrepancies in the previous studies.

The second part of this research was concerned with the effect of alloying elements on the activity of oxygen in molten copper and for this reason it is of interest to compare the behaviour of oxygen in other pure metal systems with that found for copper. The free energy equation for the reaction $\frac{1}{2}\ O_2 = [O]$ at 1 at. per cent concentration and the heat of formation of the oxides from O_2 gas per oxygen atom at 25°C is shown in Table 6. The second part of Table 6 shows corresponding data for sulphur in metals and metal sulphides.

Richardson (ref. 83) found as empirical correlation between the difference of $\Delta H^o_{25^oC}$ for Fe O and many of the oxides of interest in deoxidation of steel and the effect of the deoxidising element on the activity coefficient of oxygen in molten iron. Alcock (ref.19) postulated from this correlation and the behaviour of halogens in liquid sodium that the free energies of

TABLE 6

Solvent	ΔG^{o}(cal)	$\Delta G^{o}_{540^{o}C}$(cal)	Reference	$\Delta H^{o}_{25^{o}C}$(cal/mole)	
Ag	-2,700+10.0T	15,430	Lumsden (ref.75)	Ag_2O	-7,200
Cu	-20,450+1.77T	-17,250		Cu_2O	-41,800
Pb	-28,540+3.40T	-22,380	Alcock (ref.78)	PbO	-52,400
Co	-14,730-4.88T	-23,580	Belton (ref.76)	CoO	-57,100
Ni	-18,290-1.48T	-20,980	Bowers (ref.77)	NiO	-57,300
Fe	-28,890-3.02T	-34,370	Belton (ref.76)	FeO	-63,500
Sn	-43,870+6.59T	-31,920	Alcock (ref.79)	SnO	-68,350
Ag	-16,400+1.0T	-14,290	Rosenqvist (ref.80)	Ag_2S	-22,970
Cu	-29,200+5.0T	-20,140	Alcock (ref.4)	Cu_2S	-34,900
Co		-21,400	Cheng (ref.81)	CoS	-36,200
Sn	-24,940+5.11T	-15,680	Cheng (ref.81)	SnS	-37,100
Ni		-26,860	Cheng (ref.81)	NiS	-37,100
Pb	-23,140+4.59T	-14,820	Cheng (ref.81)	PbS	-37,700
Fe	-30,000+3.59	-23,490	Chipman (ref.82)	FeS	-37,820

solution of gaseous species in liquid metals were proportional to the heats of formation of the compounds. The order of the elements for decreasing ΔG^{o} at 1540°C is Ag, Cu, Ni, Pb, Co, Sn, Fe, for oxygen and Ag, Pb, Sn, Cu, Co, Fe, Ni, for sulphur. The results in Table 6 show that the empirical relationship suggested by Alcock is only of limited applicability and that changes in the nature of the bond between different metals and oxygen must be considered. It also shows that the manner of bonding for oxygen and sulphur is different and that the change in bonding for the series of metals is different for oxygen and sulphur. This would indicate that the behaviour of dilute solutions of oxygen in molten ternary systems may be markedly different from that of sulphur.

CHAPTER 6

DILUTE SOLUTIONS OF OXYGEN IN LIQUID COPPER ALLOYS

1. Introduction

The reaction under study may be represented by the equation;

$$CO\ (g) + [O]\ \text{Alloy} = CO_2\ (g)$$

for which,

$$K = \frac{P_{CO_2}}{P_{CO} \cdot f_O \cdot \text{atom\%O}}$$

and

$$K' = \frac{P_{CO_2}}{P_{CO} \cdot \text{atom\%O}}$$

The reference state for oxygen is the same as that selected for pure copper. From this it is evident that,

$$\log f_O = \log K' - \log K$$

where K is the true equilibrium constant for the reaction,

$$CO\ (g) + [O]\ \text{Pure copper} = CO_2\ (g)$$

Previous work in the field of alloying elements by Chipman and co-workers (ref. 84) has shown that the activity coefficient of a very dilute solute determined in the presence of an alloying element x may be conveniently separated into factors as in the relation;

$$\log f_O = \log f'_O + \log f_O^{(x)}$$

in which f_O refers to the ternary alloy Cu-O-x, f'_O is the activity coefficient for a binary Cu-O alloy of the same oxygen concentration and $f_0^{(x)}$ is the contribution of the alloying element. Chipman found that $f_0^{(x)}$ is a function of the concentration of x but is wholly or nearly independent of the concentration of O.

In very dilute solutions of alloying elements it has been frequently found that a linear relationship exists between log $f_0^{(x)}$ and the concentration of x. In this range it has been convenient to employ the interaction parameters;

$$\varepsilon_0^{(x)} = \partial \ln f_0^{(x)} / \partial N_x$$

to compare the behaviour of alloying elements on the same solute.

Alcock (ref. 3) used a slightly different method of presentation for his results on the activity of sulphur in molten copper alloys. The experimental procedures used in his research provided data on the solubility of sulphur in molten copper alloys of different compositions in equilibrium with the same H_2S/H_2 gas mixtures. From this it is apparent that

$$f_s' \text{ wt\%S pure copper} = f_s \text{ wt\%S in alloy}$$

and $$D_s = \frac{f_s}{f_s} = \frac{\text{wt\%S in copper}}{\text{wt\%S in alloy}}$$

Alcock examined the results of his research by means of plots of D_s versus concentration of alloying element.

The results of the present investigation are presented by means of the relationship $f_0^{(x)}$ where,

$$f_0^{(x)} = \frac{f_0}{f'_0}$$

and f'_0 is the activity coefficient of oxygen for a binary copper + oxygen solution at the same oxygen concentration as is present in the alloy. If Henry's law is obeyed by the solute it is evident,

$$f_0^{(x)} = D_0 = \frac{\text{atom\% O in copper}}{\text{atom\% O in alloy}}$$

and that for small deviations from Henry's law, such as found in the present investigation, the error in assuming $f_0^{(x)} = D_0$ is negligible compared with the experimental errors. The results of this research and comparisons with other relevant data will be made by means of these relationships.

The results for each alloy system will first be described and discussed from an experimental point of view. This will be followed by a general discussion which will include the relevant previous work in this field.

2. Results

a) Copper - Nickel. The activity coefficient of oxygen was measured for compositions ranging from pure nickel to pure copper at 1500°C by means of the flowmeter apparatus. The effect of small amounts of nickel on the activity coefficient of oxygen in molten copper was also determined at 1200°C by means of the circulating apparatus.

The possible extent of carbon contamination in the pure nickel beads at 1500°C was calculated from the $(CO)^2/CO_2$ ratio used in this research and the tabulated thermodynamic data listed by Elliot and Gleiser (ref. 48) for the equilibria between graphite and carbon monoxide, carbon dioxide gas mixtures. The activity of carbon relative to graphite in the nickel beads was calculated to be 5×10^{-6}. A similar calculation for the pure cobalt beads at 1500°C gave an activity of 1.4×10^{-5}. Schenck et al (ref. 85) have recently determined the saturation solubilities of carbon in pure molten nickel and cobalt. Assuming Henry's law is obeyed to saturation the calculated activities of carbon in the nickel and cobalt beads correspond to 5.4×10^{-5} and 1.9×10^{-4} at. per cent carbon respectively. These values are negligible compared to the oxygen concentrations and may be safely neglected.

Preliminary experiments at 1500°C with pure nickel showed that the alumina boat was slightly attacked by the metal beads. This was indicated by a thin green deposit on the alumina and is similar to the crucible attack described by Chipman and Wriedt (ref. 86) and Bowers (ref. 77) in their investigations on the solubility of oxygen in molten nickel. From X-ray analysis they showed that the deposit was the spinel $NiAl_2O_4$. The small extent of attack found in the present investigation was unlikely to affect the equilibrium seriously but created experimental difficulties in the removal of the equilibrated beads from the alumina boat. The beads strongly adhered to the deposit and it was frequently found necessary to break the entire alumina holder to remove them. An attempt was made to overcome the crucible attack by lining the alumina boat with a slurry of thoria powder and firing at 1500°C. Although this method was unsuccessful in sintering the thoria to the alumina it was found that the reaction between the metal beads and refractory was decreased and the equilibrated beads could easily be removed from the boat.

The preliminary experiment also showed that the hydrogen reduction method for oxygen analysis was unsatisfactory for pure nickel. In order to obtain a reasonable rate of reduction it was found necessary to raise the temperature to 1200°C and at this temperature it was found that the reproducibility of the analysis was very poor, values ranging from 0.036 to 0.057 wt % oxygen were obtained for similar equilibrated beads. For this reason it was decided to send similar specimens to the B.N.F.M.R.A.and I.R.S.I.D. for oxygen analysis and build an inert carrier gas apparatus for oxygen analysis.

From the results which are shown in Table 7 it can be seen that the oxygen analysis values obtained by the B.N.F.M.R.A., I.R.S.I.D.and the author are in reasonable agreement. The value of log K' for pure nickel was found to be 1.263 with a standard deviation of ±0.027. The previous work on the solubility of oxygen in molten nickel has been recently discussed by Bowers (ref. 77) and Fig. 21 is reproduced from this publication.

FIG. 21.

EQUILIBRIUM CONSTANT FOR THE REACTION

$CO(g) + [O]_{Ni} = CO_2(g)$

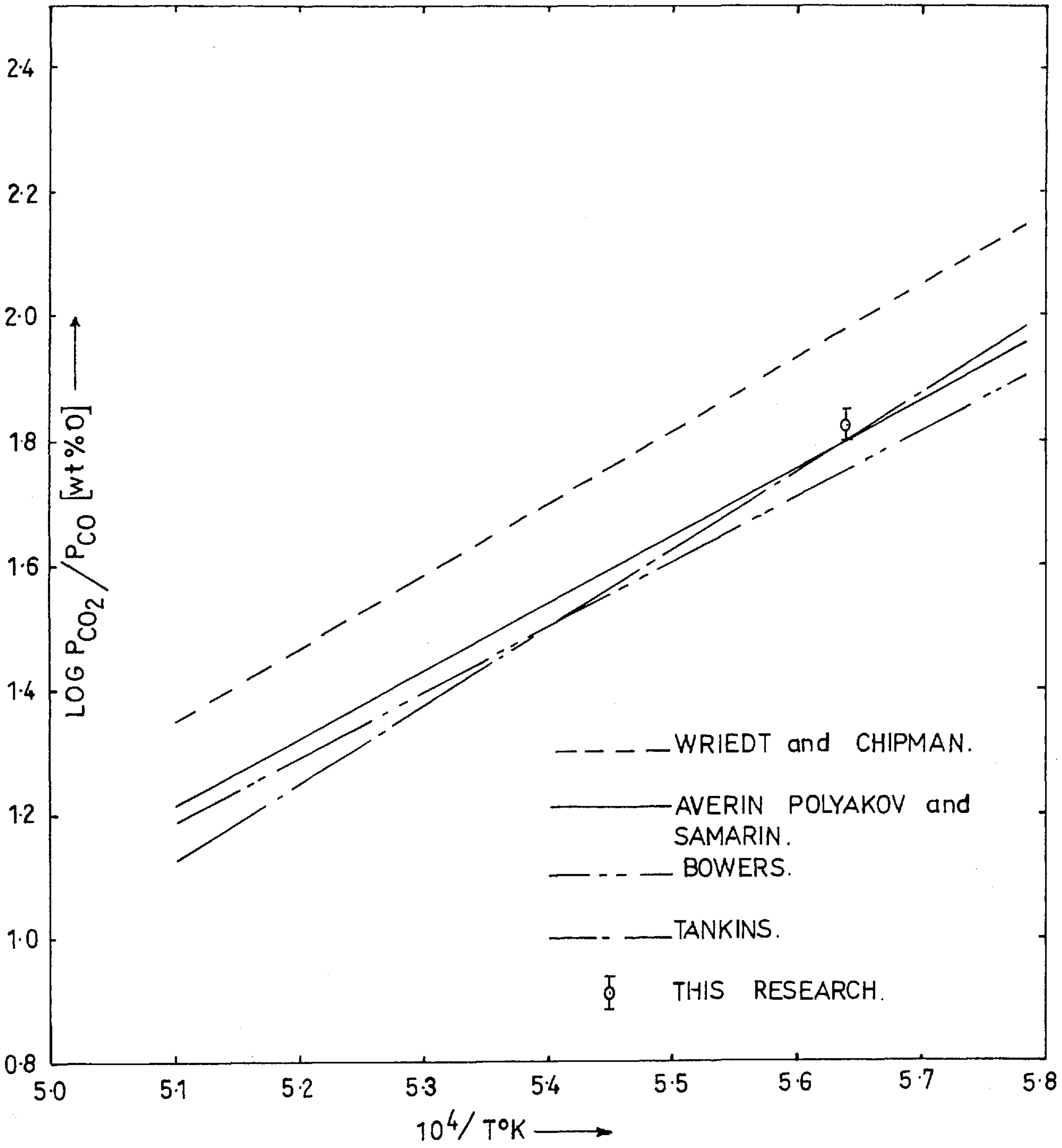


TABLE 7

Experimental results of studies of the effect of alloying nickel on the activity coefficient of oxygen in liquid copper at 1500°C.

Run No.	Atom% Cu	$\frac{P_{CO_2}}{P_{CO}}$	Atom% O	K'	LogK'	$\mathrm{Log}f_O$	$\mathrm{Log}f_O^{(Ni)}$
1NIr	0	3.63	0.205	17.7	1.248	-0.382	-0.374
2NA	0	..	0.213	17.0	1.230	-0.400	-0.392
2NB	0	..	0.198	18.3	1.262	-0.368	-0.360
3N	0	..	0.183	19.8	1.297	-0.333	-0.326
1NFA	0	3.72	0.183	20.3	1.308	-0.322	-0.315
1NFB	0	..	0.205	18.1	1.258	-0.372	-0.364
1NFA	0	..	0.220	16.9	1.228	-0.402	-0.394
2NFB	0	..	0.209	17.8	1.250	-0.380	-0.374
3NF	0	..	0.191	19.5	1.290	-0.340	-0.332
1NCIr	8.2	3.85	0.240	16.0	1.204	-0.426	-0.417
2NCA	8.4	..	0.251	15.3	1.185	-0.445	-0.455
2NCB	8.4	..	0.266	14.5	1.161	-0.469	-0.459
1NDIr	16.6	4.14	0.286	14.5	1.161	-0.469	-0.458
2NDA	17.1	..	0.272	15.2	1.182	-0.448	-0.438
2NDB	17.1	..	0.338	12.3	1.090	-0.540	-0.526
1NEIr	27.2	4.67	0.349	13.4	1.127	-0.503	-0.489
2NEA	27.0	..	0.360	13.0	1.114	-0.516	-0.502
2NEB	27.0	..	0.352	13.3	1.124	-0.506	-0.492
1NGIr	33.8	4.67	0.358	13.1	1.117	-0.513	-0.499
2NGA	35.9	..	0.351	13.3	1.124	-0.506	-0.492
2NGB	35.9	..	0.366	12.8	1.107	-0.532	-0.509
1NHIr	46.4	5.21	0.411	12.7	1.104	-0.526	-0.521
2NHA	46.5	..	0.468	11.1	1.045	-0.585	-0.566
2NHB	46.5	..	0.457	11.4	1.057	-0.573	-0.554
1NJA	65.7	5.82	0.332	17.5	1.243	-0.387	-0.374

TABLE 7 (Contd.)

Run No.	Atom% Cu	$\frac{P_{CO_2}}{P_{CO}}$	Atom% O	K'	$\text{Log}K'$	$\text{Log}f_O$	$\text{Log}f_O^{(Ni)}$
1NJB	65.7	5.82	0.352	16.5	1.217	-0.413	-0.399
1NKA	75.1	5.90	0.288	20.5	1.312	-0.318	-0.306
1NKB	75.1	"	0.284	20.7	1.314	-0.316	-0.304
1NK	76.9	"	0.277	21.3	1.328	-0.302	-0.291
1NM	84.7	5.82	0.216	26.9	1.430	-0.200	-0.192
2NM	85.4	"	0.200	29.1	1.462	-0.168	-0.160

Run No. ending in A or B oxygen analysis determined by B.N.F.M.R.A., Ir. by I.R.S.I.D., remainder by author.

TABLE 7 (Contd.)

Experimental results of studies of the effect of alloying nickel on the activity coefficient of oxygen in liquid copper at 1200°C.

Run No.	Atom% Ni	P_{CO_2}/P_{CO}	Atom% O	K'	$\log K'$	$\log f_O$	$\log f_O^{(Ni)}$
Ni1	0	107	0.163	656	2.817	-0.013	
..	3.23	..	0.208	514	2.711	-0.119	-0.110
..	4.99	..	0.229	467	2.669	-0.161	-0.152
Ni2	0	109	0.167	652	2.814	-0.016	
..	6.84	..	0.273	400	2.602	-0.228	-0.219
..	9.0	..	0.296	368	2.566	-0.264	-0.252
Ni3	0	94.2	0.143	659	2.819	-0.011	
..	5.36	..	0.206	457	2.660	-0.170	-0.162
..	7.80	..	0.237	397	2.599	-0.231	-0.221

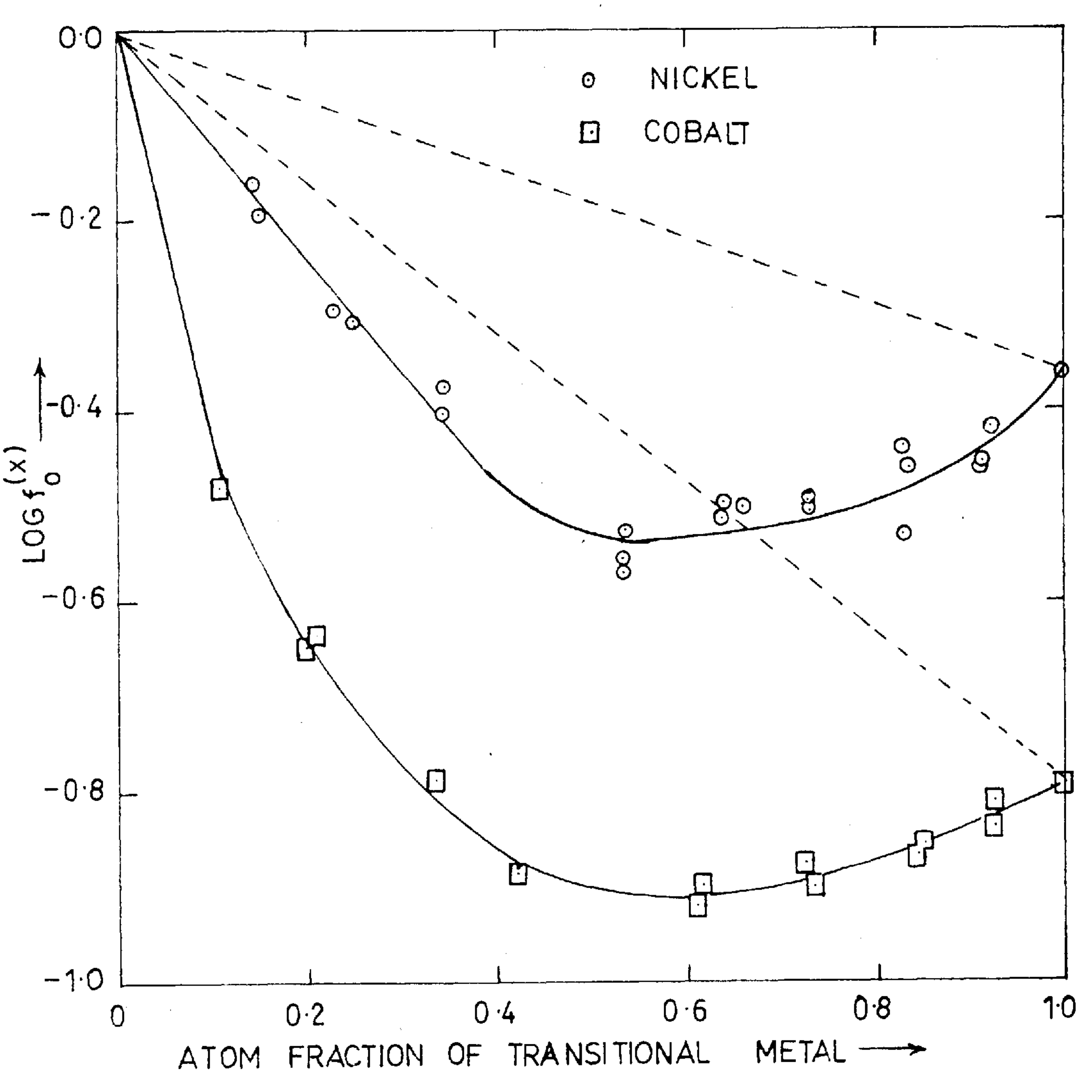
From Fig. 21 it can be seen that the result of the present investigation is in good agreement with the investigations of Averin, Polyakov and Samarin (ref. 87), Bowers (ref. 77) and Tankins (ref. 88), and contains more oxygen than may be expected from Wriedt and Chipman's study (ref. 86). The discrepancy of Wriedt and Chipman's results has been discussed by Bowers and is thought to be caused by a non-random error in their temperature measurements. The good agreement between the results of the present investigation and the majority of the previous studies on the solubility of oxygen in molten nickel indicated that the experimental procedure used in this research was satisfactory.

The variation of log $f_O^{(Ni)}$ with nickel content for the copper + nickel alloys at 1500°C and 1200°C are shown in Fig. 22 and Fig. 23 respectively.

b) <u>Copper - Cobalt</u>. The activity coefficient of oxygen was measured for compositions ranging from pure cobalt to pure copper at 1500°C by means of the circulating apparatus. The alumina crucibles were found to be attacked in a similar manner to that observed for the nickel experiments and the use of thoria lined crucibles was investigated. Again it was found that the extent of attack, which was indicated by a purple deposit was reduced and the beads could be readily removed from the boat. The

FIG. 22

EFFECT OF NICKEL AND COBALT ON ACTIVITY COEFFICIENT OF DISSOLVED OXYGEN IN MOLTEN COPPER AT 1500°C.



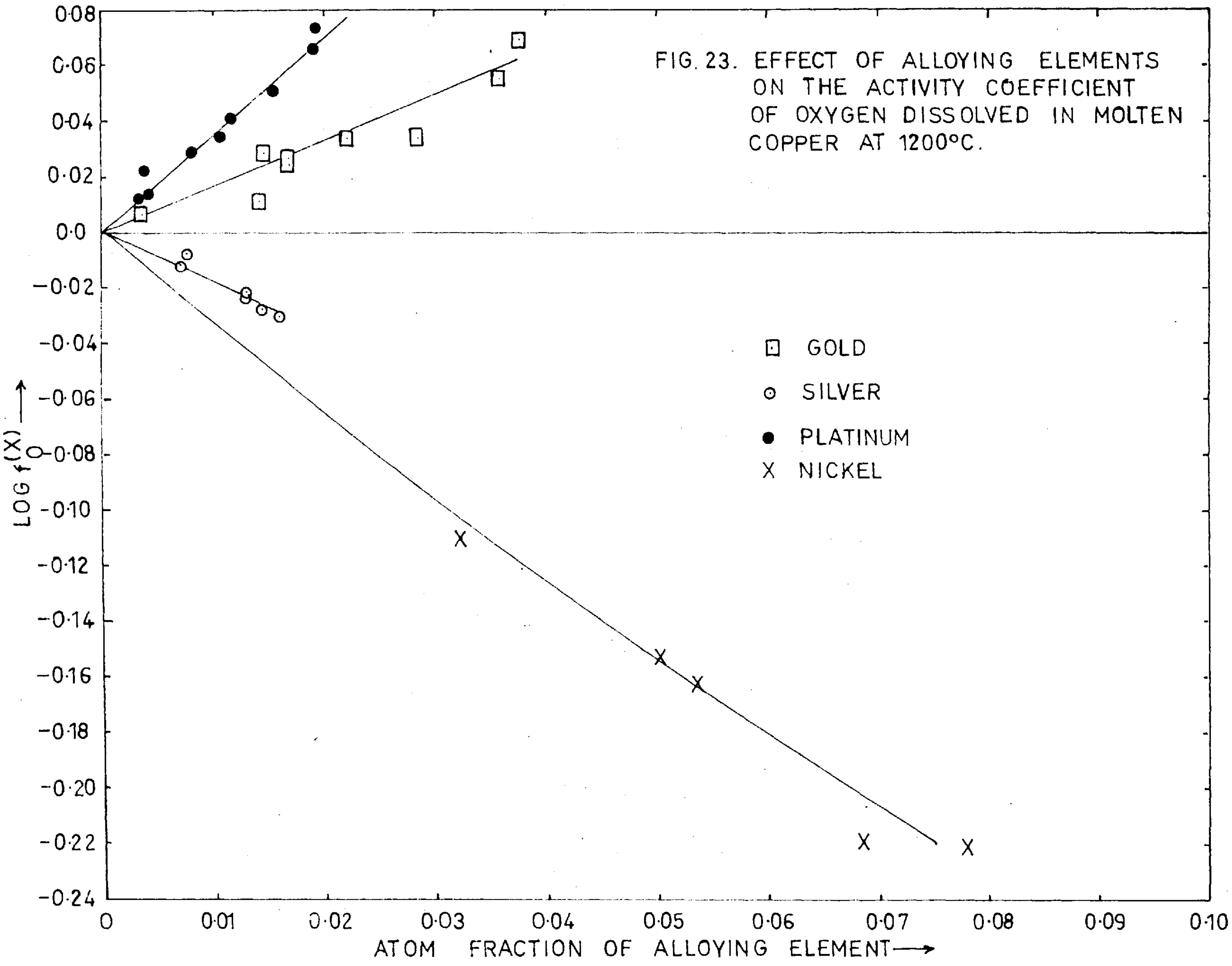


FIG. 23. EFFECT OF ALLOYING ELEMENTS ON THE ACTIVITY COEFFICIENT OF OXYGEN DISSOLVED IN MOLTEN COPPER AT 1200°C.

TABLE 8

Experimental results of studies of the effect of alloying cobalt on the activity coefficient of oxygen in liquid copper at 1500°C.

Run No.	Atom% Cu	$\frac{P_{CO_2}}{P_{CO}}$	Atom%O	K'	LogK'	Logf$_0$	Logf$_0^{(Co)}$
1C	0	2.02	0.309	6.52	0.814	-0.816	-0.804
2C	0	..	0.295	6.83	0.834	-0.796	-0.784
3C	0	..	0.302	6.68	0.825	-0.805	-0.793
2CA	7.6	2.02	0.311	6.48	0.812	-0.818	-0.806
3CA	7.7	..	0.334	6.04	0.781	-0.849	-0.836
1BC	14.7	2.02	0.339	5.95	0.775	-0.855	-0.851
3BC	15.5	..	0.354	5.69	0.755	-0.875	-0.861
1CC	27.6	2.02	0.376	5.51	0.741	-0.889	-0.874
2CC	26.6	..	0.387	5.21	0.717	-0.913	-0.898
2DC	38.4	2.02	0.386	5.22	0.718	-0.912	-0.897
3DC	39.0	..	0.405	4.98	0.697	-0.933	-0.917
3FC	57.9	2.02	0.373	5.41	0.733	-0.897	-0.882
2GC	66.6	2.71	0.398	6.81	0.833	-0.797	-0.784
2HC	80.0	3.39	0.366	9.27	0.967	-0.667	-0.649
3HC	79.2	..	0.352	9.62	0.983	-0.647	-0.633
1JC	89.2	3.39	0.245	13.8	1.140	-0.490	-0.479

oxygen analysis was carried out by the carbon reduction inert carrier gas apparatus.

The results are summarized in Table 8. The variation of log $f_O^{(Co)}$ with cobalt content for copper cobalt alloys at 1500°C is shown in Fig. 22.

c) <u>Copper - Iron</u>. The experimental methods used in this research were found to be unsuitable for studies on the solution of oxygen in molten iron + copper alloys and no satisfactory results were obtained. The following discussion describes the approach made to this system and the reasons for the failure of the experimental method.

It was evident from the previous studies on the solubility of oxygen in molten iron by Chipman and Floridis (ref. 89) and the solubility of carbon by Phragmen and Kalling (ref. 90) that at low oxygen concentrations a significant amount of carbon is also in equilibrium with CO_2/CO gas mixtures. From the data of these workers the carbon and oxygen concentration in equilibrium with molten iron at 1550°C and a gas mixture consisting of 203 ml argon, 15.4 ml carbon dioxide and 288 ml carbon monoxide were calculated to be 0.02 wt % and 0.05 wt % respectively. In order to overcome the problem of the high carbon potential of CO_2/CO gas mixtures in equilibrium with small amounts of oxygen in molten iron it was decided to investigate the properties of

H_2/CO_2 gas mixtures. From the thermodynamic data of Kubaschewski and Evans (ref. 36) for the reaction,

$$H_2\ (g) + CO_2\ (g) = H_2O\ (g) + CO\ (g)$$

and the equilibrium data for the solubility of oxygen and carbon in molten iron at 1550°C the concentration of these elements in equilibrium with a metered gas mixture consisting of 90%A, 8.41%H_2 and 1.59%CO_2 was calculated to be 0.05 wt % oxygen and 0.00054 wt % carbon. It was deduced from this calculation that this gas mixture was suitable for this investigation. On equilibrating 3 gm iron beads held in sintered alumina crucibles with this gas mixture it was found that the alumina refractory was heavily attacked and water vapour condensed in the quenching chamber. Further experiments showed that the extent of the crucible attack could be reduced by lining the boat with thoria powder but no method could be found of preventing the water vapour condensing in the apparatus. The condensation of water in the cold parts of the apparatus caused several experimental problems. First the flowmeters were found to oscillate erratically and it was difficult to maintain a metered gas mixture of known composition and secondly on quenching the surface of the specimens oxidised from reaction of the hot metal beads with the condensed water in the quenching chamber. In order to overcome these problems it would have been necessary to completely redesign the flowmeter apparatus and in view of the fact that Chipman and Floridis (ref. 89) had recently obtained data on the solubility of oxygen in molten Fe +Cu alloys it was decided to abandon any further attempts on this system.

d) Copper - Platinum. The effect of small amounts of platinum on the activity coefficient of oxygen in molten copper at 1200°C was studied by means of the circulating apparatus. No experimental difficulties were encountered with this system and the methods used were the same as for pure copper. The results are summarized in Table 9 and Fig. 23 by a plot of log $f_0^{(Pt)}$ versus atomic percentage platinum. It can be seen from Fig. 23 that platinum raises the activity coefficient of oxygen in copper and that $\varepsilon_0^{Pt} = \frac{\partial \ln f_0^{(Pt)}}{\partial N_{Pt}} = +8.2$.

e) Copper - Gold. The effect of small amounts of gold on the activity coefficient of oxygen in molten copper at 1200°C was studied by means of the circulating apparatus. No experimental difficulties were encountered with this system and the methods used were the same as for pure copper. The results are summarized in Table 10 and Fig. 23.

TABLE 9

Experimental results of the effect of alloying platinum on the activity coefficient of oxygen in liquid copper at 1200°C.

Run	Atom%	$\frac{P_{CO_2}}{P_{CO}}$	Atom%O	K'	LogK'	$\log f_O$	$\log f_O^{(Pt)}$
Pt1	0.35	484	0.742	666	2.823	-0.007	+0.023
"	0.29	"	0.749	648	2.812	-0.018	+0.013
"	0.40	"	0.747	650	2.813	-0.017	+0.014
Pt2	0.80	438	0.645	679	2.832	+0.002	+0.028
"	1.14	"	0.626	700	2.845	+0.015	+0.041
"	1.04	"	0.637	688	2.838	+0.008	+0.034
Pt3	1.92	698	0.952	732	2.865	+0.035	+0.074
"	1.89	"	0.972	718	2.856	+0.026	+0.066
"	1.53	"	1.01	692	2.840	+0.010	+0.051

TABLE 10

Experimental results of studies of the effect of alloying gold on the activity coefficient of oxygen in liquid copper at 1200°C.

Run	Atom%	$\frac{P_{CO_2}}{P_{CO}}$	Atom%O	K'	LogK'	Logf$_O$	Logf$_O^{(Au)}$
Au3	1.45	477	0.707	674	2.829	-0.001	0.028
"	1.68	"	0.710	672	2.827	-0.003	0.026
"	1.67	"	0.714	668	2.825	-0.005	0.025
Au4	0	465	0.730	637	2.804	-0.026	0.004
"	0.36	"	0.727	640	2.806	-0.024	0.006
"	3.75	"	0.621	749	2.874	+0.044	0.069
Au5	0	436	0.683	639	2.806	-0.024	0.004
"	1.4	"	0.669	652	2.814	-0.016	0.011
"	2.85	"	0.635	688	2.838	+0.008	0.034
Au6	0	505	0.801	630	2.799	-0.031	0.002
"	2.19	"	0.742	681	2.833	+0.003	0.033
"	3.59	"	0.704	717	2.856	+0.026	0.055

TABLE II

Experimental results of the effect of alloying silver on the activity coefficient of oxygen in liquid copper at 1200°C.

Run No.	Initial Wt. of Cu gm.	Initial Wt. of Ag gm	Final Wt. gm	Atom % Ag.	Atom % O	$\frac{P_{CO_2}}{P_{CO}}$	log K'	Log f_o	log f_o^{Pg}
Ag 1	0.90911	0.01248	0.92110	0.76	0.734	454	2.792	-0.038	-0.008
	0.97060	0.01352	0.98327	0.76	0.734		2.792	-0.033	-0.008
	0.01986	0.01266	1.03150	0.67	0.740		2.788	-0.042	-0.012
Ag 2	1.05040	0	1.05012	0	0.506	322	2.803	-0.027	–
	1.00368	0.02565	1.02595	1.27	0.530		2.784	-0.046	-0.024
	0.85724	0.02436	0.87834	1.43	0.535		2.780	-0.050	-0.028
Ag 3	0.94510	0	0.94490	0	0.541	346	2.806	-0.024	
	0.94904	0.02826	0.97502	1.58	0.579		2.776	-0.054	-0.030
	0.99735	0.02532	1.01921	1.28	0.567		2.785	-0.045	-0.022

by a plot of log $f_O^{(Au)}$ versus atomic percentage gold. It can be seen from Fig. 23 that gold raises the activity coefficient of oxygen in copper and that

$$\varepsilon_O^{Au} = \frac{\partial \ln f_O^{(Au)}}{\partial N_{Au}} = +3.8.$$

f) <u>Copper - Silver</u>. The effect of small amounts of silver on the activity coefficient of oxygen in molten copper at 1200°C was studied by means of the circulating apparatus. The results of these experiments can only be regarded as qualitative because of the high vapour pressure of silver at this temperature and the observed weight losses of the beads after equilibration. It was assumed that the weight loss was due solely to silver and from a mass balance the final alloy compositions were calculated. The results are summarized in Table 11 and Fig. 23 by a plot of log $f_O^{(Ag)}$ versus atomic percentage silver. It can be seen from Fig. 23 that silver decreases the activity coefficient of oxygen in molten copper and that

$$\varepsilon_O^{Ag} = \frac{\partial \ln f_O^{(Ag)}}{\partial N_{Ag}} = -3.8$$

3. <u>Discussion</u>

a) <u>Copper - Nickel</u>. The results for the activity of oxygen in copper + nickel alloys at 1500°C deviate considerably from the ideal relationship suggested by Wagner (ref. 91) and shown by a dotted line in Fig. 22. According to Wagner, for a ternary system consisting of components

1,2 and 3 where 3 is only slightly soluble the relationship;

$$\ln N_3 = (1-N_2)\ln N_3^{(1)} + N_2 \ln N_3^{(2)} \ldots\ldots\ldots\ldots\ldots (7.1)$$

may be used. The theoretical basis of this relationship is based on the following assumptions:

1. The solubility of component 3 is assumed to be so small that $N_3 \ll 1$, $N_2 + N_1 = 1$.
2. The atomic volumes of components 1 and 2 are supposed to be virtually equal, so that the number z of nearest neighbours of an atom is independent of the ratio of 1 to 2.
3. The heat of mixing of components 1 and 2 is assumed to be small, so that the behaviour of the 1-2 system is nearly ideal.

Equation (7.1) may be rewritten as;

$$\ln D_3 \text{ (alloy)} = N_2 \ln D_3 \text{ (metal 2)} \ldots\ldots\ldots\ldots\ldots (7.2)$$

where $D_3 \text{ (alloy)} = \dfrac{N_3 \text{ (metal 1)}}{N_3 \text{ (alloy)}} = \dfrac{f_3 \text{ (alloy)}}{f'_3 \text{ (metal 1)}}$

and $D_3 \text{ (metal 2)} = \dfrac{N_3 \text{ (metal 1)}}{N_3 \text{ (metal 2)}} = \dfrac{f_3 \text{ (metal 2)}}{f'_3 \text{ (metal 1)}}$

It is also evident that for small deviations from Henry's law for solute 3 in pure metal 1 the following approximation may be used.

$$\ln f_3^{\text{(alloy)}} = N_2 \ln f_3^{\text{(pure metal 2)}} \ldots\ldots\ldots\ldots (7.3)$$

where $f_3^{\text{(alloy)}} = \dfrac{f_3}{f'_3 \text{ (metal 1)}}$

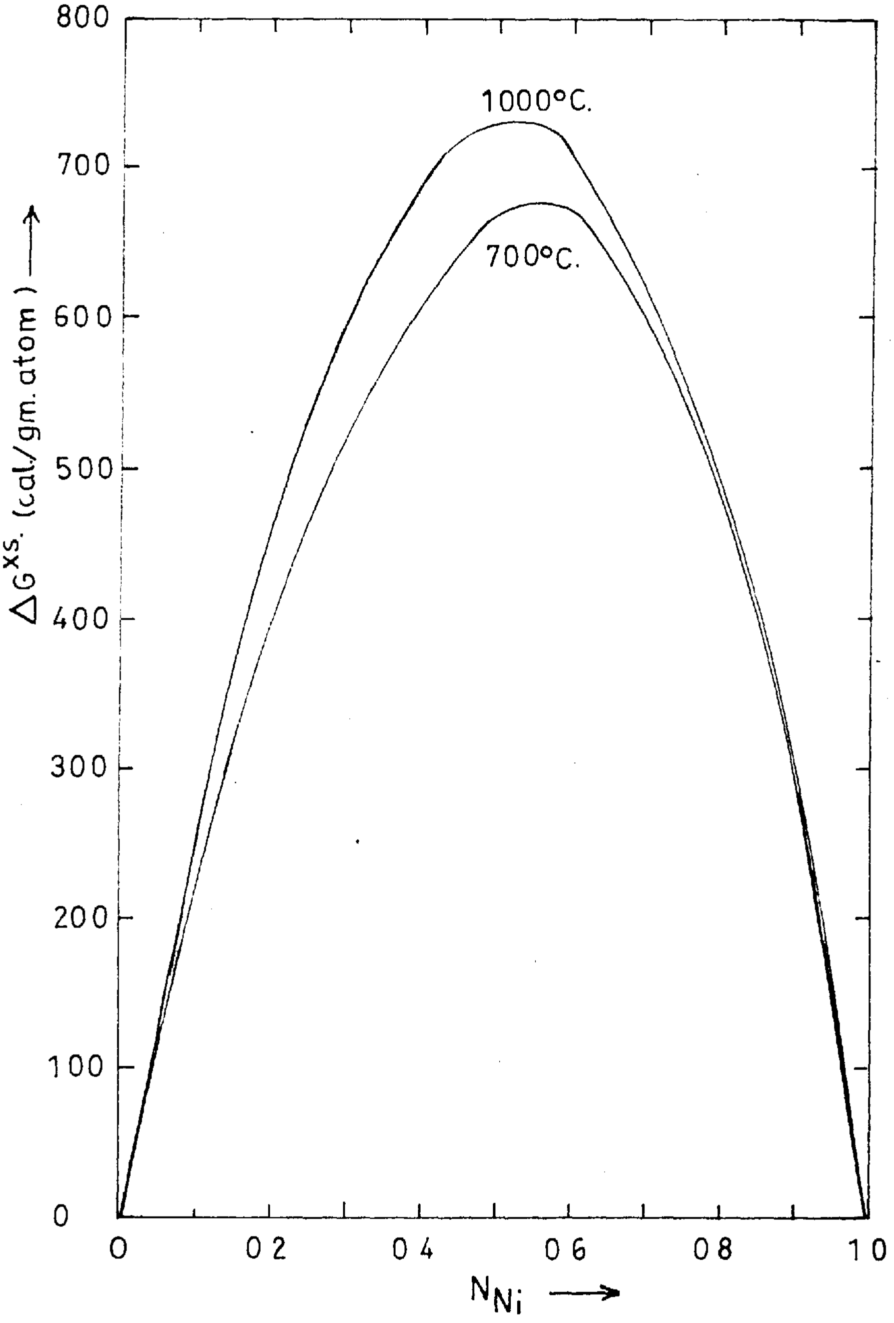
$$\text{and} \quad f_3^{(\text{pure metal 2})} = \frac{f_3 \ (\text{metal 2})}{f_3' \ (\text{metal 1})}$$

The ratios of the activity coefficients for equation (7.3) refer to the same concentration of solute 3. It may be recognised from equation (7.2) and (7.3) that for Wagner's approximation to be applicable a plot of log D_s or log $f_3^{(\text{alloy})}$ versus N_2 should be a straight line.

The failure of equation (7.1) for the Cu-Ni system with dilute solutions of carbon (ref. 92) and hydrogen (ref. 93) has already been discussed by Wagner (ref.55). Wagner deduced from the form of the Cu-Ni phase diagram, Hansen (ref. 54), that large deviations from ideality are not probable for this system and ascribed the failure of equation (7.1) to the inapplicability of the nearest neighbour hypothesis. Recent work by Rapp and Maak (ref. 94) however, has shown that the activity of nickel in solid copper-nickel alloys at 1000°C and 700°C deviates positively from Raoult's law. From the results of their investigation which are shown in Fig. 24 it is evident that the copper-nickel system does not fulfill the condition of ideality required by Wagner's approximation and hence deviations may be expected from equation (7.1).

The equation postulated by Alcock and Richardson (ref. 3) for a ternary random solution in which one of the components is present as a dilute solute may be represented by the relationship;

FIG. 24.
INTEGRAL EXCESS FREE ENERGIES OF MIXING FOR SOLID COPPER NICKEL ALLOYS.



$$\ln \frac{f_O(\text{Cu-Ni})}{f'_O\ (\text{Cu})} = N_{Ni} \ln \frac{f_O(\text{Ni})}{f'_O\ (\text{Cu})} - \frac{\Delta G^{xs(\text{Cu-Ni})}}{RT} \quad \text{....(7.4)}$$

for the copper + nickel + oxygen system. From equation (7.4) it is evident that;

$$\ln D_O(\text{alloy}) = N_{Ni} \ln D_O(\text{Ni}) - \frac{\Delta G^{xs(\text{Cu-Ni})}}{RT} \quad \text{........(7.5)}$$

and $$\ln f_O^{(\text{alloy})} = N_{Ni} \ln f_O^{(\text{Ni})} - \frac{\Delta G^{xs(\text{Cu-Ni})}}{RT} \quad \text{.......(7.6)}$$

The excess integral molar free energies of mixing of the copper + nickel system at the equimolar composition was calculated to be +3000 cals/mole from the experimental data for the copper + nickel + oxygen system at 1500°C by means of equation (7.6). A similar calculation for the Cu+Ni+S data determined by Alcock (Ref.4) gives a value of +1780 cals/mole. Rapp and Maak (Ref. 94) obtained values of +750 cals/mole at 1000°C and +680 cals/mole at 700°C for $\Delta G^{xs(Cu+Ni)}$ at the equimolar composition. If it is assumed that $\Delta G^{xs(Cu+Ni)}$ is a linear function of temperature the value at 1500°C is +870 cals/mole. It is evident from the large difference in the calculated values for $\Delta G^{xs(Cu+Ni)}$ from Alcock's data for the Cu+Ni+S system, the author's data for the Cu+Ni+O system and Rapp and Maak's data for the Cu+Ni system that the nature of the interactions between neighbouring atoms in the ternary solutions are not the same as in the binaries and that the random solution model does not explain the thermodynamic behaviour of these systems.

Alcock and Richardson (Ref. 5) further developed the random solution model to take into account the possible non-random distribution of the two types of metal atoms about the solute atom. From the data obtained by the author for the Cu+Ni+O system and Alcock's data for the Cu+Ni+S system it is apparent that the differences between the activity coefficient of sulphur in pure copper and pure nickel at 1500°C is greater than the corresponding difference for oxygen in pure copper and nickel at 1500°C. It may be deduced from this that the probability of clustering of nickel atoms around the solute atoms is greater in the Cu+Ni+S system than the Cu+Ni+O system. If this is the case it would be expected that the deviation from the random solution model would be greater for the Cu+Ni+S system than the Cu+Ni+O system whereas the experimental data show the reverse. The failure of the random solution and quasi-chemical models to adequately explain the thermodynamic behaviour of the Cu+Ni+O system indicates that the assumptions on which these models are based are only of limited applicability. Further discussion on the possible reasons for the failure of these models will be presented after discussing the results of the other systems investigated in this research.

One of the interesting features of the $\ln f_S^{(Ni)}$ versus composition plots for the Ni+Cu+O, Ni+Cu+S and

Ni+Cu+C systems is the rapid change in slope which occurs in the vicinity of 0.55 to 0.60 N_{Cu}. Saturation magnetisation data (ref. 95) indicates that the number of unfilled holes in the "3d band" for nickel decreases linearly from 0.6 of an electron per atom for pure nickel to zero at 60 atomic percentage copper. Recent work by Pollock (ref. 96) on the thermoelectric properties of nickel+copper alloys at 1000°C also shows a maximum in the absolute thermoelectric power for this system at approximately 57 atomic percentage copper. Pollock also found that there was a correlation between the effects of small amounts of alloying elements on the absolute thermoelectric power of a 57 atomic percentage copper 43 atomic percentage nickel alloy and the position of the solute in the periodic table. It would appear from these observations that the change in solubility of a dilute solute in the copper + nickel system is related in some manner to the change in the number of electrons in the "3d band" of nickel.

The interaction parameters $\varepsilon_0^{(Ni)}$ and $\varepsilon_0^{(Cu)}$ at 1500°C were calculated to be -2.8 and -1.8 respectively. These values were calculated from one experiment on a copper rich alloy and one experiment on a nickel rich alloy. For this reason the accuracy of the ε values is low and was estimated to be ± 1.0. The value of $\varepsilon_0^{(Ni)}$ at 1200°C was calculated to be -7.8.

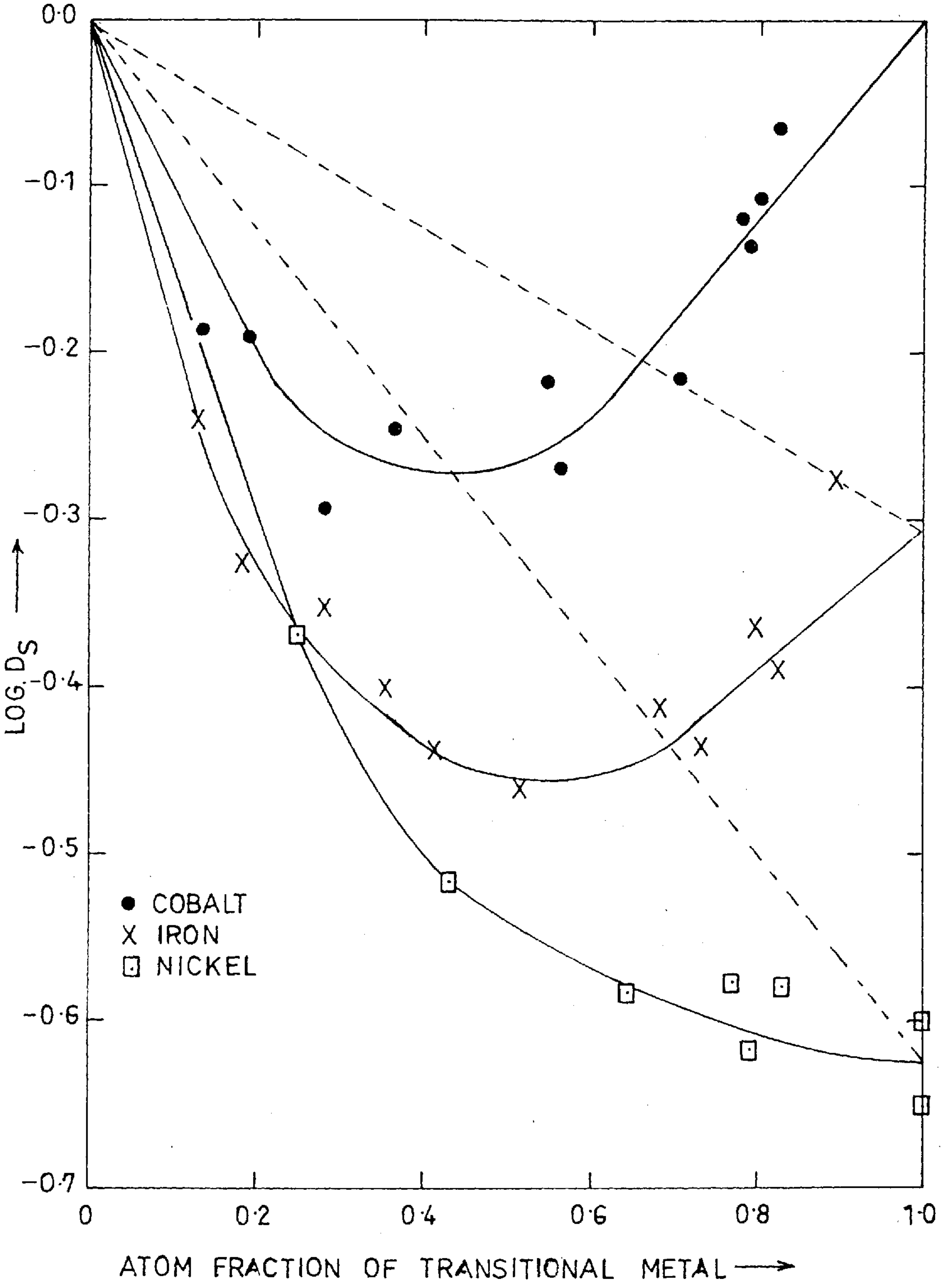
b) Copper -Cobalt. The results for the Cu+Co+O system are similar to those for the Ni+Cu+O system in that they deviate considerably from the ideal relationship suggested by Wagner. No data is available on the activities of copper and cobalt in liquid copper+cobalt alloys but from the flat liquidus of the phase diagram, Hansen (Ref. 54), it may be deduced that this system will show marked positive deviations from ideality. At the equimolar composition $\Delta G^{xs(Cu+Co)}$ was calculated by the random solution model to be +4050 cals/mole for the Cu+Co+O data and +2170 cals/mole for the Cu+Co+S data determined by Alcock (Ref.4). The data from which these calculations were made are shown in Figs. 22 and 25. The large difference in the $\Delta G^{xs(Cu+Co)}$ values calculated for the Cu+Co+O and Cu+Co+S systems again indicates the failure of the random solution model. It is also evident from the very large positive deviation from ideality of the Cu+Co+O system that the quasi-chemical model cannot adequately explain the thermodynamic behaviour of this system.

The values of $\varepsilon_{O}^{(Co)}$ and $\varepsilon_{O}^{(Cu)}$ were calculated to be -10 ± 1.5 and -1.0 ± 1.0 respectively.

c) Copper - Iron. The following discussion is based on the results of Chipman and Floridis (Ref.89) for this system. The data of these workers for the activity coefficient of oxygen in molten copper+iron alloys at

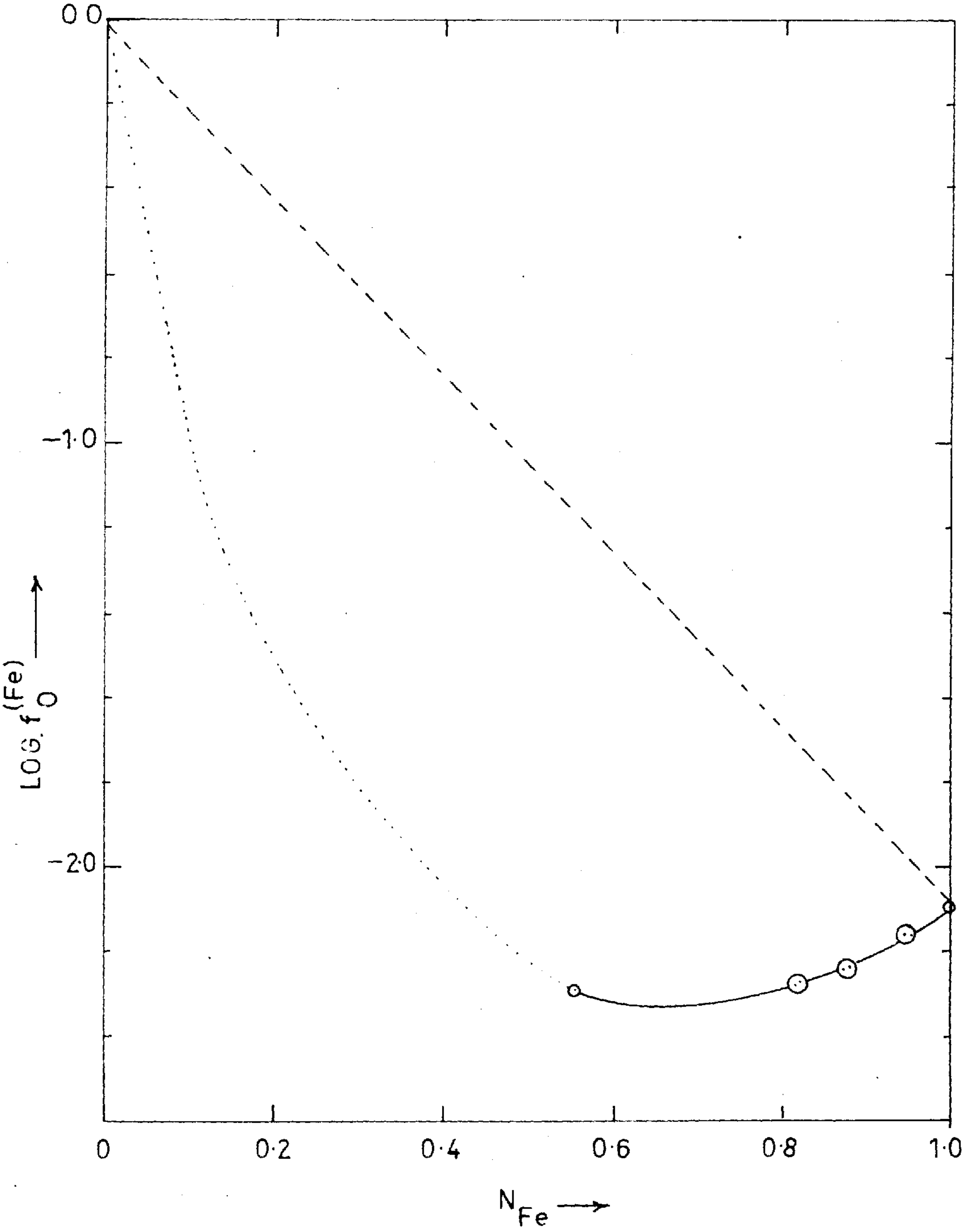
FIG. 25.

EFFECT OF IRON, COBALT AND NICKEL ON THE ACTIVITY COEFFICIENT OF SULPHUR DISSOLVED IN MOLTEN COPPER AT 1500°C.



1550°C is shown in Fig. 26. Alcock's data (Ref. 4) for the activity coefficient of sulphur in copper+iron alloys at 1500°C is shown in Fig. 24. From Figs. 25 and 26 it may be recognised that both these systems show large positive deviations from Wagner's ideal relationship and at the equimolar composition $\Delta G^{xs(Cu+Fe)}$ was calculated by the random solution model to be +2,200 cals/mole for the Cu+Fe+S data and 10,000 cals/mole for the Cu+Fe+O data. Vapour pressure measurements on the binary Cu+Fe system by Morris and Zellars (ref. 97) show that $\Delta G^{xs(Cu+Fe)}$ at the equimolar composition is 1900 cals/mole at 1550°C. It is evident from these values that the nature of the interactions between the atoms in the ternary solution is far more complicated than may be expected from the random or quasi-chemical theory. The behaviour of oxygen however is not so surprising when compared with the reported effects of other solutes on the Fe+Cu system. Hansen (Ref.54) in his review of the Cu+Fe phase diagram reports that carbon concentrations greater than 0.02 - 0.03 wt% produce a miscibility gap in the liquid state. Similar behaviour for small amounts of silicon has also been observed. From the behaviour of these elements it may be deduced that the interatomic forces between atoms in a binary solution can be considerably changed by the addition of a dilute solute.

FIG. 26.
ACTIVITY COEFFICIENT OF OXYGEN IN MOLTEN COPPER + IRON ALLOYS AT 1550°C.



d) Copper - Platinum. The behaviour of oxygen in copper + platinum alloys is qualitatively the same as that observed by Alcock (Ref.4) for sulphur. The effect of nickel on the activity coefficient of oxygen in molten copper is opposite to that observed for platinum and it is apparent that the simple free electron:atom ratio theory proposed by Himmler (Ref.93) is not satisfactory for these systems. The major weakness of the free electron:atom ratio theory is that it never considers the interactions between the ions in the solution and until such time that a better understanding of this problem has been obtained the approach adopted by Himmler would appear to be restricted.

e) Copper - Gold and Copper - Silver. The small range of alloy compositions investigated in this research does not allow a detailed discussion of these systems. Qualitatively the behaviour of oxygen is similar to that found for sulphur in these systems (Ref's.4 and 81). This behaviour may be expected when one considers that copper, silver and gold have the same number of free electrons per metal atom and the relative affinities of oxygen and sulphur for these elements follows the same order.

4. General Discussion

The approach adopted in this research has been to compare the thermodynamic behaviour of a dilute solute oxygen in a series of copper alloys with that previously found for sulphur in the same alloys. The object of this comparison was to try and obtain a better understanding of the nature of the interatomic forces in a ternary system where one component was present in a dilute amount. In order to obtain this information from the thermodynamic data it is evident that an atomic model has to be postulated for these solutions. The models selected in this research were the random and quasi-chemical models developed by Alcock and Richardson (Ref. 5).

On applying the random solution model to the experimental data for the Cu+Ni+O and Cu+Co+O systems it was found that the calculated values for the integral molar excess free energies of mixing for the binary metallic solutions at the equimolar composition were much more positive than the values previously calculated by Alcock and Richardson (Ref.3) from the data for the Cu+Ni+S and Cu+Co+S systems. The dissimilar behaviour of oxygen and sulphur compared with that predicted by the random solution model also occurs in the Fe-Ni and Fe+Cu systems. It is evident from the data for these systems that the random solution model is not generally applicable.

The data in Table 6, page 110, indicates that the behaviour of oxygen and sulphur in Fe,Co,Ni and Cu are significantly different. The order of decreasing free energy of solution for oxygen at 1540°C is Cu,Ni,Co and Fe and sulphur Cu,Co,Fe, and Ni. It is therefore not so surprising to find that the behaviour of oxygen in Cu+Ni, Cu+Co, and Cu+Fe solutions is very different to that of sulphur. In order to understand the different behaviour in the ternary systems the reasons for the different order of sulphur and oxygen in the binary systems must be first determined. The complexity of this problem may be realised if one considers that there is no general agreement on the electronic state of the simplest solute, hydrogen, in the transitional metals. McQuillan (Ref.98) and Bagshaw et al (Ref.99) have recently discussed the problem of hydrogen solution in transitional metals. The former suggests from preliminary results on the magnetic susceptibility changes in the transitional metals, that hydrogen contributes its electron to the valence band of the metal when in solution where as the latter postulates that hydrogen is present as an H^- ion. The latter conclusion was arrived at from consideration of metal hydride structures and the concept of crystal field stabilisation energy. Further progress in developing a theoretical model to adequately explain the behaviour of these systems would appear to depend on the building up of systematic data on the physical properties relating to the electronic structure. Until this data has been obtained it would appear unlikely that parameters to cover the conclusions listed by Alcock and Richardson (Ref.5), page 18 of this thesis, for the failure of the random and quasi-chemical models, can be included in a theoretical treatment.

In order to overcome the difficulties of the above problem Alcock and Richardson (Ref.5) and Gokcen (Ref.25) suggested that the most fruitful approach from a chemical metallurgical viewpoint would be to examine the thermodynamic data to find out if there was any empirical correlation between the effect of different alloying elements on the activity coefficient of a solute in a solution. The data obtained in this study on the effect of alloying elements on oxygen dissolved in metals is summarised in Table 12 by means of the relationship $\varepsilon = (\partial \ln fo/\partial X)$ where X is the atom fraction of the alloying element. Similar data for sulphur is shown in the second part of this table.

TABLE 12

The effect of alloying elements on oxygen dissolved in copper alloys.

Solvent	Alloying Element	Temp °C	ε	Ref.
Cu	Ag	1200	-3.8	
Cu	Au	1200	+3.8	
Cu	Pt	1200	+8.2	
Cu	Ni	1200	-7.8	
Cu	Ni	1500	-2.8	
Cu	Co	1500	-10.0	
Ni	Cu	1500	-1.8	
Co	Cu	1500	-1.0	
Cu	S	1206	-18.5	59
Cu	Sn	1206	-3.2	59
Cu	Sn	1155	-4.2	59

Cont'd. over...

TABLE 12 Cont'd

The effect of alloying elements on sulphur dissolved in copper alloys.

Solvent	Alloying Element	Temp ^{o}C	ε	Ref.
Cu	Ag	1085	small negative	81
Cu	Au	1115	+6.9	4
Cu	Pt	1200	+11.1	4
Cu	Ni	1300	-6.6	4
Cu	Co	1300	-4.8	4
Cu	Fe	1300	-7.4	4
Cu	Si	1200	+6.9	4
Cu	Pd	1300	+2.8	4
Cu	Pd	1400	+1.1	4
Ni	Cu	1600	0 ± 1	4
Fe	Cu	1600	negative	4
Co	Cu	1500	-4	4

The number of alloys in Table 12 is too small to make any accurate observations on empirical trends for the effect of alloying elements on the activity coefficient of oxygen and sulphur in copper alloys. One possible way of partially overcoming this problem is to examine the behaviour of more widely investigated solutes and determine if there is any empirical trend for the effect of alloying elements. The data on oxygen and sulphur can then be examined to determine if there is any similar trend.

TABLE 13

INTERACTION PARAMETERS ε

Co-X-C										3·67			
Fe-X-H										3·0	4·0		
X										B	C	N	O
Fe-X-N											7·2	0·8	4·0
Fe-X-O											-5·6	4·0	-12·3
Co-X-C										2·38	3·16	3·94	4·75
Fe-X-H										2·0	3·7	1·9	1·5
X										Al	Si	P	S
Fe-X-N										0·8	5·9	7·0	2·1
Fe-X-O										-105	-15·8	9·4	11·6
Co-X-C		-4·00	-2·94	-0·68	-0·23		0·22	1·70			2·12	4·81	
Fe-X-H	-16·0	-9·6	-0·41	-0·30		0·38	0·0	0·0			3·3	5·2	
X	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se
Fe-X-N	-12·0	-21·0	-9·5	-4·5		2·6	2·4	2·3					-0·4
Fe-X-O	-37	-56	-8·7	0		1·6	1·4	-2·6					
Co-X-C			-2·62		-1·02	0	1·01				3·50		5·63
Fe-X-H		-1·5									1·5	3·3	
X	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te
Fe-X-N		-26·4	-5·2								2·3	3·3	
Fe-X-O		-54	0·7								-1·1		
Co-X-C		-3·68	-1·70					2·03					
Fe-X-H		-17·2											
X	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po
Fe-X-N		-27·2	-0·8										
Fe-X-O			4·1				1·1	-5·5					

H.Schenk et al (Ref. 85) have recently determined the effect of a large number of alloying elements on the saturation solubility of carbon in molten cobalt. The Fe + X + O, Fe + X + H and Fc + X + N systems where X is an alloying element have also been fairly widely investigated and the data summarized by Elliot and Gleiser (Ref. 100). These data are summarised in Table 13 in the form of a periodic table.

It may be readily recognised from Table 13 that the values of $w_c^{(x)} = (\partial \ln \gamma_c / \partial Nx)\ a_C = 1,\ Nx \rightarrow 0$, for cobalt as solvent behave in a periodic manner and become more positive on going from group 111B to group V1A across the periodic table. The values of $w_c^{(x)}$ also become more positive in going down the elements from a particular group with two exceptions in group V111 and 1VA where Ru is more negative than Fe and Ge more negative than Si. It can also be seen that all elements to the left of cobalt in the periodic table have negative values for $w_c^{(x)}$ and all elements to the right positive values. The same linearity has been observed for carbon in solution in alloys with Fe, Mn and Ni as solvents (Ref. 101,25, and 102).

The values for $\varepsilon_H^{(x)} = (\partial \ln f_H / \partial N_x)\ p_{H_2} = 1$ atm, $Nx \rightarrow 0$ with iron as the solvent indicate a similar type of periodicity. The major differences are that the values become more negative in going down the elements from the same group and Co,Ni,Cu, in the fourth period and P and S in the second period behave anomalously. The values for P and S may be regarded as doubtful since Elliot and Weinstein (Ref. 103) were unsure of the composition for the sulphur melts and could not obtain a constant hydrogen reading for the phosphorus determinations. The values for Co and Ni however have been determined by several workers (Ref's. 104, 105, 106) and the results of all these investigations show that $\varepsilon_{H}^{(Ni)}$ is less positive than $\varepsilon_{H}^{(Co)}$. The solubility of hydrogen at 1 atm. pressure in pure Fe, Co, Ni and Cu at 1600°C is 28, 22, 47 and 14 cm^2/100g respectively (Ref. 99). The much greater solubility of hydrogen in Ni compared with Fe and Co indicates that the type of bonding of hydrogen in Ni is different to that of Fe and Co. It is therefore not so surprising to find a breakdown in the linear relationship for ε and the atomic number in this period. For the Co + X + C systems where periodicity is observed in this period it has been shown that the saturation solubility of carbon decreases in the order Mn, Fe, Co, Ni and Cu, (Ref. 85).

The Fe + X + N data again indicate that within the same period the value of ε increases with atomic number. Previously it was observed for the Fe + X + H data that the values for S and P were too low to conform with the periodic relationship. In a similar manner the $\varepsilon_{N}^{(x)}$

values for O, S and Se would also appear to be low. If the experimental values are accepted it is apparent that the type of bonding of hydrogen and nitrogen undergoes a distinct change on reaching group V1A. The order of $\varepsilon_{N}^{(x)}$ for Co, Ni and Cu is also similar to that found for hydrogen and indicates the complex problem of understanding the bonding of alloys with group V111 metals.

The data for the Fe + X + O system is particularly relevant to this research and from Table 13 it may be recognised that there are several distinct features compared with the previous systems. Negative values for $\varepsilon_{O}^{(x)}$ are no longer restricted to elements left of iron in the periodic table and the sequence in the fourth period is far more complicated. The $\varepsilon_{O}^{(x)}$ values for V and Cu are more negative than the alloying element to the left of them in the periodic table. The negative value for Cu cannot be explained in terms of a change in the sequence for the solubility of oxygen in the pure metals since the free energy of solution data indicate the order Fe, Co, Ni and Cu. The negative value for Au also indicates the failure of the periodic relationship. In order to determine the reasons for the behaviour of these systems a better understanding of the nature of the outer electron interactions, the effect of ions on the electrons and the possible non-random distribution of the solute ions must be obtained.

It may be expected from the similarity in the chemical behaviour of Fe, Co and Ni that the effect of dilute solutions of Cu on the activity coefficient of oxygen in molten Ni and Co would follow a similar trend to that shown by the Fe + Cu + O system. The data for oxygen in copper alloys, Table 12, shows this to be the case. The effect of dilute solutions of copper on the activity coefficient of sulphur in molten Fe, Co, and Ni shows a similar type of trend to that of the oxygen data in that Cu decreases the activity coefficient of sulphur in molten Fe and Co. The zero value for nickel is slightly different to that of the oxygen data but this may be related in some manner to the previously noted difference in the orders of the free energy of solution of oxygen and sulphur in molten Fe, Co, Ni and Cu. The effect of gold on the activity coefficient of oxygen and sulphur in molten nickel and cobalt have not been measured so no comparison can be made with the Fe + Au + O data to determine if there is a similar trend of negative interaction coefficients. The data in Table 12 also indicates that the value of $\mathcal{E}$ with copper as solvent becomes more positive in going down the elements from group V111 and IB. The value for the Cu + Pd + O system has not been measured but by analogy to the sulphur data it may be expected to be approximately zero.

Further discussion on empirical trends is fruitless until such time that more thermodynamic data is available. This data however will not provide reasons for the failure of the random, quasi-chemical and periodic relationships and to overcome this problem a better understanding of the electronic structure of alloys must be obtained. Until such time that these advances have been made all the available methods should be used to obtain the best estimate of an unknown interaction parameter.

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