

THERMODYNAMICS OF SOME METAL OXIDE
CONTAINING MELTS.

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by
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ABSTRACT

The thermodynamics of pure PbO and the systems n PbO.SiO₂, n PbO.P₂O₅ and n PbO.PbCl₂ have been studied using a cell of the type:-



A further study was undertaken on the n PbO.PbCl₂ system using a vapour entrainment technique, since the volatility of the lead chloride only enabled the composition range N PbO=1 to N PbO=0.5 to be studied using the E.M.F cell. It was found in this system that the presence of chloride ions lowered the oxygen ion activity appreciably, whereas the presence of fluoride ions only effected the oxygen ion activity by a small amount.

A high temperature calorimeter has been used to determine the heat of fusion of lead oxide, which was found to be 6.37 ± 0.4 Kcals/mole. The calorimeter was also used to measure the partial heats of PbO in the system n PbO.P₂O₅ by a drop technique.

It is suggested from the study on the PbO.SiO₂ system that firstly polymerisation reactions of the type $2\text{SiO}_4^{4-} \rightleftharpoons \text{Si}_2\text{O}_7^{6-} + \text{O}^{2-}$ begins at compositions richer in PbO than the orthosilicate composition, and secondly on the basis of Masson's molecular size distribution, the value of k_{11} is between 0.42 and 0.55 compared with $k_{11} = 0.196$ previously suggested.

The thermodynamic data obtained for the lead

phosphate system support the suggestion that PO_5^{5-} ions exist at very rich PbO compositions.

The heats of formation of sodium Maddrell and Kurrol salts were also measured with the calorimeter, with reference to cyclic sodium trimetaphosphate. The heat of transformation from Kurrol to Maddrell salt was found to be $-2.16 \pm 0.36 \text{Kcals/NaPO}_3$. A treatment of the thermodynamic data available for the sodium phosphates supports the evidence that long chains are likely to contain a certain proportion of rings.

In the appendix, an unsuccessful attempt to study the silicate structures by direct esterification, and then liquid gas chromatography is described.

TABLE OF CONTENTS.

PART A.

GENERAL INTRODUCTION.

	<u>Page.</u>
<u>Chapter 1.</u>	
Thermodynamics and Structural aspects of solutions containing metal oxides.	7
1. Introduction.	7
2. Simple ionic models.	9
3. Theories considering ionic equilibrium in polyanionic melts.	11
4. Theories considering molecular size distributions in multichain polymers.	19
<u>Chapter 2.</u>	
Techniques used for the determination of activities in PbO melts.	24
1. Synopsis of E.M.F. cells containing Lead polyanionic melts of relevance to this study.	24
2. The entrainment method.	27
<u>Chapter 3.</u>	
Calorimetry past and present.	33

<u>PART B.</u>	<u>Page.</u>
<u>EXPERIMENTAL WORK.</u>	<u>45</u>
<u>Chapter 4.</u>	
E.M.F. technique for the measurement of activities in melts.	47
1. The E.M.F. cell.	47
2. Experimental technique.	51
3. Reversibility tests.	52
4. Choice of electrolyte.	54
5. Materials.	55
6. Analysis of the melts.	56
<u>Chapter 5.</u>	
Results from the E.M.F. experiments.	58
1. Treatment of results.	58
2. Pure lead oxide (yellow).	59
3. n PbO.SiO ₂ melts.	64
4. n PbO.P ₂ O ₅ melts.	74
5. n PbO.PbCl ₂ melts.	81
6. Errors.	88
<u>Chapter 6.</u>	
Calorimetry.	91
1. Calorimeter.	91
2. (a) Materials.	93
(b) Preparation of samples for calorimetry.	93
3. Calorimetry technique and calibration.	94

Chapter 7.

The determination of the latent heat of fusion of lead oxide.	100
1. Experimental.	100
2. Results.	103
3. Discussion.	103

Chapter 8.

Calorimetric studies of $n \text{ PbO} \cdot \text{P}_2\text{O}_5$ melts.	108
1. Introduction.	108
2. The determination of the heat of formation of $\text{PbO} \cdot \text{P}_2\text{O}_5$ ($N \text{ PbO} = 0.5$).	110
3. Results.	111
4. Calorimetric determination of ΔH_{PbO} in $\text{PbO} \cdot \text{P}_2\text{O}_5$.	115
5. Experimental.	117
6. Results.	118
7. Discussion.	125

Chapter 9.

Calorimetry on $(\text{NaPO}_3)_n$.	127
1. Materials.	127
2. Method of preparation of the sodium metaphosphates.	128
3. Experimental procedure.	129
4. Results.	131

	<u>Page.</u>
<u>Chapter 10.</u>	
Vapour entrainment in the system n PbO.PbCl ₂	133
1. Apparatus.	133
2. Materials.	136
3. Experimental.	136
4. Results.	140
5. Discussion.	146
 <u>PART C.</u>	
<u>GENERAL DISCUSSION.</u>	150
 <u>Chapter 11.</u>	
Thermodynamics of some PbO melts.	151
1. Thermodynamics of pure PbO.	151
2. Thermodynamics of n PbO.SiO ₂ melts.	156
3. Thermodynamics of n PbO.P ₂ O ₅ melts.	177
4. Thermodynamics of n PbO.PbCl ₂ melts.	185
 <u>Chapter 12.</u>	
Ring-Chain equilibria in the sodium metaphosphates.	200
 <u>Chapter 13.</u>	
Conclusions.	206
Appendix.	210
References.	213
Acknowledgements.	219

Part A

General Introduction

Chapter I.

THERMODYNAMICS AND STRUCTURAL ASPECTS OF
SOLUTIONS CONTAINING METAL OXIDES.

1. Introduction:

A knowledge of the thermodynamics and structure of polyanionic melts and other metal oxide containing melts is of special interest to the extraction metallurgist in the consideration of slag metal equilibria in industrial processes, and is also of interest to the ceramicist and glass technologist.

The physical properties of the polyanionic melts such as the densities, surface tensions and viscosities have been studied extensively by various workers. The electrical conductivity of liquid silicates has been studied by Bockris^(1), and these melts have been shown to be ionic in nature. Also from these studies it can be seen that the polyanions exist as ions of varying size in the melt with the cations and free oxygen ions being responsible for the transport of current through the melt. The structural studies of the phosphates by Meadowcroft^(2), Cripps Clarke^(3) and Sridhar^(4) and the distribution of ethyl silicates which can also be demonstrated (see Appendix) ties in with the above picture.

Sridhar (4) has studied the thermodynamics of various polyanionic melts containing the same cation by an E M F technique; the PbO system was chosen because of its relatively lower melting points. The validity of Sridhars E M F cell was in doubt because of the assumption that the electrical conductivity in PbO was completely ionic. A modified cell has been used in the present study to check this validity in the Lead silicate and phosphate systems. Since this technique can produce only reliable free energy data, a knowledge of the heats of mixing is desirable by a calorimetric technique.

A high temperature calorimeter has recently been developed by Kleppa (5) and modified by Jeffes (6) and its versatility has been demonstrated in this study by the determination of the heats of mixing in $n \text{ PbO} \cdot \text{P}_2\text{O}_5$, the determination of the latent heat of fusion of PbO (which was in dispute) and its applicability to the determination of the heats of formation of various sodium metaphosphates. Kleppa (7,8) has measured the heats of mixing in the systems $n \text{ PbO} \cdot \text{SiO}_2$ and $n \text{ PbO} \cdot \text{B}_2\text{O}_3$ to complete the thermodynamic picture of the lead polyanionic melts.

The thermodynamics of the system $\text{PbO} - \text{PbCl}_2$ was also measured to study the effect of the chloride ion on the oxygen ion activity compared with the effect

due to a fluoride ion on the oxygen ion activity, which has special relevance to slag-metal equilibrium considerations.

2. Simple Ionic Models:

A molten salt is a name used to cover a host of high temperature liquids ranging from alkali metal halides, sulphates, nitrates, carbonates to the polyanionic melts such as the aluminates, silicates, borates and phosphates. In this study the treatment of these polyanionic melts is the primary interest, but a greater understanding of these melts can initially be obtained by a consideration of the ionic models which are applicable to the simpler molten salt mixtures.

Herasymenko^(9) put forward the first theory which introduced ionic concentrations into activity considerations and he assumed complete dissociation. The expression that he obtained relating the activity of a molten salt to the number of cations and anions present implies a random distribution of ions regardless of charge or type, which is generally unrealistic from energetic considerations.

A more realistic approach was put forward by Temkin^(10) who also considered complete dissociation

but postulated two interlocking sublattices are present. On one sublattice the cations can distribute themselves at random, and likewise the anions can be randomly distributed on the other. Then the activity of components M_1A_1 in M_1A_1 , M_2A_2 is given by:-

$$a_{M_1A_1} = \frac{n_{M_1+}}{n_{M_1+}} \cdot \frac{n_{A_1-}}{n_{A_1-}} = N_{M_1+} \cdot N_{A_1-}$$

where N_{M_1+} and N_{A_1-} are the cation and anion fractions, n_{M_1+} and n_{A_1-} are the number of cations and anions respectively. Sridhar has applied this model to lead silicates, borates and phosphates with success only in the lead rich compositions. The objection to the Temkin model is the case when the charges in the melt are not all the same; in other words in a melt containing a monovalent and a divalent ion.

Forland (11) modified Temkin's equation in terms of equivalent ionic fractions. Then: $a_{M_1A_1} = N_{M_1+}' \cdot N_{A_1-}'$ in a solution consisting of M_1A_1 and M_2A_2 .

$$\begin{aligned} \text{The equivalent ionic fraction} &= N_{M_1+}' \\ &= \frac{n_{M_1+}}{n_{M_1+} + n_v + n_{M_2^{2+}}} \\ &= \frac{n_{M_1+}}{n_{M_1+} + 2n_{M_2^{2+}}} \end{aligned}$$

In a liquid however this effect of different charges is small since there are a large number of vacancies created on melting. Temkins model was further treated by Flood, Forland and Grjotheim^(12) with a regular solution model such that the activity of component M_1A_1 in M_1A_1, M_2A_2 becomes:-

$$\begin{aligned} a_{M_1A_1} &= N_{M_1+} \cdot N_{A_1-} \cdot Y \\ &= N_{M_1+} \cdot N_{A_1-} \cdot \exp \left(\frac{N_{M_2+} \cdot N_{A_2-} \cdot z\Delta H}{RT} \right) \end{aligned}$$

$z\Delta H$ is the enthalpy change for the reaction



3. Theories considering ionic equilibrium in polyanionic melts.

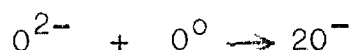
The theories so far discussed depend upon the melt consisting of definite and known ions. For example in a lead silicate melt, if one can assume that only the ions Pb^{2+} , O^{2-} and SiO_4^{4-} are present in the melt, then a Temkin model should be applicable. This can only be the case in the PbO rich melts and is certainly not the case as the silica concentration is increased, as polymerisation of the silicate ions occurs.

Toop and Samis^(13) have considered the degree of polymerisation of silicate anions in both acid and basic silicate melts. They considered the

suggestion by Fincham and Richardson⁽¹⁴⁾ that the reaction by which equilibrium polymerisation is established in a silicate melt should be the same for all compositions across the binary, and this equilibrium should be of a general form, and should not involve specific silicate anions. Oxygen in silicate melts exists in three forms; singly bonded O^- , doubly bonded O^0 and free oxygen ions O^{2-} .

The equilibrium between these forms was expressed as: $2O^- \rightleftharpoons O^0 + O^{2-}$. Thus the equilibrium constant $K = \frac{(O^0) \cdot (O^{2-})}{(O^-)^2}$, where these concentrations of the oxygen ions are the equilibrium numbers of moles of ions per mole of slag. They proposed that K is constant at a given temperature, and is characteristic of the cations present in the melt.

A consideration of the charge and material balances enabled (O^0) and (O^{2-}) to be expressed in terms of (O^-) and N_{SiO_2} . On substitution into the above equilibrium equation, the equilibrium values of (O^0) , (O^-) and (O^{2-}) versus compositions at known K can be drawn, see Fig 1. It is apparent that the shape of the (O^-) curve is similar to that of a free energy of mixing curve, although the tangents to N_{O^-} versus N_{SiO_2} at $N_{SiO_2} = 0$ and 1 do not tend to infinity. If one considers the reaction



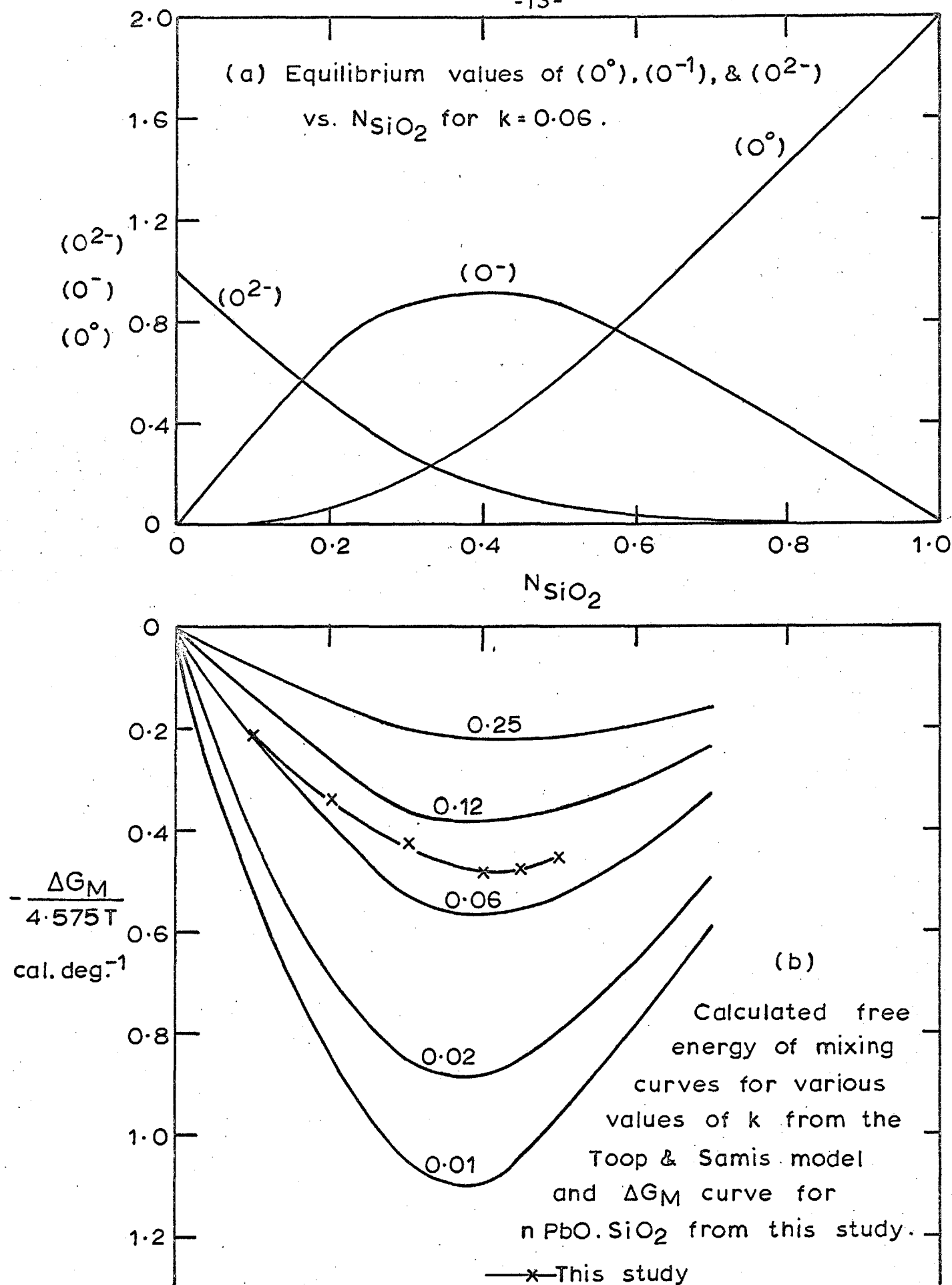


Fig. 1.

a reaction between metal oxide and silica to form two moles of singly bonded O^- ions, then the standard free energy change for this reaction is given by

$$\Delta G^0 = -RT \ln \frac{1}{K} = RT \ln K.$$

Since however the integral free energy of mixing is the free energy of mixing of the constituents to form one mole of oxides, then the number of moles of oxygen ions which have reacted in the melt is

$$\frac{(O^-)}{2}. \quad \text{Thus } \Delta G_M = \frac{(O^-)}{2} RT \ln K.$$

Toop and Samis then drew free energy of mixing curves for various values of K, as can also be seen in Fig 1. together with ΔG_M obtained in this study. A value for K of 0.09 was obtained from the present study, compared with K = 0.04 using the data of Richardson and Webb (15).

The approach of Toop and Samis does not involve specific silicate ions. Flood and Knapp (16) however have suggested specific polymeric silicate anions present in the melts, and have considered specifically $nPbO.SiO_2$ melts. In their treatment they consider ideal solutions of ions, and they chose the specific anions which forced agreement between the calculated ideal activity of PbO and experiment. Flood and Knapp considered three composition regions in $nPbO.SiO_2$:- (a) 0 - 20 moles per cent SiO_2 , (b) 20 - 40 moles per cent SiO_2 and (c) 40 - 60 moles per cent SiO_2 . Silica saturation begins at approximately 60 mole per cent silica.

In the first region (a) they considered the only anions present were O^{2-} , SiO_4^{4-} , and they found that agreement was obtained between experiment and an ideal solution containing only these anions as given by Temkin (10). In the second region (b) however they observed deviation from the ideal solution considering only SiO_4^{4-} and O^{2-} anions and the experiment. They suggested the anions present were O^{2-} , SiO_4^{4-} and $Si_3O_9^{6-}$ and again obtained agreement between experiment and theory. In the third composition region (c), they discounted the theory that the only polymeric ion formed was $Si_3O_9^{6-}$ on the grounds that the activity of PbO should approach zero at the equimolar or metasilicate composition. Since this is not the case they have considered a more highly polymerised ion is formed in this composition range. The ion $Si_6O_{15}^{6-}$ was found to force the best fit between experiment and theory. This theory is not meant to prove that the only anions present are O^{2-} , SiO_4^{4-} , $Si_3O_9^{6-}$ and $Si_6O_{15}^{6-}$. This is unlikely since the treatment involves the assumption of a completely ideal solution of anions.

Meadowcroft and Richardson (2) have considered the problem of ionic equilibria in liquid phosphates, which is analogous to the liquid silicates, in a more general manner than has been previously postulated.

They considered equilibria of the type:-

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

The equilibrium constant K_n is given by the equation:-

$$K_n = \frac{(N_{P_{n-1}O_{3n-2}})^{-n-1} \cdot N_{(P_{n+1}O_{3n+4})^{-n-3}}}{N_{(P_nO_{3n+1})}^2 \cdot (-n-2)} \dots (2)$$

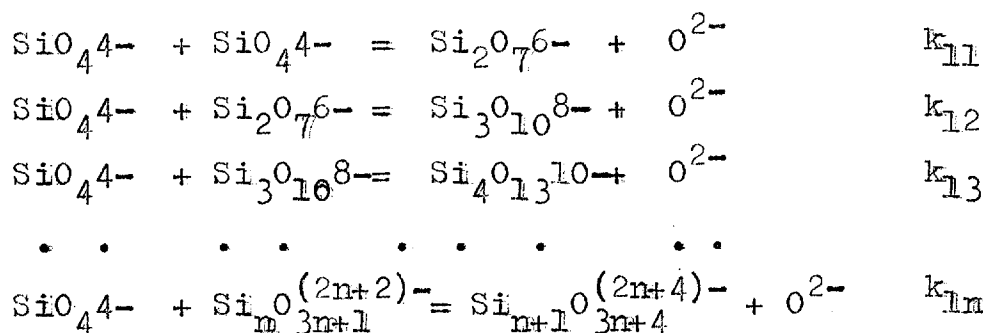
They then considered the Flory distribution which is discussed later in this chapter. For the Flory (17)

distribution, and in a melt in which the mean phosphate chain contains $\bar{n}$ phosphorus atoms, then the mole fraction $N_{P_nO_{3n+1}}^{-n-2} = \frac{1}{\bar{n}} \left(\frac{\bar{n}-1}{\bar{n}} \right)^{n-1}$ ref (2) .. (3)

If one combines equations (2) and (3), then $K_n=1$ is obtained for all values of n .

This is not however the case in practice. The values of K_n approach unity as one passes from K_2 to K_6 , and this value of unity is more rapidly approached with the smaller cations.

Masson (18) has considered the problem of ionic equilibria in liquid silicates in a similar manner to Meadowcroft and Richardson. He considers a binary melt $MO - SiO_2$ and the general reaction by which the monomer reacts with any constituents to produce the next higher member of the series. When the metal oxide to silica ratio is high, the silica is present in entirety as SiO_4^{4-} ions. As the silica content increases polymerisation begins according to the reactions:-



Assuming the activity coefficients are the same or unity, then the ion fraction of each ion can be expressed in terms of its lower members and its equilibrium constant. For example:-

$$N_{\text{Si}_2\text{O}_7^{6-}} = \frac{k_{11} N_{\text{SiO}_4^{4-}}}{N_{\text{O}^{2-}}} \cdot N_{\text{SiO}_4^{4-}} \quad \text{and so on.}$$

The assumption was then made that

$$k_{11} = k_{12} = k_{13} = \dots = k$$

$$\text{such that } \frac{N_{\text{Si}_2\text{O}_7^{6-}}}{N_{\text{SiO}_4^{4-}}} = k_{11} \frac{N_{\text{SiO}_4^{4-}}}{N_{\text{O}^{2-}}} = r \dots (1)$$

It can be shown that for all reactions between two silicate ions in which the O^{2-} is eliminated, the equilibrium ratios between a silicate ion and its next highest member is unity. The activity of the metal oxide is related by the Temkin equation $a_{\text{MO}} = N_{\text{M}^{2+}} \cdot N_{\text{O}^{2-}}$. Since $N_{\text{M}^{2+}} = 1$ in a binary system (containing one cation), then $a_{\text{MO}} = N_{\text{O}^{2-}}$.

If k_{1m} is known for a particular system then $N_{\text{O}^{2-}}$ as a function of composition is given by the equation (18)

$$\frac{1}{N_{\text{SiO}_2}} = 3 - k_{1n} + \frac{N_{\text{O}^{2-}}}{1 - N_{\text{O}^{2-}}} + \frac{k_{1n}(k_{1n} - 1)}{\left(\frac{N_{\text{O}^{2-}}}{1 - N_{\text{O}^{2-}}}\right) + k_{1n}}$$

The sum of the silicate ions is given by:-

$$\begin{aligned}\sum N_{\text{Silicate}} &= N_{\text{SiO}_4^{4-}} + N_{\text{Si}_2\text{O}_7^{6-}} + N_{\text{Si}_3\text{O}_{10}^{8-}} + \dots \\ &= N_{\text{SiO}_4^{4-}} + \frac{k N_{\text{SiO}_4^{4-}}}{N_{\text{O}^{2-}}} (\sum N_{\text{Silicates}})\end{aligned}$$

$$\text{Therefore } \sum N_{\text{Silicates}} = \frac{N_{\text{SiO}_4^{4-}}}{1 - \frac{k N_{\text{SiO}_4^{4-}}}{N_{\text{O}^{2-}}}} = 1 - N_{\text{O}^{2-}}.$$

assuming that the only anions present are O^{2-} and silicate ions.

$$\text{Then } N_{\text{SiO}_4^{4-}} = \frac{1 - N_{\text{O}^{2-}}}{1 + k \left(\frac{1}{N_{\text{O}^{2-}}} - 1 \right)}$$

Using equation (1) above, then the mole fractions of all the other ionic species can be determined. It is apparent that the equilibrium constant used by Masson is the product of k_1, k_2, k_3 etc. used by Meadowcroft and Richardson (2). It was suggested by Sridhar (4) that k_1 and k_2 vary slightly with composition, which means that k_{1n} from Masson will vary slightly with composition. A serious limitation to this theory and that of Meadowcroft and Richardson, is that only linear and branched chains have been considered and no allowance has been made for condensation between pairs of singly bonded oxygen atoms attached to the same polyanion.

4. Theories considering molecular size distributions
in multichain polymers.

Flory (17) was the first to consider the most probable distribution of molecular sizes in multichain polymers formed by the condensation of monomers of the types $A - R - B_{f-1}$ and $R - A_f$. This study is only concerned with condensation of polymers of the type $R - A_f$. f is the functionality and A is the functional group. Thus SiO_4^{4-} is a tetrafunctional monomer, and PO_4^{3-} is a trifunctional monomer.

Flory made the first assumption of equal reactivity of all functional groups, and this reactivity is independent of the size of the molecule involved. The second assumption made was that intramolecular condensations do not occur. The problem of treating intramolecular condensations is very complex, but because the theory developed ignoring these condensations fits well with the experiment, the latter assumption has been made.

Flory considers the probability that a given functional group has reacted is equal to α which is the fraction of functional groups that have condensed. Similarly the probability that another functional group has reacted is also equal to α from the principle of equal reactivity. The probability that $(x-1)$ additional identical units are attached according to a specific pattern to the unit containing

this functional group is $\alpha^{x-1} (1-\alpha)^{(f-2)x+1}$ since there are $x-1$ linkages and $(f-2)x + 1$ additional unreacted groups. The total number of specific configurations ω_x is given by Flory⁽¹⁷⁾

$$\omega_x = \frac{(fx - x)!}{(fx - 2x + 1)! x!}$$

Thus the probability P_x that the unreacted A group selected at random is part of an x -meric structure of any configuration is given by

$$P_x = \omega_x \alpha^{x-1} (1-\alpha)^{fx-2x+1}$$

$$\text{But } P_x = \frac{\text{Number of unreacted A's on } x\text{-mers}}{\text{Total unreacted A's}}$$

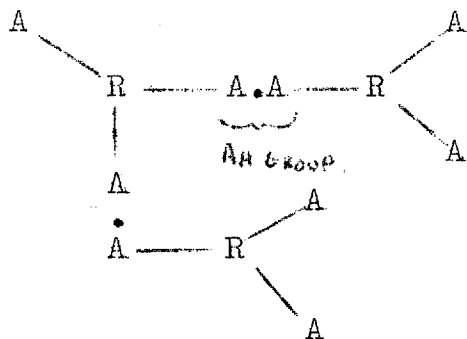
The number of unreacted A's on an x -mer = $(f-2)x+2$

$$\text{Therefore } P_x = \frac{((f-2)x+2)}{N_0 f(1-\alpha)} N_x = \omega_x \alpha^{x-1} (1-\alpha)^{fx-2x+1}$$

$$\text{Therefore } N_x \text{ (per mole)} = \frac{f(fx-x)! \alpha^{x-1} (1-\alpha)^{fx-2x+2}}{((f-2)x+2) (fx-2x+1)! x!}$$

where N_x is the number of x -mer molecules.

Flory's approach however is not strictly correct and it suffers from two sources of error. Consider the polymer formed by the self condensation of the monomer RA_f for $f = 3$



Flory has considered these AA groups as if they were only A groups. He has considered that the probability is unity for finding the second A of an AA group since he has equated this probability directly to α , which violates the assumption of equal reactivity. Masson⁽¹⁹⁾ has instead called this probability p_{AA} and he has related this to the extent of the reaction α by the equation

$$p_{AA} = \frac{\alpha f}{2(f-1)}.$$
 Secondly Flory's approach requires the singling out of a particular functional group on each configuration. In other words he chose the functional group at random from a set of functional groups consisting of one functional group from each molecule, rather than from all the functional groups that are available.

If p is the probability of a favourable outcome of each trial, then the probability P that in n trials an event will be favourable exactly $(n-r)$ times and unfavourable r times is given by:-

$$P = \frac{n!}{r!(n-r)!} p^{n-r}(1-p)^r.$$

In this situation $p = p_{AA}$. The number of trials is equal to the number of sites in an x -mer where such a choice is made, and is equal to $(fx-x)$. Number of favourable events is equal to $(x-1)$ and number of unfavourable choices is equal to $(fx-2x+1)$.

$$\text{Thus } P_x = \frac{(fx-x)!}{(fx-2x+1)!(x-1)!} \cdot p_{AA}^{(x-1)} \cdot (1-p_{AA})^{fx-2x+1}$$

This probability is directly related to the mole fraction of x-mer by taking into account the number of unsuccessful sequences.

$$\begin{aligned} \text{Thus } N_x &= \frac{P_x}{x} \\ &= \frac{(fx - x)!}{(fx - 2x + 1)!x!} \cdot p_{AA}^{(x-1)} \cdot (1 - p_{AA})^{fx-2x+1} \end{aligned}$$

$$\text{But } p_{AA} = \frac{\alpha f}{2(f-1)}$$

$$\text{Therefore } N_x = \frac{(fx-x)!}{(fx-2x+1)!x!} \cdot \left[\frac{\alpha f}{2(f-1)} \right]^{x-1} \cdot \left(1 - \frac{\alpha f}{2(f-1)} \right)^{fx-2x+1}$$

The difference between the two approaches becomes apparent when one considers the mole fraction according to the two theories as $\alpha \rightarrow \alpha_{MAX}$. For an RA_f monomer $\alpha_{MAX} = \frac{2}{f}$. Flory's mole fraction approaches infinity as $\alpha \rightarrow \alpha_{MAX}$, whereas Masson's mole fractions are finite up to the value for α_{MAX} . The mole fraction of monomer versus the extent of the reaction for $f = 3$ is shown in Fig 2 and illustrates the last point.

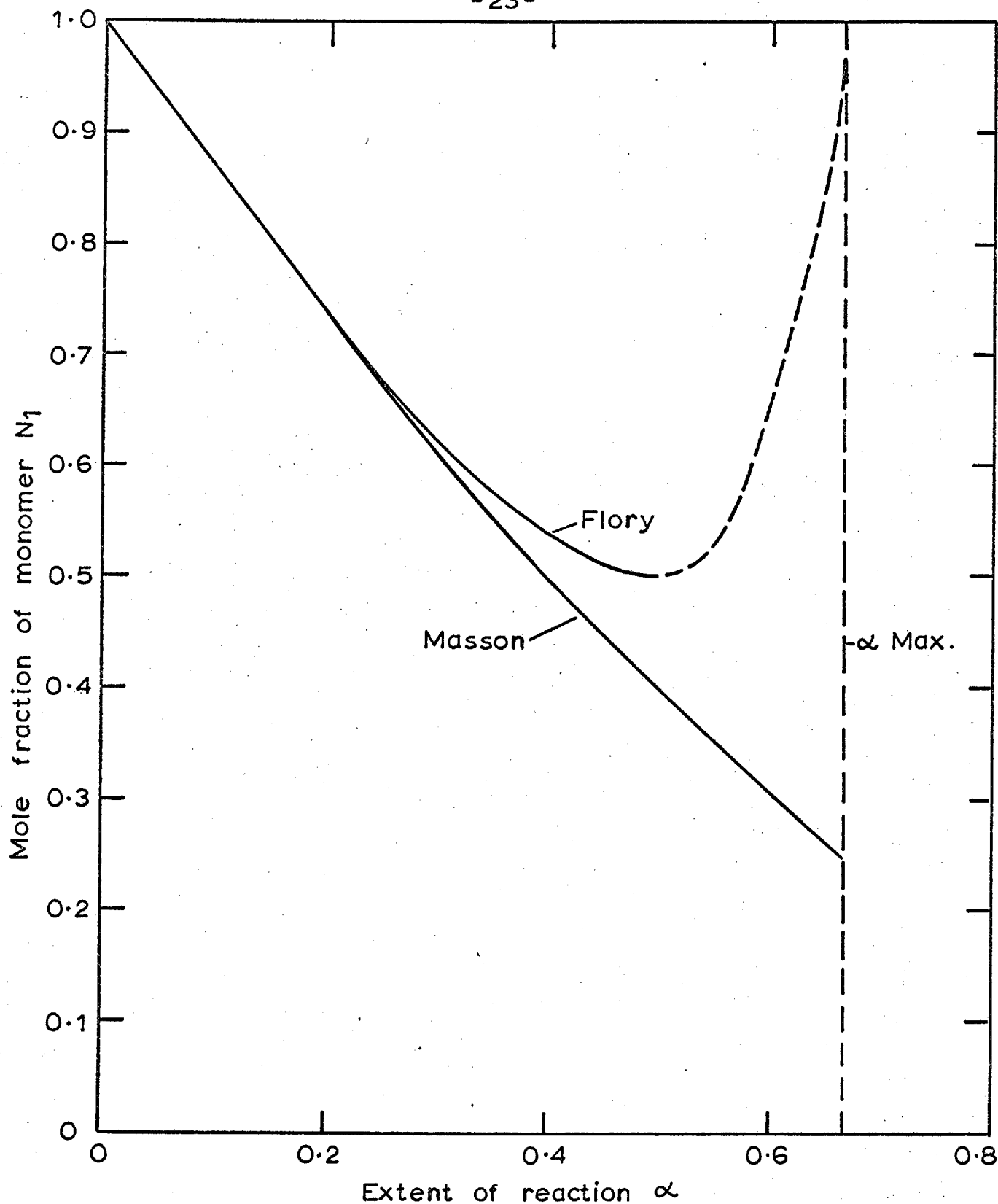


Fig. 2. MOLE FRACTION OF MONOMER vs. EXTENT OF REACTION ACCORDING TO FLORY & MASSON.

Chapter 2

TECHNIQUES USED FOR THE DETERMINATION OF ACTIVITIES IN PbO MELTS.

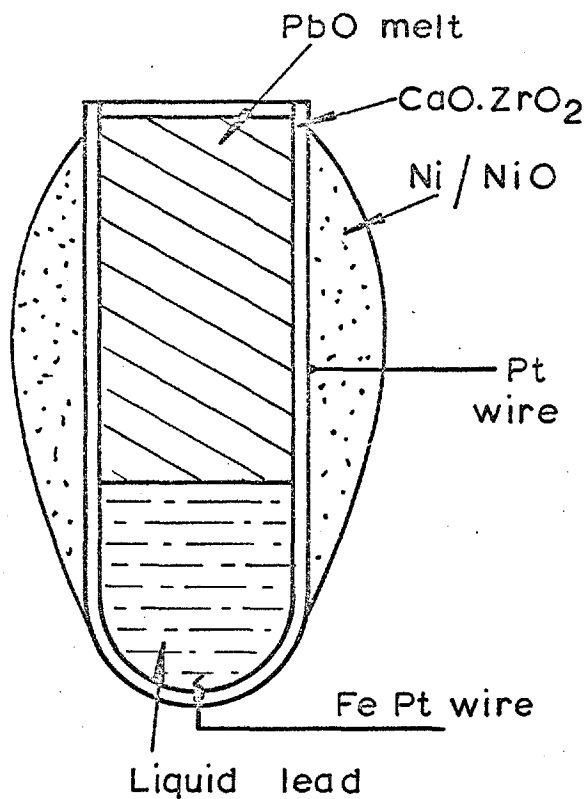
Various methods are available for the measurement of activities in melts, and in the present study two techniques have been used for this purpose.

The systems $n \text{ PbO} \cdot \text{SiO}_2$, $n \text{ PbO} \cdot \text{P}_2\text{O}_5$ and $n \text{ PbO} \cdot \text{PbCl}_2$ have been studied using an E M F technique, and the system $n \text{ PbO} \cdot \text{PbCl}_2$ has also been studied by a vapour entrainment method, since the volatility of PbCl_2 allowed only E M F measurements to be made on this system in the composition range pure PbO to the equimolar composition.

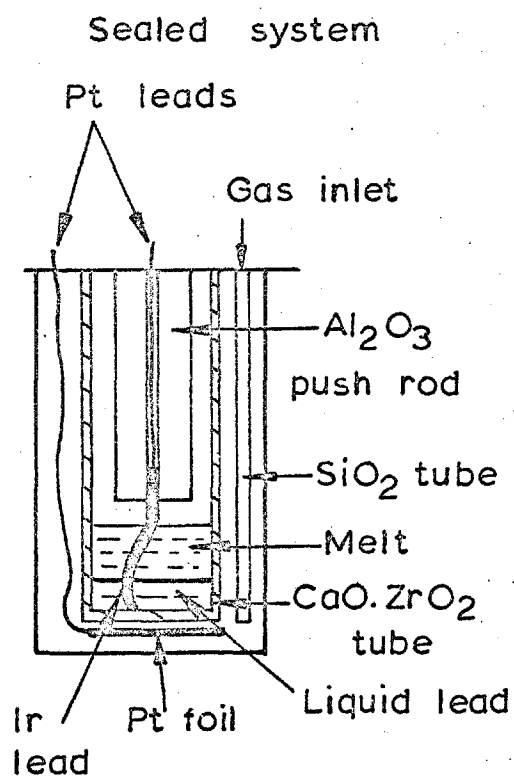
1. Synopsis of E M F cells containing lead polyanionic melts of relevance to this study.

Sridhar^(4) has given an excellent review (up to 1966) of E M F cells containing lead polyanionic melts. The majority of these cells have been discounted because of errors inherent in their design.

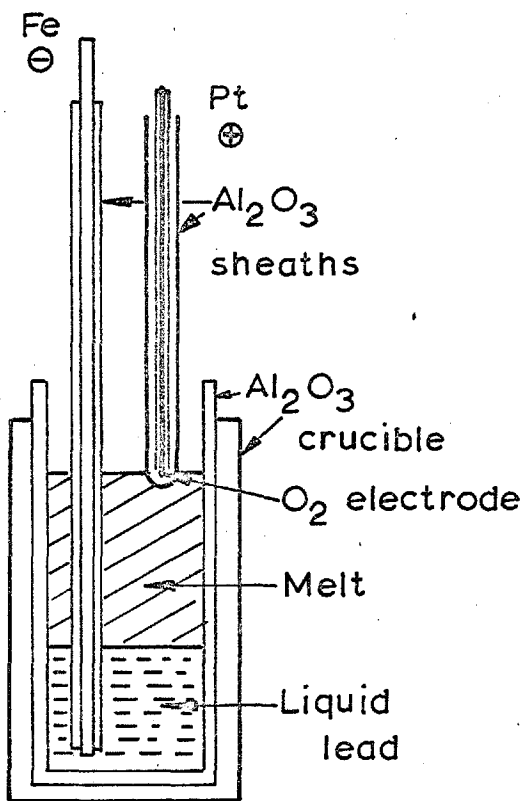
The work of Matsushita and Goto^(20) however is of interest in the study. They have used the cell;-
 $\text{Pb} | \text{PbO} - \text{SiO}_2 || \text{ZrO}_2 \cdot \text{CaO} || \text{NiO} | \text{Ni}$.
The cell used is shown in Fig 3 . The results obtained in the present study are in the best agreement with this work. Charette and Flengas^(21)



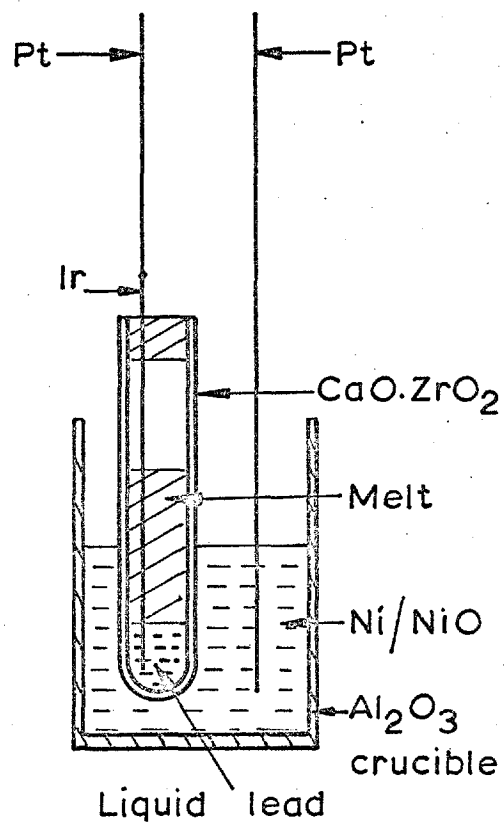
(A) MATSUSHITA & GOTO



(B) CHARETTE & FLENGAS

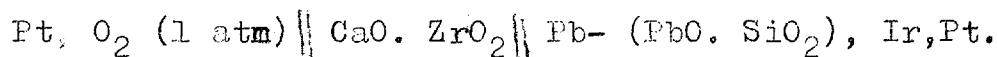


(C) SRIDHAR



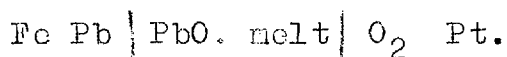
(D) JACOB

have also considered a solid electrolyte electrochemical cell with reference to oxygen at one atmosphere pressure. This cell can be represented by:-



They contain the melt in contact with liquid lead inside a sealed lime zirconia tube and maintain a flow of oxygen around the outside of the tube. A diagram of the cell is shown in Fig 3 .

Sridhar^(4) has used an almost identical cell to that used in the present study. The cell he used is represented by:-



and is also shown in Fig 3 . Sridhar considered the criteria which must be satisfied for such a cell to operate successfully. The criteria are:-

- (a) The melts must conduct electricity by ionic conduction only.
- (b) The solubility of metal in the slag and slag constituents in the metal must be small.
- (c) The free energy of formation of the metal oxide must be sufficiently less than that of the acid oxide and that the cell reaction is unambiguous.
- (d) The vapour pressure, liquid ranges and compatibility with available refractories and electrode materials of the cell components must be satisfactory.
- (e) The electrode reactions must be reversible.

He has shown that criteria (b), (c) and (d) are

all satisfied. The criterion (b) is also satisfied in the present study for PbCl_2 , since it is reported (22) that 0.12% mole of Pb dissolves in PbCl_2 at 800°C . The first criterion is in doubt however since he accepted the statement of Bockris and Mellors (1) that PbO and PbO-SiO_2 melts are completely ionic in nature. In order to check this criterion in the present study a solid oxide electrolyte replaced the oxygen electrode used in Sridhar's cell. The difference in E M F with the modified cell for pure PbO compared with that of Sridhar suggested up to 6% electronic conduction is present in pure liquid PbO . This is discussed in Chapter 11. For this reason it was decided to repeat the PbO-SiO_2 binary with the modified cell.

As a further check to the validity of the modified cell, Jacob (23) used the cell:-
 $\text{Pt, Ni - NiO} \parallel \text{CaO. ZrO}_2 \parallel \text{Pb - PbO, Ir, Pt.}$
which is shown in Fig 3 , in order to check the free energy of formation of pure PbO . His results suggest 4-5% electronic conductivity in pure PbO .

2.

The entrainment method.

It was found necessary in the present study to use a technique for the measurement of the vapour pressure of PbCl_2 in the system n PbO. PbCl_2 , in order

to complete the free energy of mixing curve for this system, since by the E M F method only the composition range pure PbO to the equimolar composition could be studied because of the volatility of the PbCl_2 .

The entrainment or transpiration method was chosen, partly for its versatility and for the fact that vapour pressures over the range 0.0003 to 0.1 atmospheres can be measured in this way.

The entrainment technique is widely used by many workers, being originated by Regnault in 1845. The uses of the method are numerous, the most important being for the measurement of vapour pressures. It can also be used for the measurement of dissociation pressures, the purification of substances, the growth of crystals, formation of non stoichiometric compounds and for the determination of the molecular formula of vapour species, amongst other applications.

An excellent review of the technique is given by Merten and Bell (24).

The method consists of passing a known volume of a carrier gas over the melt in question in such a way that the carrier gas becomes saturated with the vapour. The amount of vapour that is transported in this way can be determined by either analysis of the gas mixture after saturation, or by measurement of the loss in weight of the sample. Various gases have been used as the carrier gas by different workers,

depending upon the application. Most commonly used are inert gases, usually argon or nitrogen, but for vapour pressure measurements of metals and alloys, hydrogen has been used because of its reducing nature. Reactive carrier gases such as oxygen and the halogens have been used when dissociation of vapour species is a problem, and also when it has been necessary to form desired species. However argon gas was used in the present study, primarily because of its inertness, but also there are less problems concerning thermal segregation in a heavier carrier gas.

The volumes of the transporting gas and the vapour species carried by the gas are measured in these experiments, together with the total pressure of the system, and the temperature of the sample. If the volumes are corrected to N.T.P. then Boyle's law can be applied. The result expresses the partial pressure of the vapour species in terms of the volumes of the species and the transporting gas.

$$p_s = \frac{760 \times V_s}{V_s + V_c} \quad \text{mm. Hg.}$$

$$= \frac{760 \times n_s}{n_s + n_c} \quad \text{mm. Hg.}$$

Where **p** = partial pressure of the vapour species above the melt.

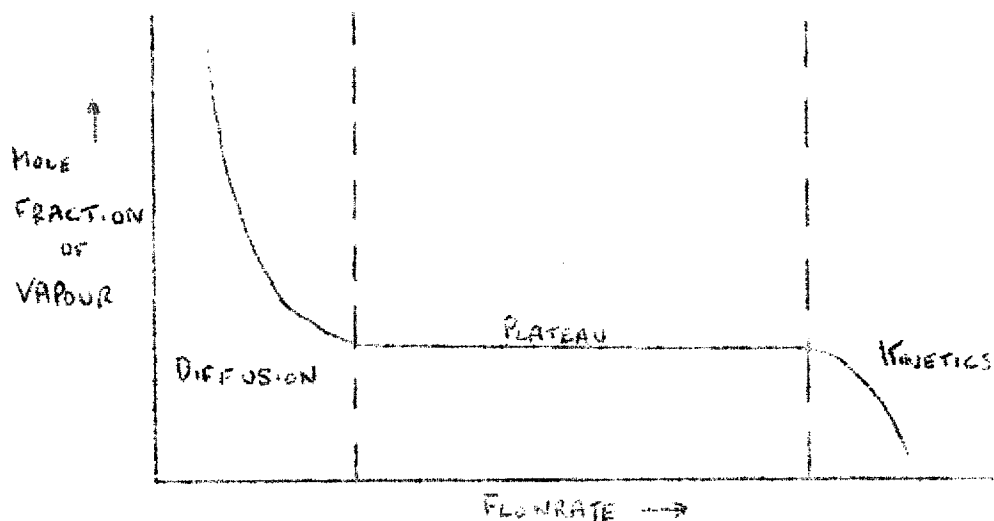
V = volume at N.T.P.

n = number of molecules at N.T.P.

s = vapour species.

c = carrier gas.

The flowrate is about the most important factor to be considered in the design of the experiment, as various effects are apparent at different flowrates. At very low flowrates there is danger of vapour diffusion with the result that $\frac{n_s}{n_s + n_c}$ becomes very large. On the other hand if the flowrate is too fast kinetics prevent complete saturation of the carrier gas, such that $\frac{n_s}{n_s + n_c}$ becomes small. For the present study, it was necessary to have the minimum possible flowrate (without any diffusion effect) such that the composition of the melt was not changed appreciably during the experiment. The intermediate region is a plateau and the flowrate must be selected to lie on this plateau as shown below.



A good isothermal region is required to contain the melt, otherwise thermal segregation could effect the experiment. The reaction tube is usually designed such that the saturated carrier gas passes through a capillary into a cooler part of the tube. In this

study the design of the reaction tube was based on that used by McClincy and Larson (25). A ceramic plug with a capillary outlet has been used to saturate the gas, and the weight loss of the sample has been measured. McClincy and Larson have measured the activity of Sb_2O_3 in $\text{PbO} \cdot \text{Sb}_2\text{O}_3$ and in $\text{PbO} \cdot \text{SiO}_2 \cdot \text{Sb}_2\text{O}_3$ melts.

A knowledge of the vapour species present above the melt is absolutely necessary for the determination of vapour pressures by this method. This knowledge is usually obtained by a mass spectrometric experiment or measurement of vapour density. Alternatively, if the vapour pressure of the monomeric species is known from a boiling point method, the vapour density can be deduced from the transpiration method. In the case of lead chloride, Barton and Bloom (26) have measured the vapour pressure by such a boiling point method. The system $\text{PbCl}_2 - \text{PbBr}_2$ has been studied using a quadrupole mass spectrometer by Bloom and Hastie (27), and only the species PbCl_2 , PbBr_2 and PbClBr were identified. It would be useful to study the system $\text{PbO} \cdot \text{PbCl}_2$ in the same way.

In the present study however for the determination of activities a ratio of vapour pressures is required. Since the experimental error is relatively large, the assumption is made that the ratio of polymeric species and any complex species to monomer is constant,

at constant temperature over the composition range studied. Thus the absolute values of partial pressure are not essential for this study.

Chapter 3

CALORIMETRY PAST AND PRESENT

The subject of calorimetry was instigated by Berthelot and Thomas a century ago and since then many types of calorimeter have been invented and modified to give the most precise thermodynamic measurements. Heats of formation and other thermodynamic quantities measured experimentally give a greater understanding of the nature of the bonding in metals, alloys and compounds, which is necessary in the concept of a great number of metallurgical problems. There is a great necessity to measure these quantities at high temperatures, in the order of 1000°C such that general principles concerning bonding, interactions and structures in melts can be deduced and tested, especially those melts closely allied to metallurgical processes. Equilibrium techniques which have also been widely developed during the last century give reliable free energy data but unfortunately unreliable heats and entropies, since these values have to be obtained from the temperature coefficients of free energy, with the introduction of relatively large errors. However combination of free energy data from equilibrium methods with heat data from calorimetry gives more precise values of entropy.

Kubaschewski (28) has carried out a review of many types of calorimeter.

There are two distinct types of calorimeter namely ~~isothermal~~ and adiabatic calorimeters. An ~~isothermal~~ calorimeter is one in which the temperature of the calorimeter is equal to the temperature of the surroundings at all times and is constant. However Kubaschewski has pointed out that the majority of calorimeters which are described to be ~~isothermal~~ calorimeters are in fact ~~isoperibol~~ calorimeters (after the Greek word for surroundings) since although the surroundings are held at a constant temperature, the temperature of the calorimeter changes during a reaction or an event. This change in temperature during a reaction is usually measured. In an adiabatic calorimeter however the temperature of the calorimeter is equal to the temperature of the surroundings at all times but is not constant depending on the amount of heat produced in the calorimeter.

The majority of ~~isoperibol~~ calorimeters consist of a single reaction vessel inside a larger but well lagged vessel. When heat is evolved or absorbed in the reaction vessel, then heat is exchanged between the reaction vessel and its surroundings. In order to calculate the heat of the event in the reaction

tube then a knowledge of this heat transfer is essential. This can be evaluated by measuring continuously the temperature difference between the reaction vessel and the jacket before, during and after the event.

Berthelot's Bomb calorimeter (28) is perhaps the best known calorimeter and it was originally designed to measure heats of combustion. The bomb is made of high tensile steel, since the heats of combustion are measured directly by burning the substance under consideration in an excess of oxygen, and the bomb must remain gas tight during the reaction. This is the most accurate type of calorimeter for measuring heats of combustion and R M S errors of $\pm 0.2\%$ have been quoted in the literature for the heat of combustion of benzoic acid. This type of calorimeter has been modified to measure heats of formation of metallic oxides, halides, carbides, nitrides and sulphides. A more recent modification is known as the fluorine bomb calorimeter developed at the Argonne National laboratory. (29)

Heats of formation and reaction which are difficult to measure directly, can be measured indirectly by the measurement of the heats of solution in a suitable solvent, and direct application of Hess' Law of constant heat summation. Often water can be used as the solvent, but more often acids have been used. Meadowcroft and

Richardson(30) for example have measured heats of solution of crystalline and glassy phosphates of sodium, lithium, calcium and zinc as well as their component oxides in 6N HCl at 35°C, with the result that the heats of formation of these phosphates could be calculated. Similarly Irving and McKerral(31-34) have measured the heats of solution of some sodium phosphates in 60% perchloric acid at 60°C, and hence calculated the heats of formation of these phosphates.

The selection of the solvent and experimental conditions for a solution experiment depends primarily on the rate of dissolution of the solute in the solvent which must be relatively fast for the greatest accuracy, and secondly in the case of the sodium phosphates on the rate of hydrolysis. At 25°C hydrolysis of the sodium triphosphates is slow, but at 60°C in 60% perchloric acid the hydrolysis is fast and complete. Platinic chloride has been used by Richards (35) to accelerate the solution of metals and alloys in HCl. Also many stirring devices have been designed to speed up the solution process. The solvent is most usually held in a Dewar flask inside a larger Dewar flask and the temperature of the solvent is measured continuously. The water equivalent of the calorimeter is usually calibrated against a known amount of heat dissipated from a heating coil in the calorimeter.

A differential solution calorimeter has been developed by Buck (36) for studying the heats of formation of alloys. The method depends on fast dissolution of the sample in the solvent. The heat effect measured is an absolute value of the heat of formation required. The calorimeter consisted of two reaction vessels, and in one a sample of the alloy was dissolved in HCl, and the relevant quantities of the constituent elements were dissolved simultaneously in the other vessel. The temperature difference between the two vessels was continuously recorded.

A knowledge of specific heats is essential for many thermodynamic calculations, and these have previously been determined by dropping samples from the desired temperature into an ice calorimeter; hence the name 'the drop method'. Rodigina (37) has used this method to determine the heat capacity of yellow lead oxide at various temperatures below and above its melting point. The difference between the heat capacity of the liquid and the solid at the melting point yield the value of the heat of fusion of lead oxide. Other types of calorimeter have been used for these measurements such that the sample does not come into contact with the liquid in the calorimeter. These designs include hollow metallic blocks which are surrounded by water, and calorimeters in which the calorimeter consists solely of a metal block.

The error in these calorimeters is ^{due to} the lower rate of heat dissipation, since forced convection is eliminated. Oelsen (38) has developed another room temperature calorimeter for the measurement of heats of formation of alloys by mixing two molten components together in the calorimeter at room temperature, and subtracting the known heat contents of the pure components. In this technique there is a risk of incomplete reaction due to the rapid cooling of the system.

All the methods mentioned so far involve working temperatures for the calorimeter in the range -100°C to $+100^{\circ}\text{C}$, and hence the necessity for high temperature calorimeters. The major problem that has to be overcome with a high temperature calorimeter is the difficulty of maintaining the calorimeter at the required temperature. This can however be overcome by designing the calorimeter such that its water equivalent is a minimum and its thermal insulation is more than sufficient. Several single cell high temperature calorimeters have been designed by various workers, and it was found that to reproduce results to $\pm 1\%$, the reaction vessel had to be contained in a metal block, the temperature of the block being recorded. This is because the temperature of the outside of a ceramic block is uncertain. Examples of this type of calorimeter are those of Wittig and

Huber (39) and Orr, Goldberg and Hultgreen (40).

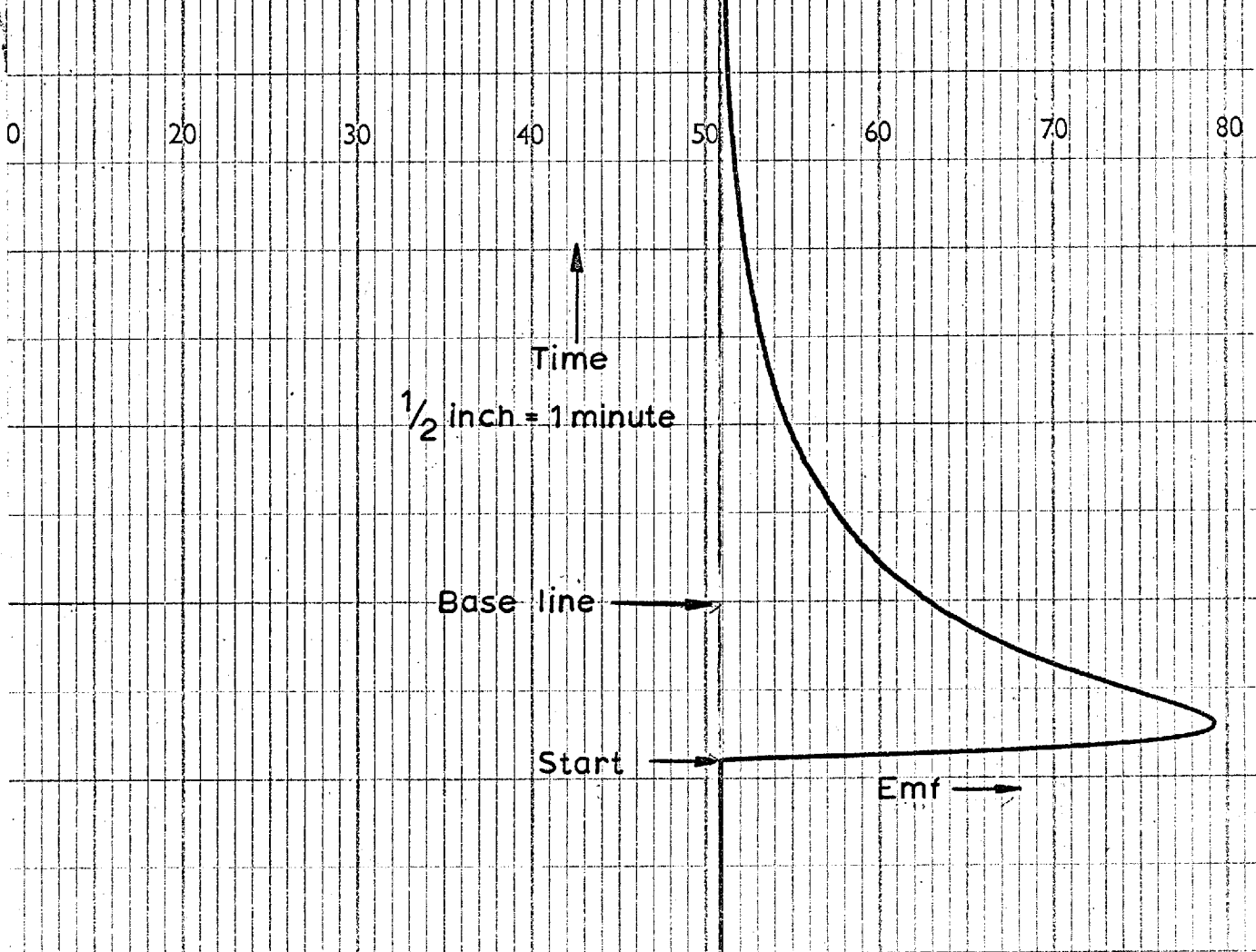
In a great number of experiments with metals and alloys, molten tin has been used as the solvent, as tin melts at 232°C . The main advantage of using tin as a solvent is that the heats of solution in liquid tin are usually of the same order of magnitude as the heats of formation which are required. In acids the heats of solution are usually several orders of magnitude larger. Using these single cell calorimeters, again a knowledge of the heat transfer is required.

Another type of isoperibol calorimeter was first introduced by Calvet (41), with the introduction of a thermopile in the calorimeter and 'twin' reaction tubes. This type of calorimeter was modified by Kleppa (5), who contained the two calorimetric units in a heavy aluminium jacket and he surrounded each unit with a 96 couple thermopile. The two thermopiles were connected in series and in opposition to each other, such that at thermal equilibrium in the calorimeter the resultant E M F was zero. This calorimeter was used initially at temperatures up to 500°C to measure the heats of mixing of various nitrates. Hersh and Kleppa (42) later modified this calorimeter by replacing the aluminium jacket with a 300 pound weight nickel block. This enabled measurements to be made up to temperatures of about 800°C . In the present study this type of calorimeter has again been

modified by Jeffes (6), by the replacement of the nickel block with an alumina block and a modified thermopile design. At present the upper operating temperature limit of this calorimeter is about 1200°C , determined by the melting point of the kanthal heating elements (1350°C). The advantage of this type of calorimeter is that since both units are contained in the same block, which is itself maintained at a uniform temperature, then the rate of heat transfer when no event is taking place in the calorimeter from each unit should be the same, such that the resultant E M F from the two thermopiles is zero. When heat is absorbed or generated in one of the units causing a thermal imbalance within the two thermopiles, then a typical curve shown in Fig 4 results. The E M F generated in the thermopile system is directly proportional to the difference in temperature between the reaction vessel and the block, and from Newton's law directly proportional to the rate of heat transfer. Thus the total area under the curve E M F versus time shown in Fig 4. between the start and termination of the disturbance is proportional to the total heat effect due to the event in the calorimeter. It is therefore possible to compare an unknown heat effect with that from a known source . For example a platinum drop, since the heat content of platinum is well known, or an

Fig. 4

TYPICAL EMF vs. TIME
CURVE FOR A DISTURBANCE
IN ONE SIDE OF THE
CALORIMETER



electrical method.

Yokokawa and Kleppa (43) initially used a lead borate melt $3\text{PbO} \cdot \text{B}_2\text{O}_3$ as a solvent for various oxides, but found that these melts attacked the platinum and gold containers. They then considered other lead borate melts as suitable solvents, and the melt $9\text{PbO} : 3\text{CdO} : 4\text{B}_2\text{O}_3$ was finally used. This melt is very viscous at its melting point of about 500°C , but quite fluid above 700°C and is a good solvent for a variety of solid oxides of acidic, basic and amphoteric character. Also this melt does not attack platinum or gold and has been widely used by Kleppa in his work and by this author in the present study.

The high temperature calorimeter can be used to determine various thermodynamic quantities namely:- $\Delta H_{T_1}^{T_2}$ where T_1 is the temperature of the calorimeter, and T_2 is usually room temperature but could be any temperature $T^\circ\text{K}$; Entropies by varying T_1 ; Heats of fusion; Heats of transformation and transition; Heats of reaction; Heats of formation and partial heats of mixing. Usually the determination of heats of reaction, formation and transformation result from measurements of heats of solution in a suitable solvent and application of Hess' law. The experiments can be conducted by dropping samples from a temperature $T_2^\circ\text{K}$ into the calorimeter, or by a solution or mixing

in the calorimeter at the temperature required. Holm and Kleppa (8) have measured the partial heats of solution of lead oxide and boron oxide at 800°C in $\text{nPbO} \cdot \text{B}_2\text{O}_3$. The free energy for the system has been studied by Sridhar (4) and the phase diagram by Geller and Bunting (44). More applicable to the study, Ostwald and Kleppa (7) have measured the partial enthalpies of lead oxide and silica in $\text{nPbO} \cdot \text{SiO}_2$ melts at 900°C .

The other type of calorimeter which is widely used today is the adiabatic calorimeter in which the temperature of the outer jacket is maintained at the temperature of the calorimeter at all times during the experiment. The heat effect in the calorimeter is directly a measure of the amount of heat required to maintain the outer jacket at the temperature of the calorimetric vessel during the experiment. An adiabatic calorimeter is usually heated at the rate of about 1°C per minute. This type of calorimeter is the most often used to measure heat capacities, for example the work of Moser (45) in the temperature range 50°C to 670°C , and various calorimeters have been designed to work at higher temperatures. At the National Physical Laboratory (46) an adiabatic calorimeter has been developed to operate up to 1600°C . Heats of reaction and heats of transformation have been measured by this technique.

The choice of calorimeter and technique must primarily depend on the nature of the heat effect that is to be measured, but also on the magnitude of the heat effect, its acceptable error, and the temperature at which the experiment must be carried out. The calorimeter used in the present study was found to be most satisfactory for the measurement of partial heats and heats of solution above 600°C and at constant temperature, since the method requires the minimum corrections.

PART B.

EXPERIMENTAL WORK.

The experimental work consisted of three experimental techniques namely E M F studies, high temperature calorimetry and vapour entrainment.

Firstly E M F work was carried out on the systems $n\text{PbO}.\text{SiO}_2$, $n\text{PbO}.\text{P}_2\text{O}_5$ and $n\text{PbO}.\text{PbCl}_2$ in order to determine the activities of lead oxide in these melts, and using a Gibbs Duhem integration to determine the activity of the other component, hence the integral free energy of mixing of these systems. Since the heats determined in this way are not very accurate, high temperature calorimetry was used to determine the integral heats of mixing of the system $n\text{PbO}.\text{P}_2\text{O}_5$, and to measure the latent heat of fusion of lead oxide. Combination of calorimetric heats with E M F free energies enables the integral entropies of mixing to be calculated. This is the best method for determining entropy data.

The heats of formation of some of the sodium metaphosphates were also determined with the high temperature calorimeter. In the system $n\text{PbO}.\text{PbCl}_2$, the lead chloride has a relatively high vapour pressure at 800°C and so the E M F technique could only be used on this system between $N \text{ PbO}=1$ to $N \text{ PbO}=0.5$.

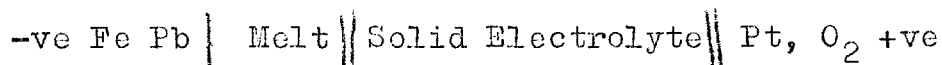
A vapour entrainment technique was therefore used in this system in order to determine the activities of PbCl_2 for the lead chloride rich end of the system. Combination of the E M F work and the entrainment work enabled the free energy of mixing of the system to be determined.

Chapter 4.

E M F TECHNIQUE FOR THE MEASUREMENT OF ACTIVITIES IN MELTS.

1. The E.M.F. cell:

The E M F cell used can be represented by:-



A diagram of the oxygen electrode assembly is given in Fig 5 . The platinum contact was carried down on twin bore alumina rod and coiled at the bottom to make the maximum contact. A platinum thirteen per cent rhodium wire was fused to the platinum contact just above the coil, and was carried up the other bore of the alumina tube. The alumina tube was weighted at the top end with a brass piston which was polished such that it could slide inside the brass head. The platinum contact was made to a brass nut set in a sindanyo plug, and the platinum thirteen per cent rhodium contact to the brass casing.

The solid electrolyte tubes were only fifteen centimetres long and this had to be cemented into the ends of eight millimetre outside diameter alumina tubes such that the overall length of the two tubes was about thirty three centimetres. The alumina tubes fitted into the brass head, using two neoprene 'O' rings. The passage of oxygen through the assembly is down the twin bore alumina tube to the platinum

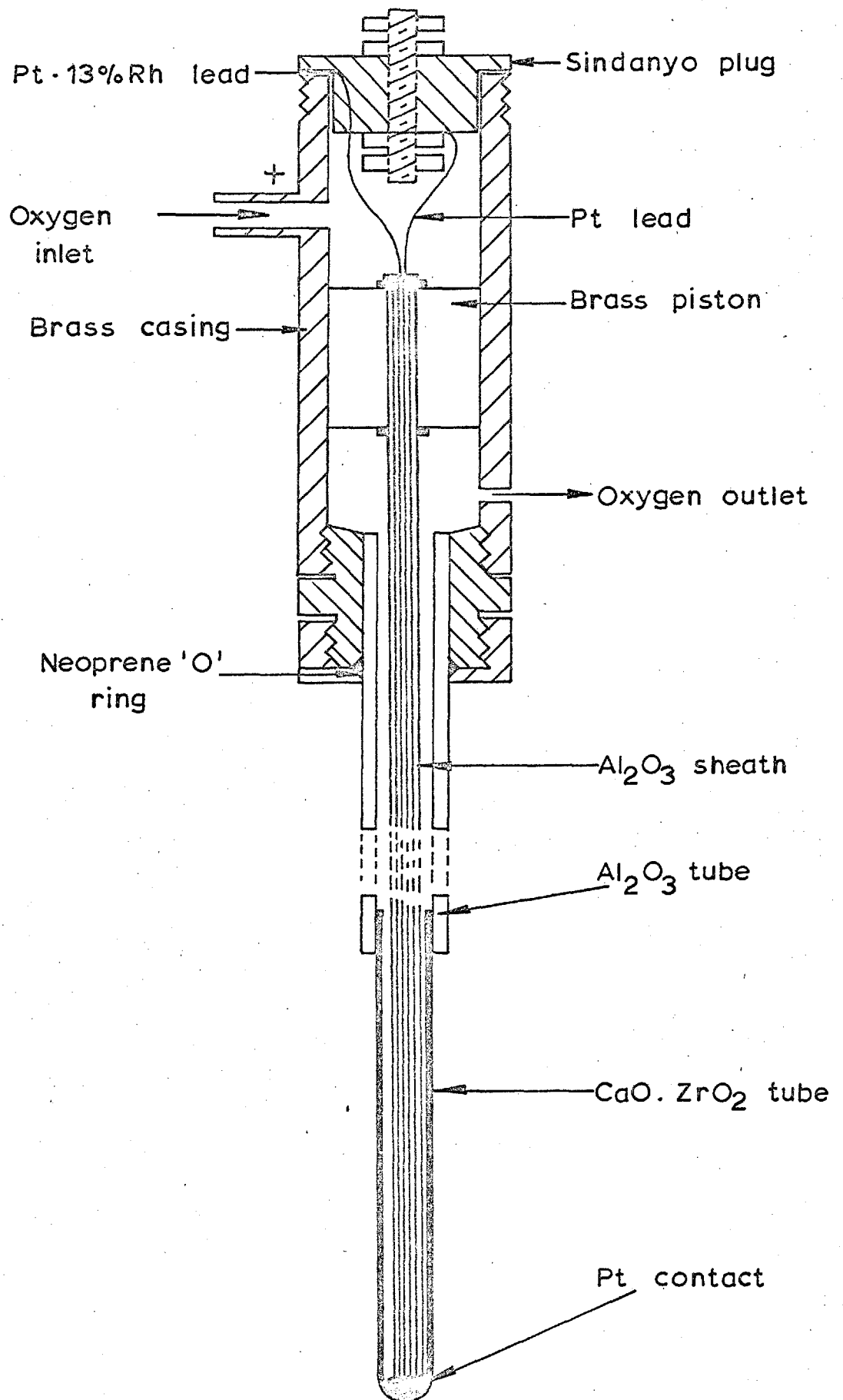


Fig. 5

OXYGEN ELECTRODE ASSEMBLY

contact and then up the inside of the electrolyte tube and out through a hole at the base of the brass head.

The alumina crucible containing the melt was contained in a larger alumina crucible which in turn was suspended in a Kanthal wire cage in the hot zone of the furnace. The temperature of the cell was measured with a platinum/platinum thirteen per cent rhodium thermocouple attached to the wire cage external to the crucible, and also with the platinum/platinum thirteen per cent rhodium thermocouple in the oxygen electrode. These thermocouples were checked against a third held in an empty alumina crucible in the assembly.

The furnace consisted of a two inch diameter non inductive crusilite element, with lagging of alumina powder, and was controlled with a proportional band controller operated by a platinum/platinum thirteen per cent rhodium thermocouple at the bottom of the hot zone in the furnace. In this way the hot zone was controlled to $\pm 1^{\circ}\text{C}$, although the temperature across the two inch hot zone varied by about $\pm 2^{\circ}\text{C}$.

The cell itself consisted of a three centimetre tall by fifteen millimetre diameter alumina crucible with one centimetre of liquid lead in the bottom and the melt floating on top of the lead. The iron electrode passed through the melt into the liquid lead, being protected from the melt by an alumina tube.

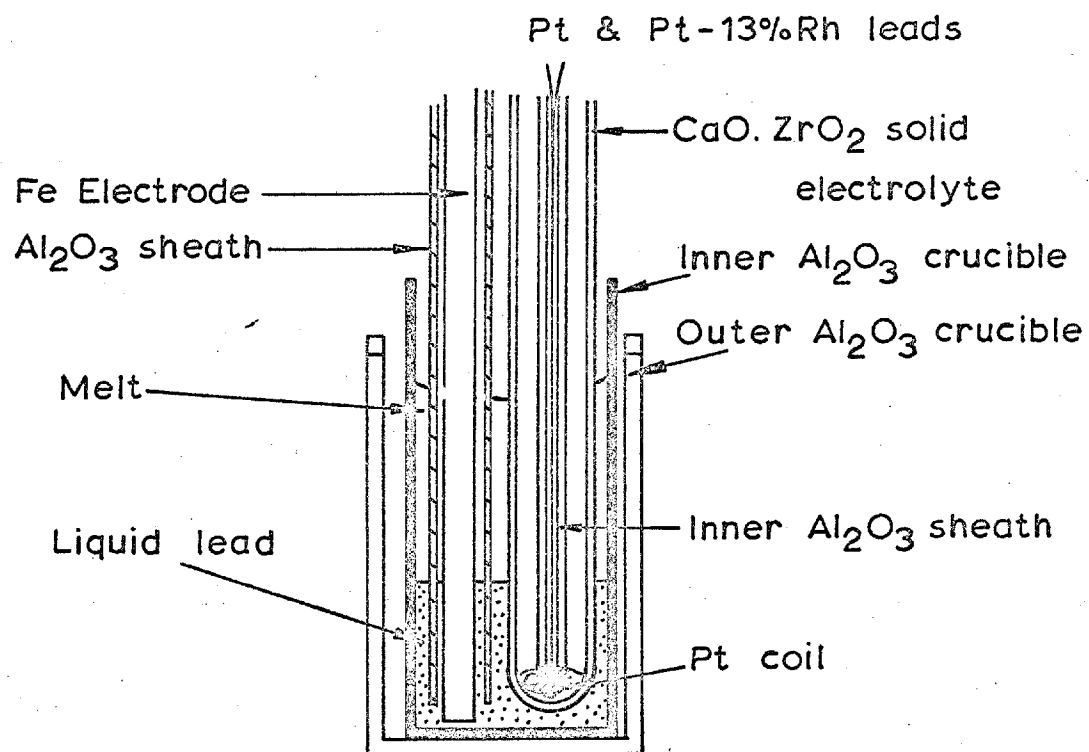


Fig. 6

EMF CELL

There was no appreciable attack observed on the refractories as was also observed by Sridhar. The solid electrolyte tube was also situated in the liquid lead and passed through the melt. A schematic diagram of the cell is given in Fig 6 .

2. Experimental Technique.

Ten grams of A. R lead metal were melted into the crucible with the iron electrode in position before the experiment in a nitrogen atmosphere to prevent attack on the iron electrode by the melt. The slag to be studied was then placed in the crucible which was in turn placed in the larger crucible in the wire cage. The solid electrolyte tube assembly was then positioned such that the sealed top of the tube was located about one centimetre from the top of the melt. The furnace, already maintained at about 800°C was slowly brought up around the assembly, such that the refractory oxides did not crack from thermal shock. After thirty minutes when the melt and cell assembly were at the temperature of the furnace, the oxygen electrode was lowered, by means of a screw device through the melt into the liquid lead. In fact it was lowered to the bottom of the crucible and then raised by a few millimetres. The negative connection was made to the iron electrode and

the positive connection to the oxygen electrode. The E M F obtained was measured on a Vibron electrometer. The Vibron electrometer used was checked against another Vibron electrometer and also a Wheatstone bridge.

A very steady E M F was almost instantaneously obtained. The first reading was taken after a further thirty minutes, of E M F versus temperature. The temperature of the furnace was then changed by about 50°C and after another thirty minutes the next reading was taken. For each melt E M F versus temperature was recorded in the range 700°C to 1100°C , depending on the melt.

The E M F measured was corrected for the $\begin{smallmatrix} + & - \end{smallmatrix}$ iron-platinum couple measured by Sridhar and confirmed in this study. The E M F versus temperature of the couple is given in Fig 7.

All the experiments were conducted in an atmosphere of nitrogen to eliminate any unexpected side reactions.

3. Reversibility Tests:

The E M F results obtained from a cell can only be used to derive thermodynamic data directly if the cell is completely reversible.

Firstly it was observed that a linear relationship was obtained from the E M F versus temperature

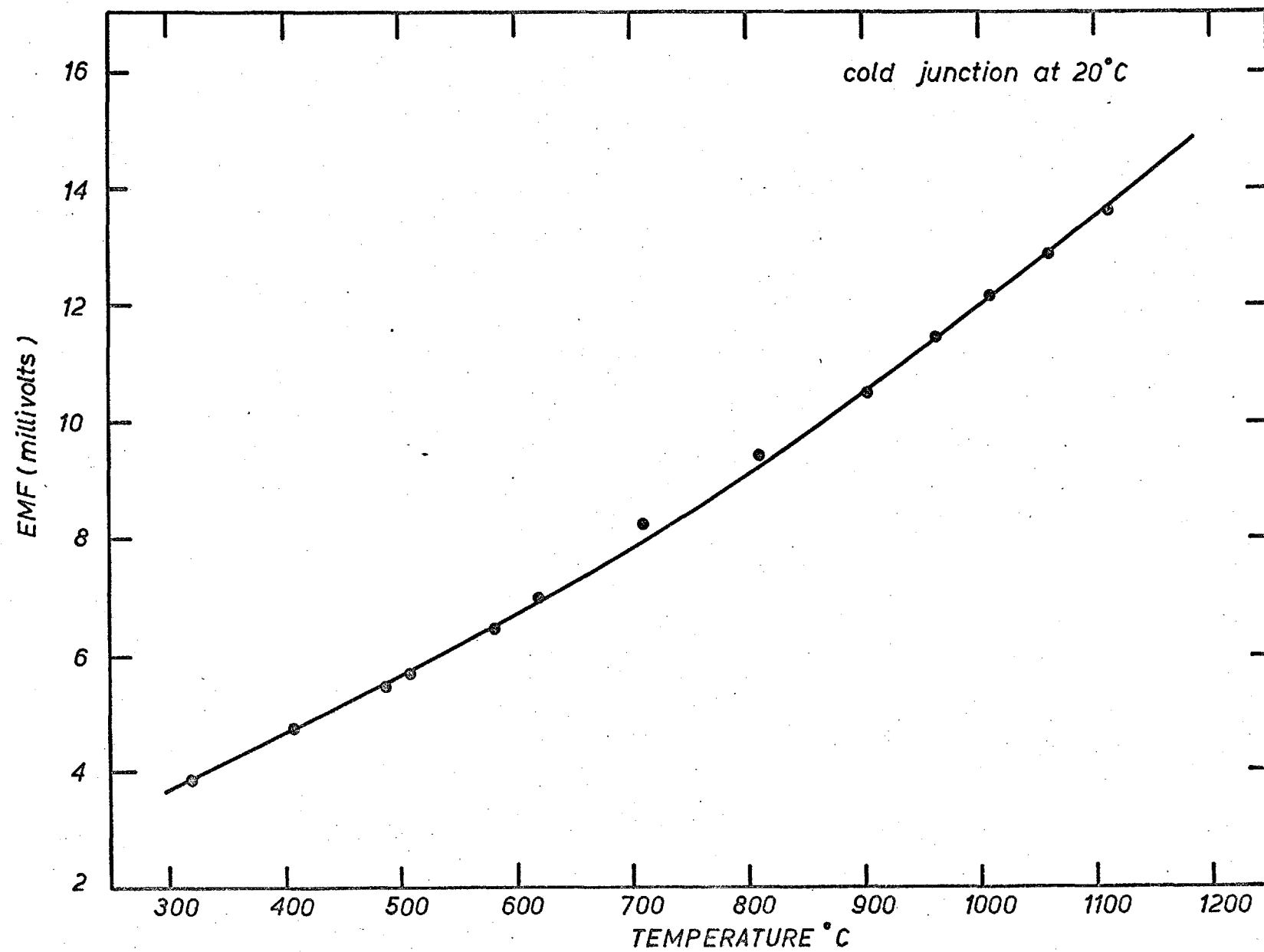


FIG.7. THERMAL EMF FOR $\text{Fe}^+ - \text{Pt}^-$ COUPLE .

results from each melt. No matter in which order the results were obtained, the linear relationship still resulted.

Secondly when a current from an external source was passed through the cell, on the removal of the constraint, the E M F of the cell immediately returned to its initial value; the temperature of the cell being held constant during this test.

Thirdly the flowrate of oxygen did not effect the E M F obtained.

The observations confirm that the cell used was completely reversible.

4. Choice of Electrolyte:

The initial experiments were to determine the most suitable solid electrolyte for this study. Using semistabilized lime zirconia tubes, the E M F versus temperature for pure lead oxide was measured. No attack of these tubes was observed and they could be reused after washing in nitric acid. Also yttria zirconia tubes were used and the same results for pure lead oxide were obtained. These tubes however shattered after only one run. Optical examination of the two tubes showed penetration of the yttria zirconia tube by the lead but no penetration in the case of the lime zirconia tubes.

In order to determine the suitability of lime

zirconia as solid electrolyte for measurements in the systems $\text{nPbO.S}_2\text{O}_2$, $\text{nPbO.P}_2\text{O}_5$ and nPbO.PbCl_2 , these melts were held in lime zirconia crucibles at 1000°C for two hours and after cooling sections across the crucibles were taken and analyzed on the microprobe analyzer. In the case of lead silicate, very slight surface penetration was observed, but in the case of lead phosphates and nPbO.PbCl_2 melts no penetration was observed.

It was decided to use semi-stabilized lime zirconia for these experiments.

5. Materials:

A.R. lead oxide (yellow), A.R. lead metal, A.R. ammonium dihydrogen orthophosphate and high purity washed quartz powder were used as the starting materials for making the relevant melts.

All the melts were made by melting the relevant amounts of the components in a platinum crucible at about 1000°C , with the exception of lead phosphate, the preparation of which is described by Sridhar.

Alumina crucibles supplied by the Royal Worcester Porcelain Company (47) were used to contain the melts.

Iron rods (99.8% Fe, 0.03%C, 0.01%Si, 0.12%Mn, 0.005%P, 0.010%S, 0.005%Cr, 0.005%Ni, 0.01%Cu, 0.002%Sn) protected from the melt by alumina sheaths

were used as the anode material in the cell. Semi-stabilized lime zirconia tubes and yttria zirconia tubes, sealed at one end, were used as the solid electrolyte materials. The electrical contact was by means of a pure platinum coil inside the tube.

Oxygen free nitrogen purified by passage through a copper oxide furnace at 500°C and then towers of silica gel, sofnolite, and magnesium perchlorate was used in the oxygen electrode.

Nitrogen also purified in a similar gas train was used as the flushing gas.

6. Analysis of the Melts:

(i) Lead Silicates:

About 0.75 grams of lead silicate to be analyzed was weighed out into a 600 millilitre beaker and 60 millilitres 1 : 1 HCl and 30 millilitres 1 : 1 HNO_3 were added. The solution was evaporated to dryness and the residue baked for half an hour. After cooling, the sides of the beaker were rinsed with 1 : 1 HCl and evaporation and baking were repeated. Solution of the residue was carried out by boiling with 80 millilitres of 1 : 1 nitric acid. The solution was then filtered through number 541 Whatman paper. The paper was then ignited in a silica crucible and the contents were weighed as silica. The analyses were within one per cent of the

precalculated compositions.

(ii) Lead Phosphates:

The analysis of the lead phosphates was carried out by the analytical services laboratory, and the results agreed to within 0.5% of the intended composition.

(iii) $n\text{PbO} \cdot \text{PbCl}_2$ Melts:

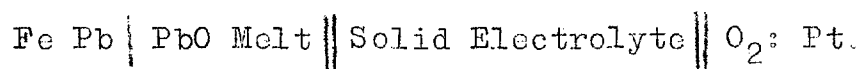
These were analyzed for chlorine by a simple silver nitrate titration using potassium chromate as the indicator. Solution of the melts was brought about by boiling with excess anhydrous sodium carbonate in 150 millilitres deionized water. Addition of concentrated nitric acid completed the solution process. Excess calcium carbonate was then added to produce a neutral solution for the titration. Again the results were within 0.5% of the intended composition.

Chapter 5.

RESULTS FROM E M F EXPERIMENTS.

1. Treatment of results.

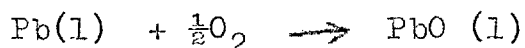
The cell that is to be considered is represented by:-



In order to determine the activity of lead oxide in the PbO melts, it is necessary to measure the standard free energy of formation of pure liquid PbO. Since the solid electrolyte that was used is a completely ionic conductor then

$$-nEF = \Delta G = \Delta G^\circ + RT \ln a_{\text{PbO}}$$

$\Delta G^\circ = -nE^\circ F$ where ΔG° is the standard free energy change of the reaction:-



$$\text{ie. } \ln a_{\text{PbO}} = \frac{-n(E-E^\circ) F}{RT}$$

where:- E is the EMF of the cell using PbO melt in equilibrium with liquid lead

E° is the EMF of the cell using pure PbO in equilibrium with liquid lead.

F is Faradays constant $nF = 46,126$ cal/volt.

R is the gas constant

T is the temperature in $^\circ\text{K}$.

$$\text{Now } \Delta G = RT \ln a_{\text{PbO}}.$$

$$\text{also } \Delta G_{\text{PbO}} = \Delta H_{\text{PbO}} - T\Delta S_{\text{PbO}}$$

$$\frac{\Delta G_{\text{PbO}}}{T} = \frac{\Delta H_{\text{PbO}}}{T} - \Delta S_{\text{PbO}}$$

Thus from a plot of $\frac{\Delta G_{\text{PbO}}}{T}$ vs $\frac{1}{T}$, the slope is equal

to ΔH_{PbO} . Knowing the values of the partial free energies, and combination with the partial enthalpies then the partial entropies of lead oxide can be determined.

Using a Gibbs Duhem integration in order to determine the activity of the second component in the system, then the partial free energies, enthalpies and entropies can likewise be determined.

The Gibbs Duhem equation for a two component system is $N_1 d \ln a_1 + N_2 d \ln a_2 = 0$

$$\therefore \ln a_2 = - \frac{N_1}{N_2} \int_{N_2=1}^{N_2=N_2} d \ln a_1$$

An integral quantity is expressed in terms of partials by the expression:-

$$\Delta G_M = N_1 \Delta G_1 + N_2 \Delta G_2.$$

Thus the integral quantities can be determined.

2. Pure lead oxide (yellow).

The E M F of the cell with the pure lead oxide in contact with liquid lead was measured over the temperature

range 700°C to 1100°C. It was possible to measure the E M F of the cell after the lead oxide had solidified since the solid electrolyte oxygen electrode passed through the melt into the liquid lead.

The results of E M F versus temperature using the lime zirconia tubes and the yttria zirconia tubes for both solid and liquid lead oxide are given in Table 1, and shown in Fig 8 as the calculated lines of linear regression.

Also shown in Fig 8 are the results obtained by Sridhar and Jeffes (48), Charette and Flengas (21) Jacob (23), and Alcock and Belford (49).

The correlation coefficient is defined as $R = \frac{(X_i - \bar{X})(Y_i - \bar{Y})}{(X_i - \bar{X})^2 (Y_i - \bar{Y})^2}$ and is a

measure of the fit of the experimental points to the line of regression. If $R = \pm 1$, then all the points lie on the line, and there is perfect correlation.

The E M F temperature relationships for pure PbO obtained in the study are given by the equations;

Solid PbO, CaO. ZrO₂ Solid electrolyte.

$$E^{\circ} = -4.906861 \times 10^{-4}T + 1.110893$$

Liquid PbO, CaO ZrO₂ Solid electrolyte.

$$E^{\circ} = -3.555616 \times 10^{-4}T + 0.957132$$

TABLE 1.

E M F as a function of Temperature for cells
containing pure PbO.

Using Lime Zirconia Solid Electrolyte				Using Yttria Zirconia Solid Electrolyte.	
Liquid PbO		Solid PbO		Liquid PbO.	
EMF	Temperature	EMF	Temperature	EMF	Temperature
Volts	°K	Volts	°K	Volts	°K.
0.504	1270	0.561	1112	0.509	1253
	1281		1123		1256
0.491	1307	0.606	1019	0.490	1307
	1319		1029		1310
0.523	1218	0.584	1068	0.477	1346
	1231		1074		1348
0.515	1238	0.570	1109	0.524	1205
	1250		1113		1206
0.534	1182	0.556	1128		
	1197		1135		
0.543	1162	0.572	1095		
	1174		1094		
0.510	1258	0.605	1035		
	1259		1031		
0.528	1201	0.6215	1001		
	1202		996		
0.538	1179	0.596	1051		
	1179		1048		

TABLE 1. continued.

Using Lime Zirconia Solid Electrolyte.			
Liquid PbO		Solid PbO	
EMF	Temperature	EMF	Temperature
Volts	$^{\circ}\text{K}$	Volts	$^{\circ}\text{K}$
0.519	1229	0.555	1137
	1231		1136
0.496	1292	0.585	1071
	1295		1069
		0.559	1124
			1122

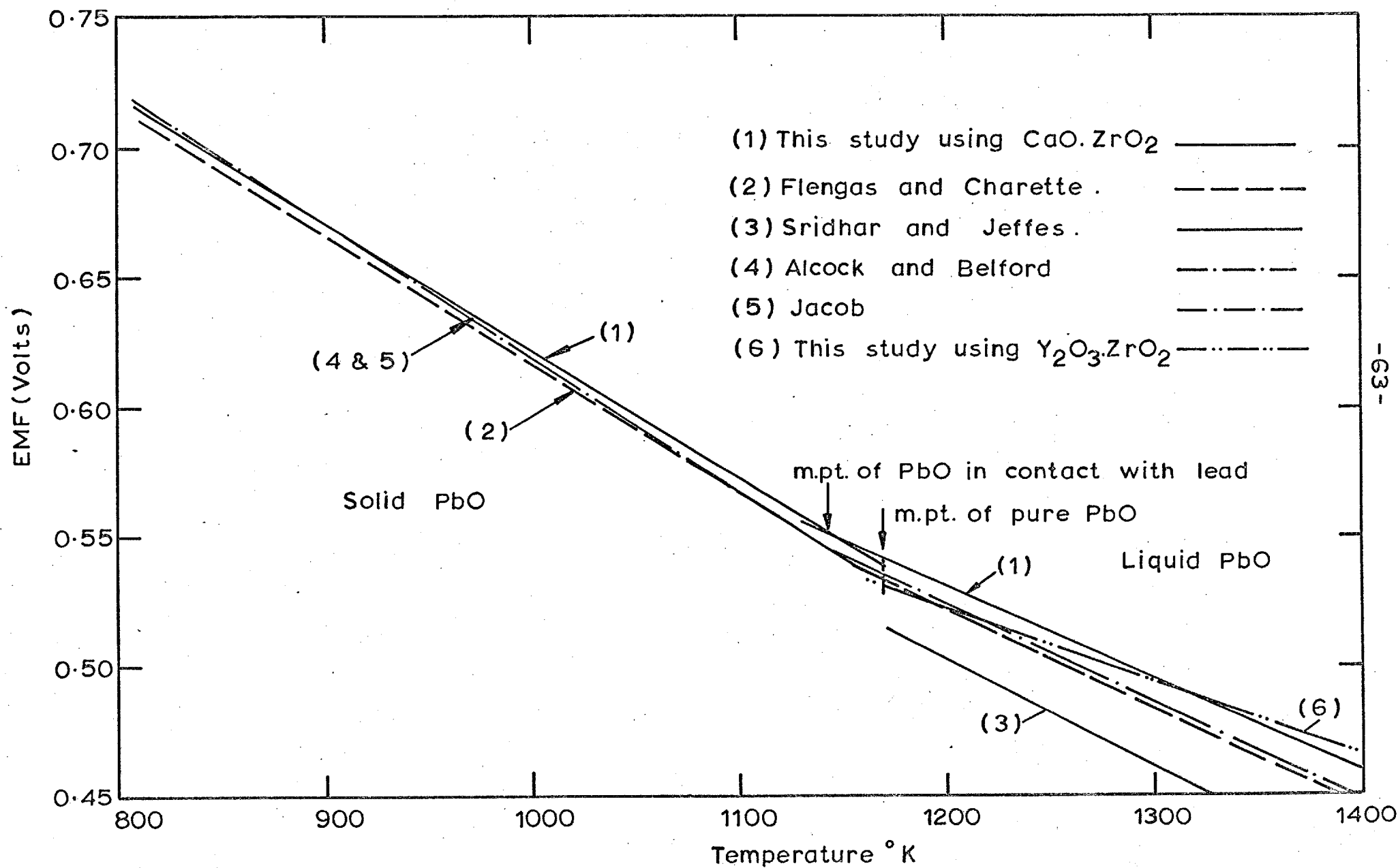


Fig. 8 EMF OF CELL $\text{Pt O}_2 \mid \text{CaO ZrO}_2 \mid \text{PbO} \mid \text{Pb Fe}$.

Liquid PbO, Y₂O₃, ZrO₂ Solid electrolyte.

$$E^{\circ} = -2.807986 \times 10^{-4}T + 0.860319.$$

The standard free energy for the reaction

Pb(l) + $\frac{1}{2}$ O₂(g) = PbO (l) was calculated from

$\Delta G^{\circ} = -2 FE^{\circ}$ and are shown in Fig 34, for comparison with other data; see chapter 11 (1).

3. nPbO. SiO₂ melts.

The E M F of the cell containing nPbO. SiO₂ melts was measured over the temperature range 700°C to 1100°C. The results E M F versus temperature for each composition are given in Table 2, and the lines of linear regression calculated for each composition are plotted in Fig 9, and given in Table 3.

The activity of lead oxide in this system was measured from N PbO = 0.5 to N PbO = 1 since there is silica saturation at about N PbO = 0.4. The liquidus as used by Sridhar shown in Fig 10 was used to determine the actual composition of the silica saturation at various temperatures. Using the Gibbs Duhem relationship the activity of silica was calculated knowing that the silica activity is unity at the silica saturation.

$$\log a_{\text{SiO}_2} = - \frac{N_{\text{PbO}}}{N_{\text{SiO}_2}} \int_{N_{\text{SiO}_2}=1}^{N_{\text{SiO}_2}=N_{\text{SiO}_2}} d \log a_{\text{PbO}}$$

TABLE 2.

E M F as a function of Temperature for cells
containing n PbO. SiO₂ melts.

N PbO = 0.9		N PbO = 0.8		N PbO = 0.7	
EMF	Temperature	EMF	Temperature	EMF	Temperature
0.548	1170	0.552	1171	0.570	1152
	1169		1174		1161
0.5295	1216	0.581	1108	0.5525	1210
	1215		1110		1214
0.5395	1192	0.5955	1065	0.560	1181
	1193		1064		1187
0.5205	1243	0.567	1146	0.543	1234
	1243		1146		1238
0.508	1286	0.6125	1024	0.5255	1281
	1288		1021		1287
0.517	1257	0.550	1198	0.535	1251
	1259		1199		1259
0.5365	1202	0.550	1179	0.5515	1206
	1205		1183		1212
0.551	1163	0.574	1123	0.5675	1165
	1163		1125		1167
0.559	1139	0.592	1068	0.586	1110
	1142		1068		1112
0.548	1167	0.6125	1023	0.5785	1137
	1170		1024		1142
0.525	1225	0.534	1247	0.5995	1075
	1227		1252		1081

TABLE 2. continued.

N PbO = 0.9		N PbO = 0.8		N PbO = 0.7	
EMF	Temperature	EMF	Temperature	EMF	Temperature
0.535	1192	0.546	1190	0.561	1180
	1197		1198		1187
0.517	1247	0.532	1240	0.546	1236
	1252		1250		1239
0.501	1292	0.536	1219	0.5515	1210
	1296		1224		1215
0.514	1260	0.519	1261	0.526	1283
	1268		1271		1293
0.532	1208	0.536	1219	0.542	1272
	1212		1225		1237
0.553	1149			0.571	1164
	1152				1159
0.567	1110			0.590	1106
	1114				1107
0.562	1119			0.579	1139
	1123				1145
				0.5995	1073
					1078

TABLE 2. continued.

N PbO = 0.6		N PbO = 0.55		N PbO = 0.5	
EMF	Temperature	EMF	Temperature	EMF	Temperature
0.640	1061	0.607	1185	0.6475	1128
	1061		1184		1126
0.6065	1141	0.588	1231	0.6145	1203
	1138		1233		1206
0.580	1217	0.599	1209	0.602	1248
	1224		1210		1249
0.5635	1267	0.6185	1145	0.623	1180
	1265		1144		1181
0.572	1235	0.613	1162	0.6365	1139
	1234		1161		1138
0.590	1168	0.635	1095	0.6555	1084
	1173		1097		1080
0.605	1125	0.6505	1061	0.644	1120
	1123		1060		1118
0.585	1183	0.628	1123		
	1184		1123		
0.5785	1211	0.610	1176		
	1216		1176		
0.613	1096	0.592	1231		
	1098		1234		
0.641	1014	0.5695	1290		
	1014		121		
0.6295	1067	0.5555	1333		
	1062		1339		

TABLE 2. continued.

N PbO = 0.6		N PbO = 0.55		N PbO = 0.55	
EMF	Temperature	EMF	Temperature	EMF	Temperature
0.588	1182	0.569	1300	0.6305	1136
	1185		1304		1137
0.596	1164	0.581	1263	0.640	1105
	1158		1265		1105
0.5615	1259	0.617	1168		
	1251		1172		
0.545	1302	0.598	1224		
	1296		1225		
0.535	1322	0.6065	1193		
	1320		1196		
0.562	1246	0.590	1239		
	1239		1242		
		0.5745	1293		
			1295		
		0.570	1310		
			1312		
		0.6045	1207		
			1207		
		0.621	1155		
			1155		
		0.614	1181		
			1184		

TABLE 3.

The lines of linear regression of E M F versus
Temperature for the system n PbO - SiO₂.

$$E = MT + C \quad \text{volts.}$$

E is the EMF in volts.

T is the temperature in °K.

Composition n PbO	M	C	Correlation Coefficient	Standard Deviation
0.5	-3.3725×10^{-4}	1.0222	0.9906	± 0.0025
0.55	-3.3948×10^{-4}	1.01108	0.9900	± 0.0029
0.6	-3.4994×10^{-4}	1.0017	0.9905	± 0.0042
0.7	-3.5259×10^{-4}	0.9791	0.9960	± 0.0019
0.8	-3.6706×10^{-4}	0.9865	0.9946	± 0.0030
0.9	-3.5284×10^{-4}	0.9594	0.9920	± 0.0017

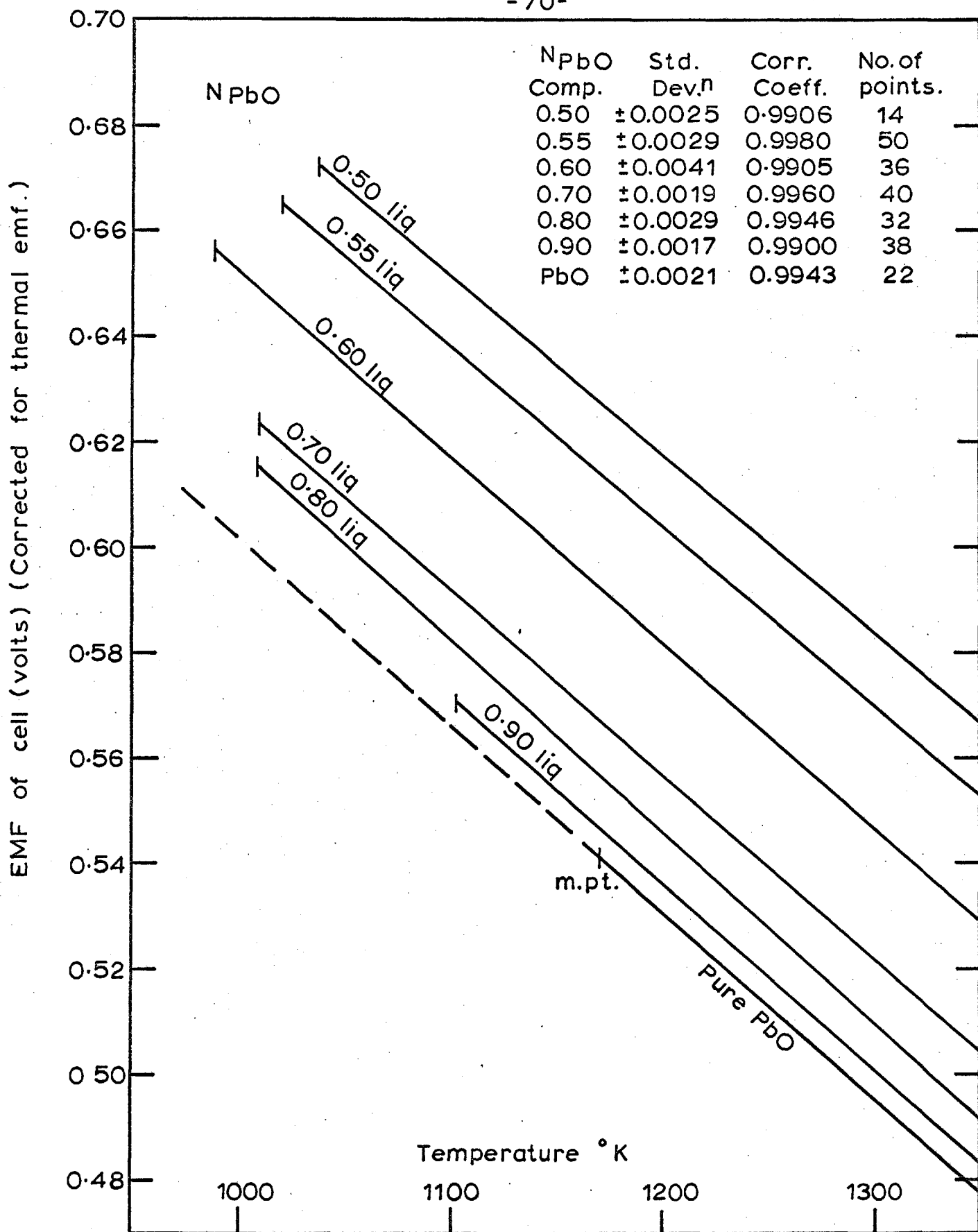
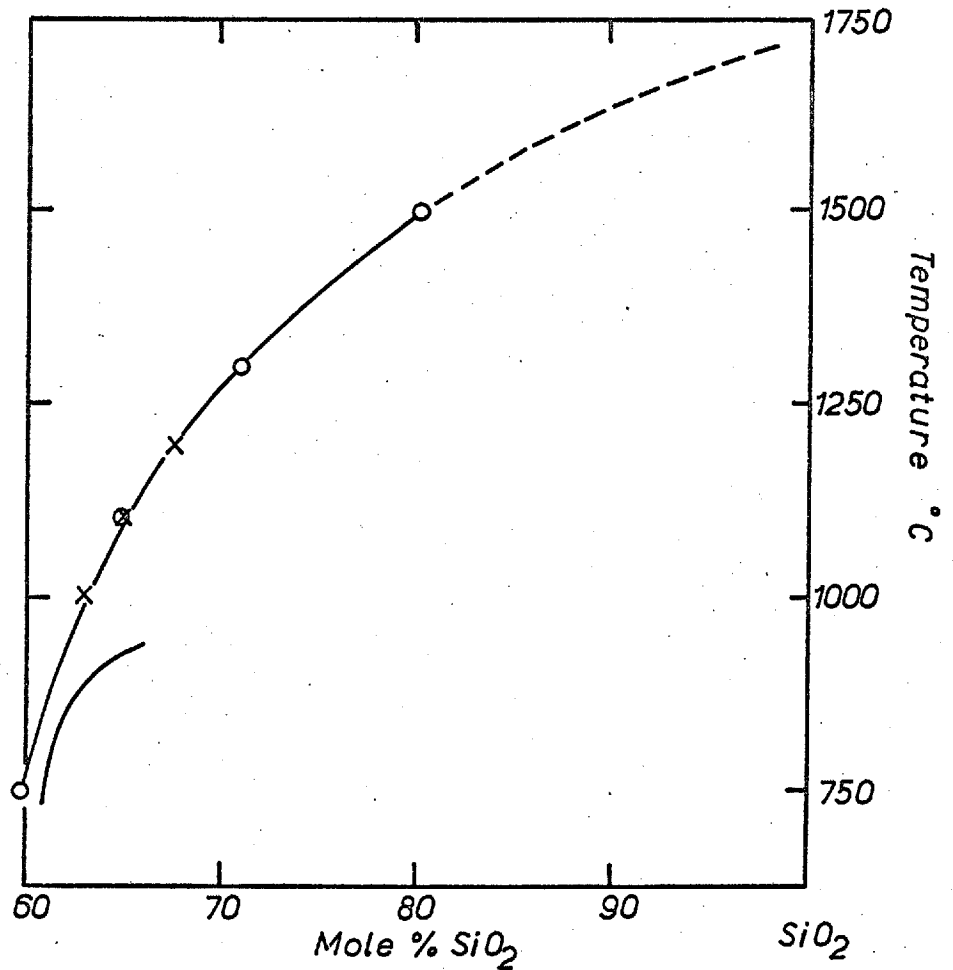


Fig.9 EMF OF CELLS CONTAINING n PbO - SiO₂ MELTS



o Krakau, Mukhin and Heinrich x Richardson and Webb
— Geller, Creamer and Bunting

FIG. 10 THE LIQUIDUS AT SILICA SATURATION FOR THE SYSTEM PbO-SiO₂

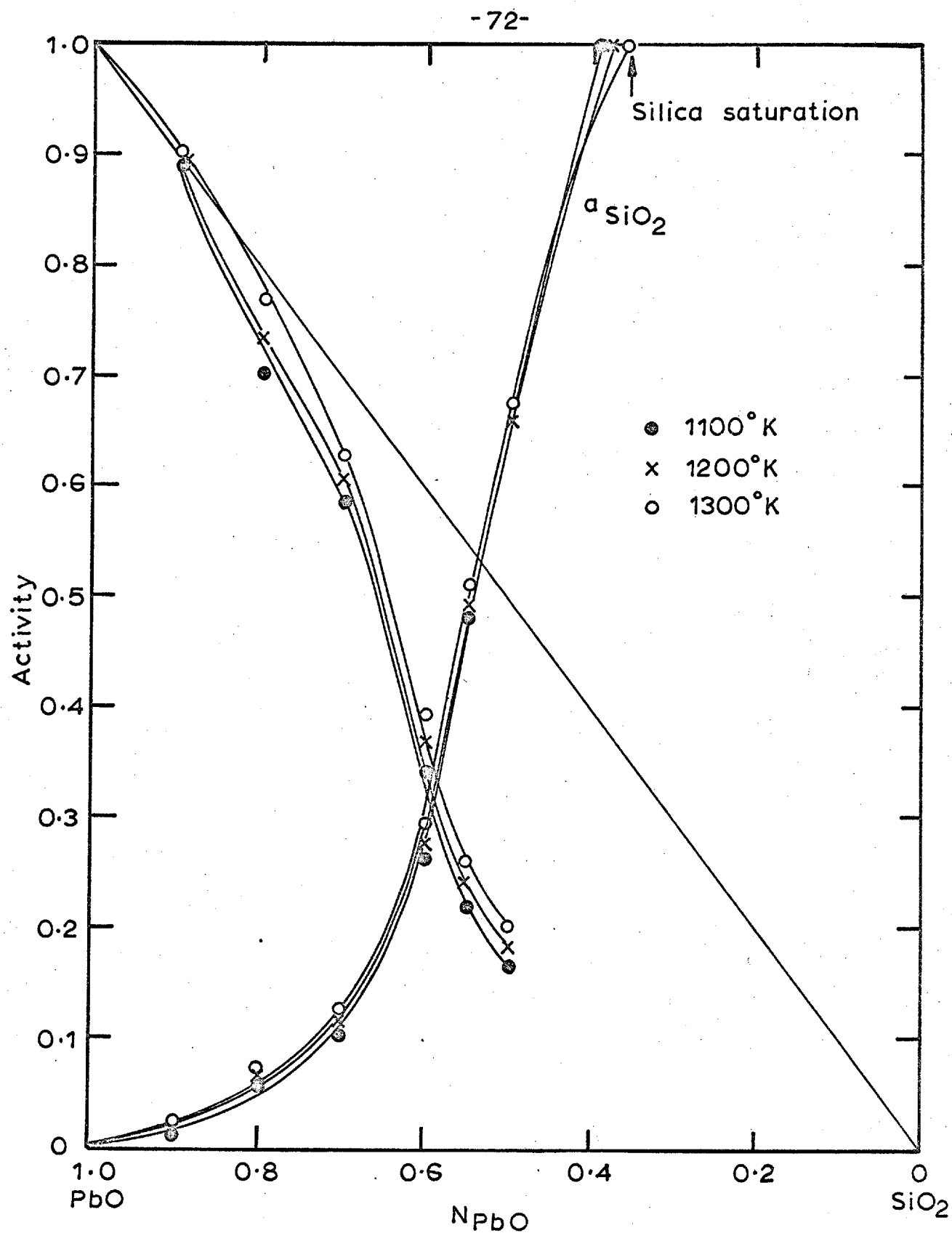


Fig. 11 ACTIVITY OF PbO & SiO₂ IN nPbO-SiO₂ MELTS

T A B L E 4

The activities, partial free energies, enthalpies and entropies of PbO and SiO₂ in n PbO SiO₂.

Tempera- ture	NPbO Composi- tion	a PbO	a SiO ₂	$\Delta\bar{G}$ PbO Kcals/ mole	$\Delta\bar{G}$ SiO ₂ Kcals/ mole	$\Delta\bar{H}$ PbO Kcals/ mole	$\Delta\bar{H}$ SiO ₂ Kcals/ mole	$\Delta\bar{S}$ PbO	$\Delta\bar{S}$ SiO ₂
1100°K	0.5	0.1656	0.661	-3.930	-0.906	-2.9978	-0.3	+0.85	+0.55
	0.55	0.2205	0.484	-3.304	-1.585	-2.4875	-0.8	+0.74	+0.71
	0.6	0.3425	0.266	-2.342	-2.894	-2.0586	-1.6	+0.26	+1.18
	0.7	0.5864	0.106	-1.166	-4.907	-1.0121	-2.8	+0.14	+1.91
	0.8	0.7024	0.0610	-0.772	-6.114	-1.355	-1.7	-0.53	+4.01
	0.9	0.8939	0.0135	-0.245	-9.411	-0.1072	-9.35	+0.126	+0.05
1200°K	0.5	0.1857	0.661	-4.014	-0.988	-2.9978	-0.3	+0.85	+0.55
	0.55	0.2425	0.490	-3.378	-1.702	-2.4875	-0.8	+0.74	+0.71
	0.6	0.3704	0.29	-2.368	-3.047	-2.0586	-1.6	+0.26	+1.18
	0.7	0.6095	0.117	-1.180	-5.106	-1.0121	-2.8	+0.14	+1.91
	0.8	0.7397	0.0661	-0.719	-6.478	-1.355	-1.7	-0.53	+4.01
	0.9	0.8975	0.0193	-0.258	-9.415	-0.1072	-9.35	+0.126	+0.05
1300°K	0.5	0.2046	0.676	-4.099	-1.011	-2.9978	-0.3	+0.85	+0.55
	0.55	0.2627	0.513	-3.453	-1.725	-2.4875	-0.8	+0.74	+0.71
	0.6	0.3958	0.298	-2.394	-3.122	-2.0586	-1.6	+0.26	+1.18
	0.7	0.6299	0.129	-1.193	-5.293	-1.0121	-2.8	+0.14	+1.91
	0.8	0.7727	0.0668	-0.666	-6.988	-1.355	-2.7	-0.53	+4.01
	0.9	0.9006	0.0260	-0.270	-9.427	-0.1072	-9.35	+0.126	+0.05

The activity of PbO and SiO_2 found in this study is plotted in Fig 11. The activity of PbO found in this study is also shown in Fig 36, along with the activities of PbO in this system determined by Sridhar and Jeffes, (48) Charette and Flengas, (21) Richardson and Webb (15), see chapter 11 (2).

A plot of E M F versus composition at 1200°K is shown in Fig 35 from this study, Charette and Flengas and Sridhar and Jeffes, also in chapter 11 (2).

The activities, partial free energies, enthalpies entropies of PbO and SiO_2 at 1100°K , 1200°K and 1300°K are given in Table 4.

The partial enthalpies are plotted in Fig 15 and the partial entropies in Fig 16. The integral free energies, enthalpies and entropies obtained from this study are plotted in Fig 40, in chapter 11 (2).

4. $n\text{PbO} \cdot \text{P}_2\text{O}_5$ melts.

As a check of the results obtained by Sridhar of the system $n\text{PbO} \cdot \text{P}_2\text{O}_5$, two compositions were studied using this cell. The results E M F versus temperature are given in Table 5 and the calculated lines of linear regression are plotted in Fig 12 and given in Table 6.

The activities of PbO are shown in Fig 13

TABLE 5.

E M F as a function of Temperature for cells
containing n PbO. P_2O_5 melts.

N PbO = 0.7		N PbO = 0.86	
EMF	Temperature	EMF	Temperature
Volts	$^{\circ}K$	Volts	$^{\circ}K$
0.939	1330	0.520	1332
	1333		1330
0.9485	1289	0.533	1293
	1292		1290
0.946	1312	0.546	1248
	1313		1246
0.9225	1316	0.5615	1201
	1362		1199
0.863	1410	0.557	1227
	1412		1224
0.926	1303	0.5405	1276
	1300		1274
0.9135	1349	0.511	1376
	1351		1374
0.922	1324		
	1326		
0.893	1372		
	1373		
0.908	1397		
	1397		

TABLE 5. continued

N PbO = 0.7	
EMF	Temperature
Volts	$^{\circ}\text{K}$
0.889	1421
	1421
0.919	1369
	1370
0.9285	1323
	1321

TABLE 6.

The lines of linear regression of E M F versus
Temperature for the system nPbO - P₂O₅ .

E = MT + C Volts

E is the EMF in Volts

T is the temperature in °K.

N PbO Composition	M	C	Correlation Coefficient	Standard Deviation
0.7	-4.9648×10^{-4}	1.5877	0.8578	± 0.0121
0.86	-3.0773×10^{-4}	0.9315	0.9932	± 0.0019

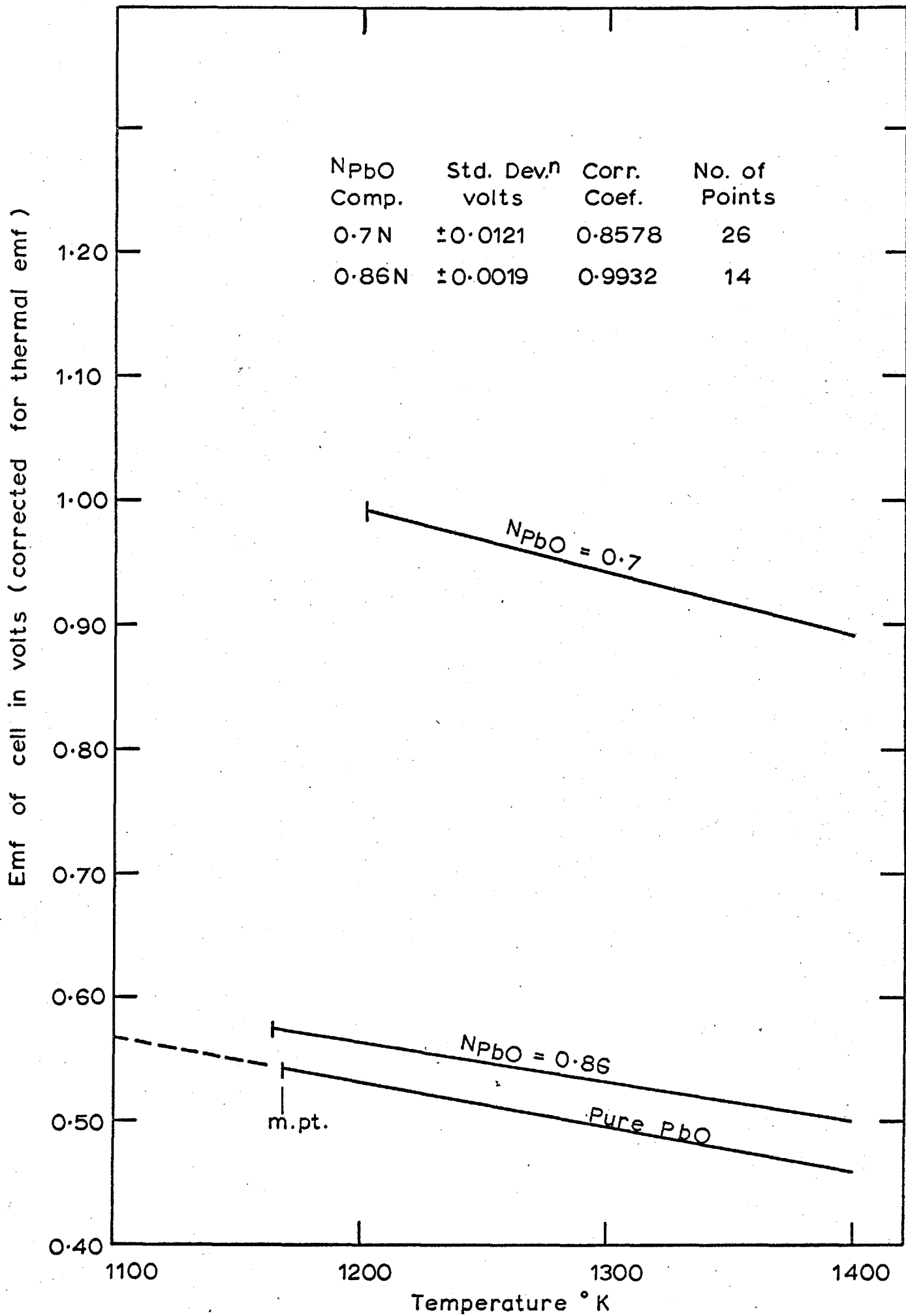


Fig. 12 EMF OF CELLS CONTAINING nPbO.P₂O₅ MELTS

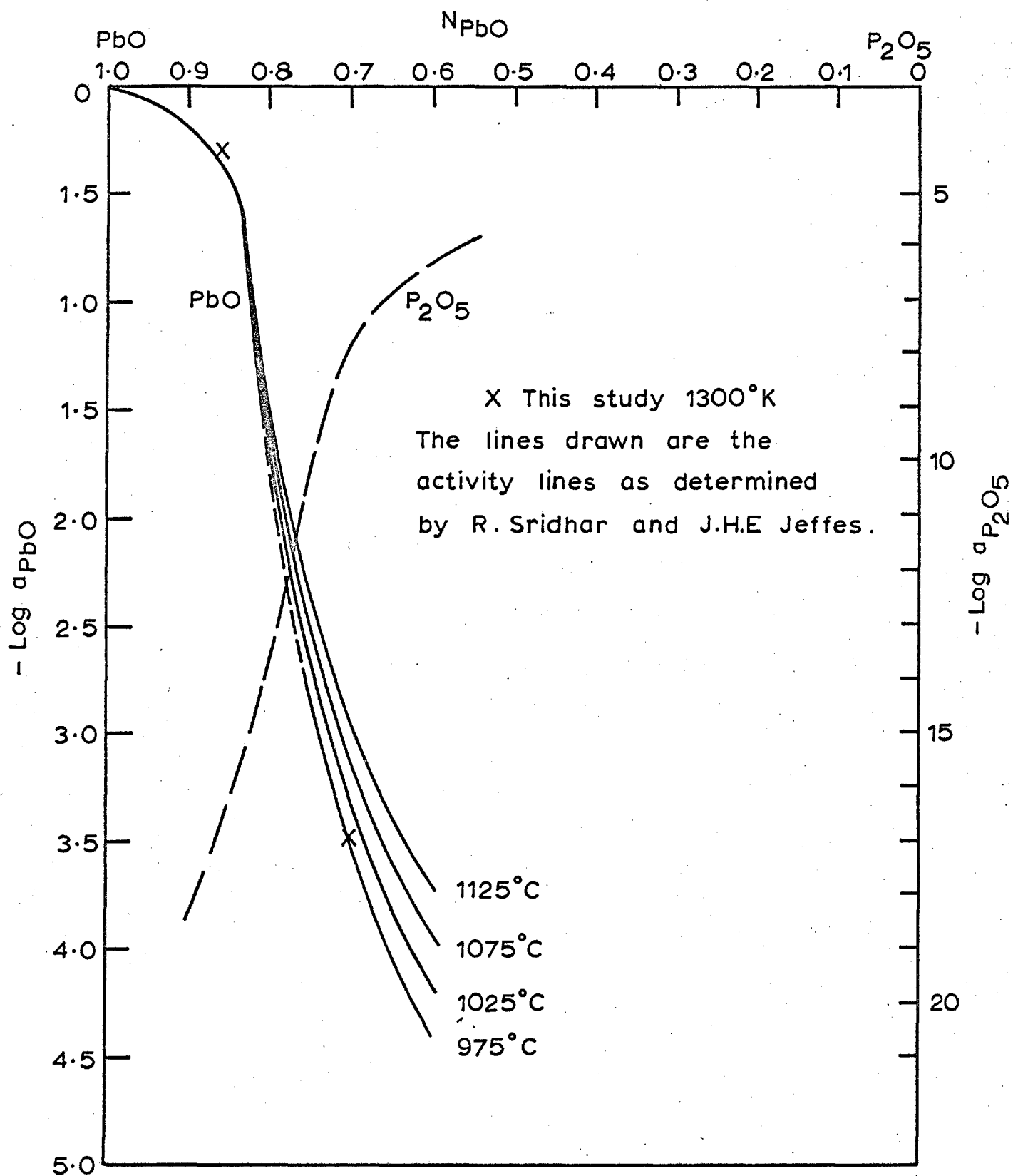


Fig.13. ACTIVITIES OF PbO AND P_2O_5 IN PbO P_2O_5 MELTS

T A B L E 2

The activities, partial free energies, enthalpies and entropies of PbO in n PbO.Pb₂O₅

Temperature	Composition N PbO	a PbO	log a PbO	$\Delta \bar{G}$ PbO	$\Delta \bar{H}$ PbO	$\Delta \bar{S}$ PbO cals/°
1100	0.7	4.376×10^{-5}	-4.359	-21.94	-29.09	-6.50
	0.86	0.5659	-0.2473	-1.244	+1.258	+2.27
1200	0.7	1.326×10^{-4}	-3.877	-21.29	-29.09	-6.50
	0.86	0.5409	-0.2668	-1.465	+1.258	+2.27
1300	0.7	3.390×10^{-4}	-3.470	-20.64	-29.09	-6.50
	0.86	0.5207	-0.2834	-1.686	+1.258	+2.27

along with the activities of PbO as determined by Sridhar. Sridhar has estimated the activity of P_2O_5 in these melts using a Gibbs Duhem equation and by estimating the activity of P_2O_5 at $N_{PbO} = 0.55$, since he observed that phosphorus was evolved from the cell at this composition. This result is also given in Fig 13 .

The activities and partial quantities of PbO at $1100^\circ K$, $1200^\circ K$ and $1300^\circ K$ are summarised in Table 7 .

The partial enthalpies are plotted in Fig 15 and the partial entropies in Fig 16 .

5. nPbO. PbCl₂ melts.

The E M F of the cell containing nPbO.PbCl₂ melts was measured over the temperature range $670^\circ C$ to $950^\circ C$. The results E M F versus temperature are given in Table 8 and the lines of linear regression calculated for each composition are plotted in Fig 14 and given in Table 9.

The activity of lead oxide could only be measured between $N_{PbO} = 1$ to $N_{PbO} = 0.5$ by this method since the lead chloride has a relatively high vapour pressure, and at mole fractions less than $N_{PbO} = 0.5$ the loss of lead chloride from the melt becomes significant.

A plot of activity of lead oxide versus composition at $1200^\circ K$ is given in Fig 46 as well as the activity-composition relationship for PbO in the system nPbO.PbF₂

TABLE 8.

E M F as a function of Temperature for cells
containing n PbO. PbCl₂ melts.

N PbO = 0.9		N PbO = 0.8		N PbO = 0.7	
EMF	Temperature	EMF	Temperature	EMF	Temperature
Volts	°K	Volts	°K	Volts	°K.
0.573	1106	0.592	1106	0.633	1044
	1103		1103		1047
0.5555	1158	0.6095	1061	0.6505	1003
	1155		1055		1006
0.5655	1138	0.6015	1082	0.640	1029
	1135		1077		1032
0.583	1095	0.619	1039	0.6185	1080
	1092		1035		1083
0.593	1070	0.6355	995	0.606	1111
	1066		992		1111
0.5935	1067	0.6295	1015	0.5955	1139
	1065		1011		1139
0.553	1168			0.631	1049
	1168				1050
0.5685	1126			0.599	1127
	1123				1128
0.586	1083			0.6175	1082
	1082				1084
0.595	1061			0.636	1037

TABLE 8. continued.

N PbO = 0.9		N PbO = 0.7	
EMF	Temperature	EMF	Temperature
Volts	$^{\circ}\text{K}$	Volts	$^{\circ}\text{K}$
0.595	1059	0.636	1036
		0.650	1001
			1002
		0.6215	1073
			1072
		0.582	1176
			1175

TABLE 8. continued.

N PbO = 0.6		N PbO = 0.5	
EMF	Temperature	EMF	Temperature
Volts	°K	Volts	°K
0.6625	1042	0.733	953
	1041		955
0.6825	1000	0.742	935
	1007		937
0.6735	1023	0.720	907
	1028		991
0.6505	1078	0.704	1018
	1075		1022
0.637	1101	0.711	1007
	1106		1009
0.629	1127	0.729	959
	1131		960
0.6755	1001	0.7125	1004
	999		1002
0.664	1051		
	1047		
0.6815	1003		
	998		
0.6855	982		
	978		
0.667	1024		
	1020		
		N PbO = 0.6 contd.	
		0.6465	1078
			1074

TABLE 9.

The lines of linear regression of E M F versus
Temperature for the system $\text{nPbO} - \text{PbCl}_2$.

$$E = MT + C \text{ volts}$$

E is the EMF in volts

T is the temperature in $^{\circ}\text{K}$.

N PbO Composition	M	C	Correlation Coefficient	Standard Deviation
0.5	-4.2735×10^{-4}	+1.1411	0.9968	± 0.0013 volts
0.6	-4.0822×10^{-4}	+1.0884	0.9892	± 0.0030 "
0.7	-4.0328×10^{-4}	+1.0545	0.9991	± 0.0008 "
0.8	-3.9841×10^{-4}	+1.0316	0.9965	± 0.0026 "
0.9	-3.9512×10^{-4}	+1.013471	0.9946	± 0.0017 "

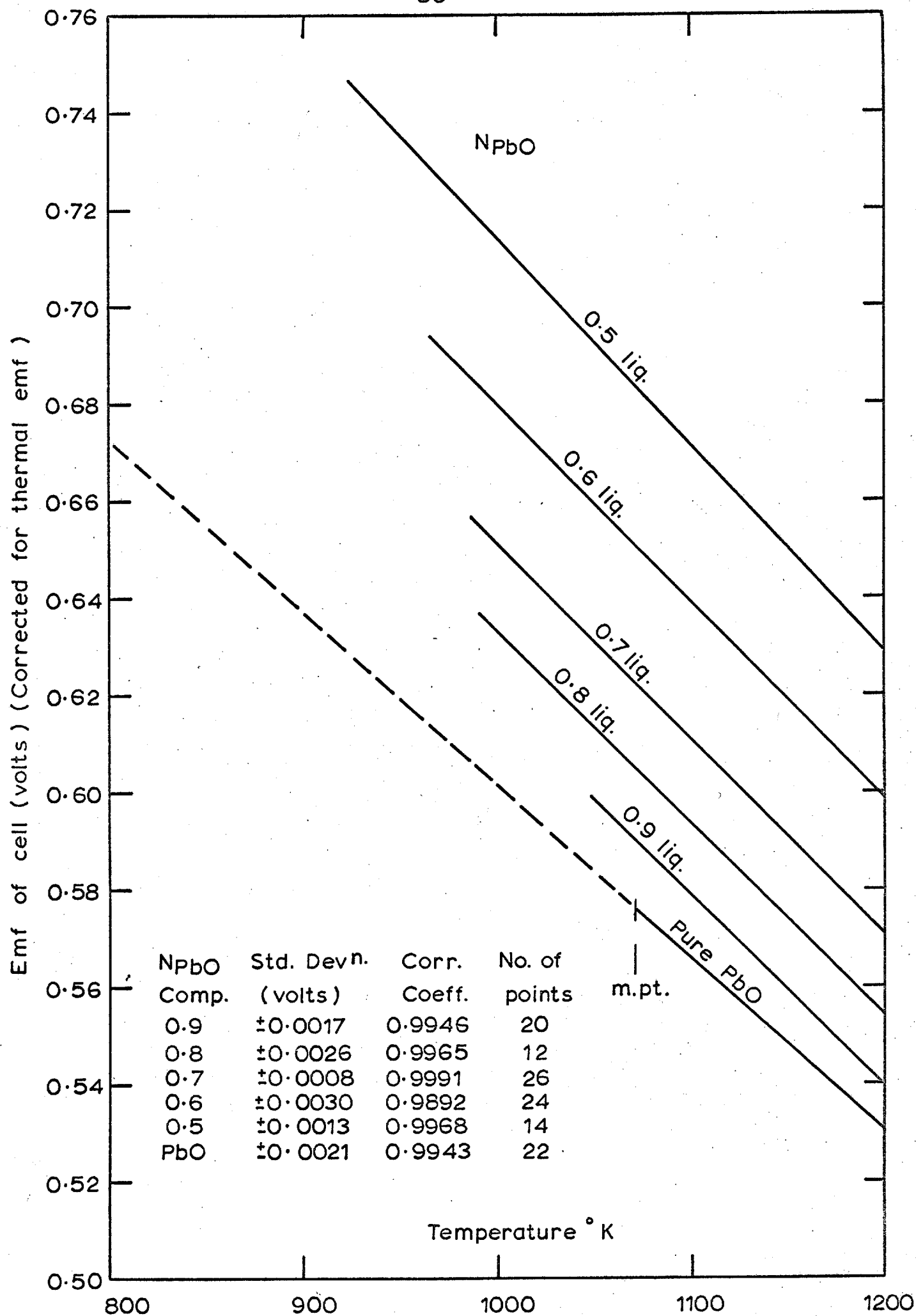


Fig.14 EMF OF CELLS CONTAINING nPbO.PbCl₂ MELTS

TABLE 10

The activities, partial free energies, enthalpies and entropies
of PbO in n PbO. PbCl₂

Temperature	Composition N _{PbO}	a _{PbO}	$\Delta \bar{G}_{\text{PbO}}$	$\Delta \bar{H}_{\text{PbO}}$	$\Delta \bar{S}_{\text{PbO}}$ cals/°
1100°K	0.5	0.1090	-4.844	-8.485	-3.31
	0.6	0.2125	-3.385	-6.054	-2.43
	0.7	0.3876	-2.071	-4.489	-2.20
	0.8	0.5619	-1.260	-3.433	-1.97
	0.9	0.7628	-0.592	-2.598	-1.82
1200°K	0.5	0.1506	-4.513	-8.485	-3.31
	0.6	0.2677	-3.141	-6.054	-2.43
	0.7	0.4621	-1.851	-4.489	-2.20
	0.8	0.6405	-1.062	-3.433	-1.97
	0.9	0.8423	-0.409	-2.598	-1.82
1300°K	0.5	0.1981	-4.182	-8.485	-3.31
	0.6	0.3255	-2.899	-6.054	-2.43
	0.7	0.5318	-1.631	-4.489	-2.20
	0.8	0.7155	-0.865	-3.433	-1.97
	0.9	0.9159	-0.227	-2.598	-1.82

as determined by Sridhar at 1170°K.

The activities and partial quantities of PbO in mPbO. PbCl₂ melts at 1100°K, 1200°K and 1300°K are given in Table 10.

The partial enthalpies are plotted in Fig 16 and the partial entropies in Fig 16.

6. Errors.

A complete analysis of errors using this technique has been given by Sridhar^(4). Since the RMS of the E M F of the cell is approximately $\pm 2\text{mV}$, then this produces an error in $\Delta\bar{G}_{\text{PbO}}$ of ± 130 calories.

$\Delta\bar{G}_{\text{PbO}} = RT \ln a_{\text{PbO}}$, then with an error of $\pm 1^\circ\text{C}$ in the temperature readings, the error in the activity results is about 5%. The errors in $\Delta\bar{G}_{\text{SiO}_2}$ are slightly larger due to the additional error involved in a Gibbs Duhem integration and are about ± 150 calories.

The errors in the partial heats and entropies are much larger since they involve the measurement of slopes of $\frac{\Delta\bar{G}}{T}$ versus $\frac{1}{T}$ and are estimated to be about ± 700 calories and ± 0.5 calories/ degree respectively.

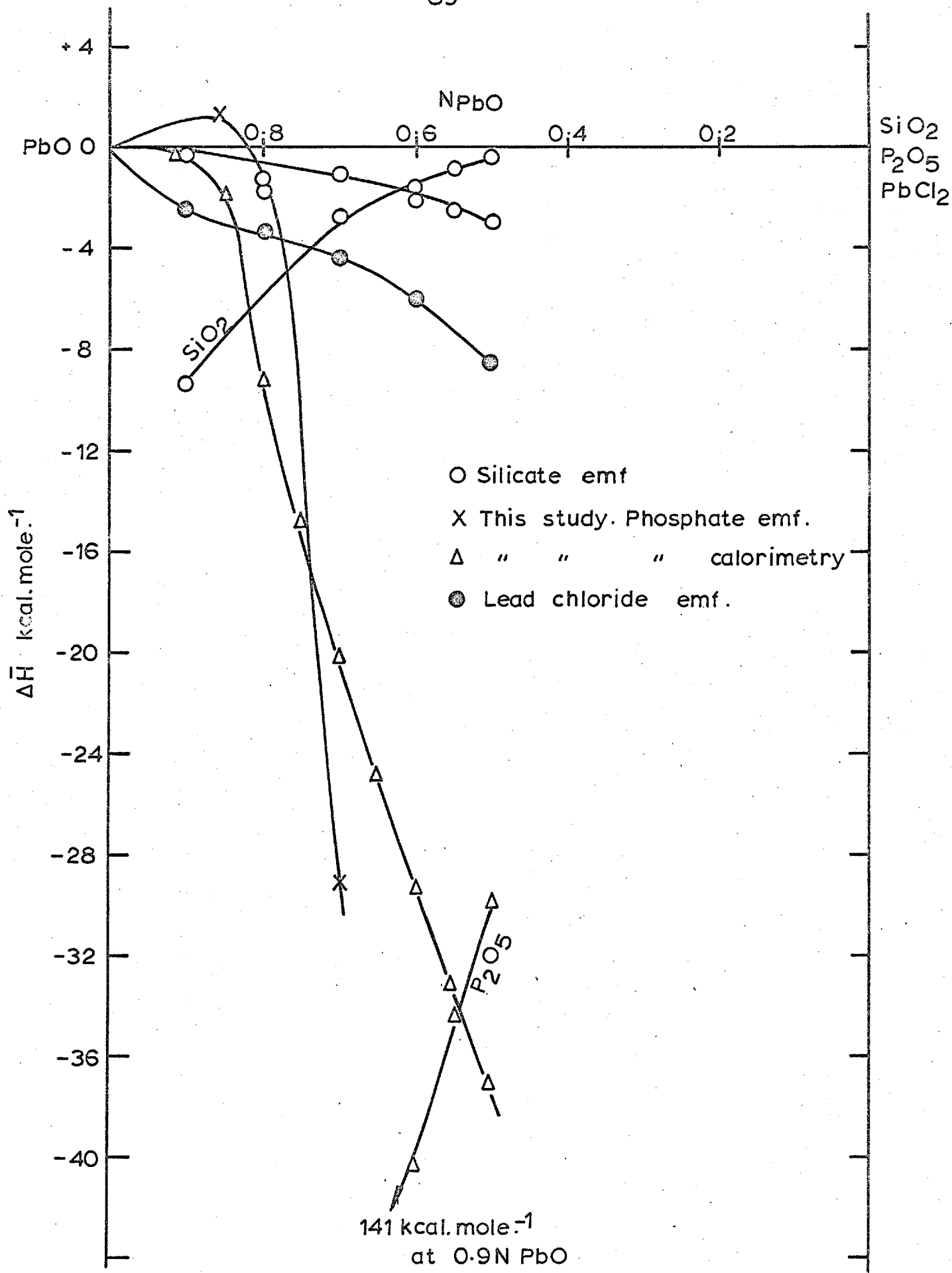


Fig. 15

THE PARTIAL HEATS OF SOLUTION IN $n\text{PbO} \cdot \text{SiO}_2$,
 $\text{PbO} \cdot \text{P}_2\text{O}_5$, & IN $\text{PbO} \cdot \text{PbCl}_2$ MELTS.

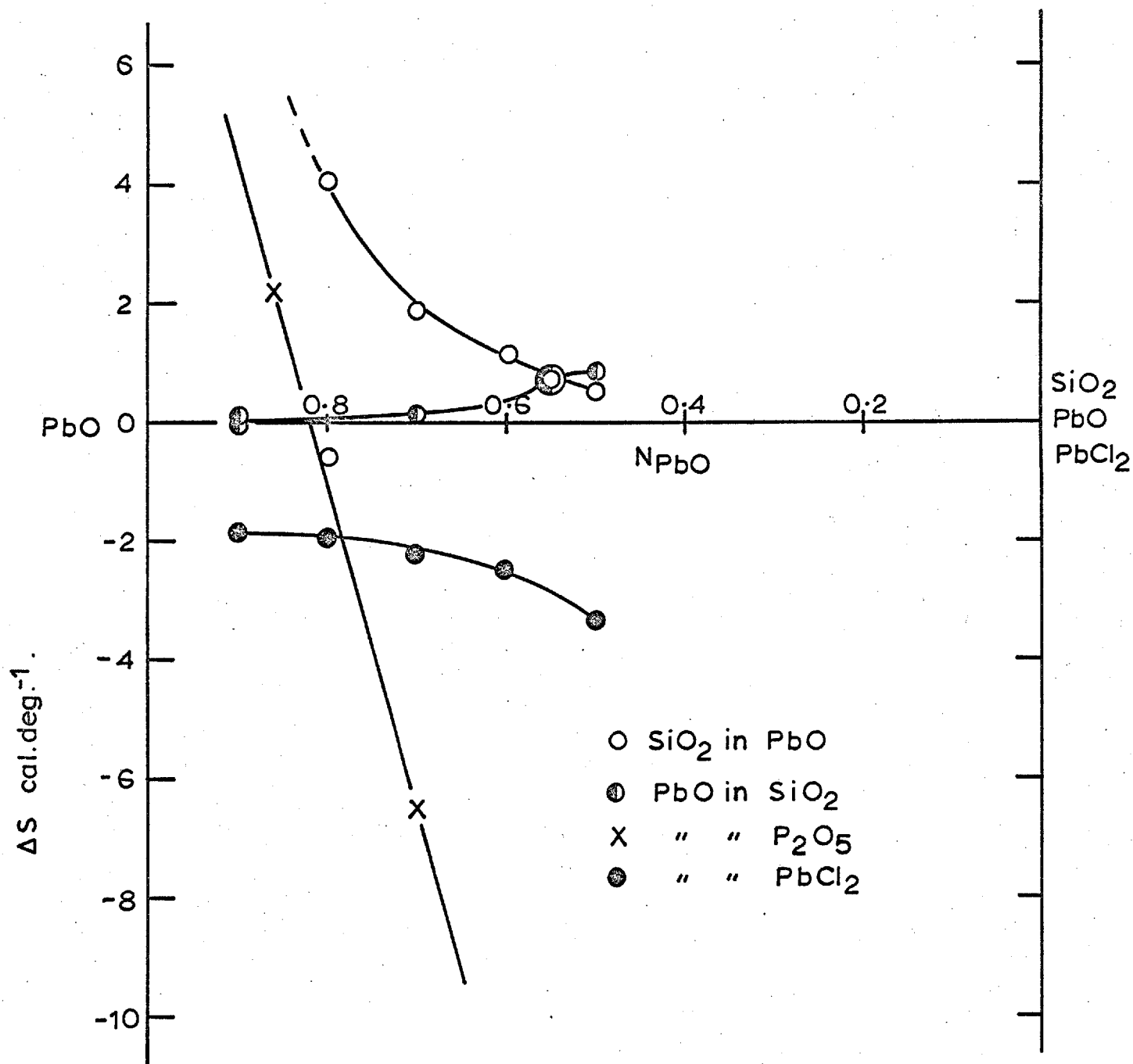


Fig.16 PARTIAL ENTROPIES OF SOLUTION IN
 $n \text{ PbO} \cdot \text{SiO}_2$, $n \text{ PbO} \cdot \text{P}_2\text{O}_5$, & IN $\text{PbO} \cdot \text{PbCl}_2$
 MELTS

Chapter 6.

CALORIMETRY

1. Calorimeter:

A Calvet type of Differential calorimeter which has recently been developed by O. J. Kleppa (5) was used for these experiments.

A diagrammatical cross-section is shown in Fig 17 . This diagram is not to scale since there is more lagging around the calorimeter.

The differences between the calorimeter and the 'Kleppa' calorimeter are, firstly that the block has been made of a material with the trade name 'Deranox' which is 93.4% alumina fired at 1650°C. Secondly, the thermopile units consists of Platinum - Platinum 13% Rhodium thermocouples. The two thermopiles each containing sixty four thermocouple junctions are connected 'back to back' so that a small difference of temperature in either of the tubes is directly converted into an emf which is recorded on a Leeds and Northrup pen recorder. The details of the calorimeter and thermopile construction are to be published by M. P. Roye and J. H. E. Jeffes.

At present the upper temperature limit is 1200°C which is the limit of the Kanthal windings. In these experiments the ~~max~~imum temperature at which the calorimeter was maintained was 1000°C.

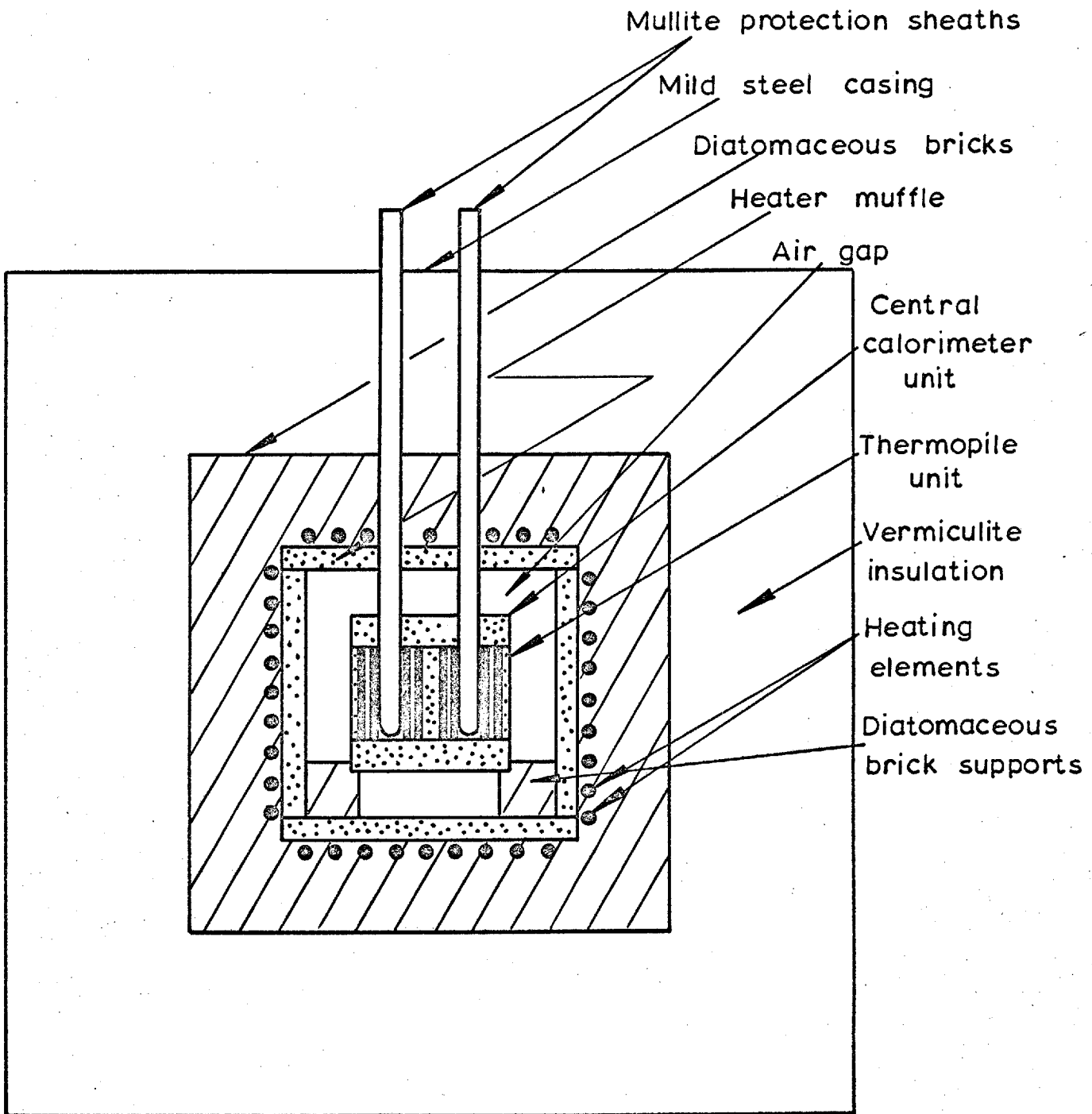


Fig.17. CROSS SECTION OF THE HIGH TEMPERATURE CALORIMETER

2. (a) Materials:

Analar grade PbO (yellow) was used after drying in all the PbO experiments, and for making the lead phosphates.

Analar $\text{NH}_4\text{H}_2\text{PO}_4$ was used as the source of P_2O_5 to make PbO. P_2O_5 melts and ZnO. P_2O_5 melts as described by Sridhar (4).

Analar zinc oxide was used after drying. Pure Platinum, single and poly-crystals of alumina were used for the calibration. Analar Cadmium oxide and Analar Boric acid were used for making Kleppa solvent PbO. CdO. B_2O_3 .

(b) Preparation of samples for calorimetry.

The pure Platinum for the calibration was pre-melted into a spherical shape in a induction furnace, on a piece of ceramic.

The PbO and ZnO powdered samples were pressed at forty to fifty tons on a ten inch diameter ram in a mould made from 'Vinamold' to produce spherical samples. Each mould was made by pouring the molten polymer onto nine Nickel spheres on a flat surface and contained in a two and a half inch diameter brass cylinder; each Nickel sphere being slightly raised from the surface with a little plasticine. No Vinamold was found in these samples after pressing.

The PbO. P_2O_5 and ZnO. P_2O_5 samples however

could not be made in this way because of contamination by the Vinamold. Each of these samples were pre-melted in bulk and then poured onto an Aluminium quenching block. The resulting glasses were then broken up to produce four to six millimeter cubic samples.

3. Calorimetry Technique and Calibration.

All the experiments were of the drop calorimetry type. The samples were dropped into 6 centimetres tall Platinum crucibles contained in 1.3 centimetre outside diameter silica tubes which were inserted at least two hours before each experiment into the calorimeter.

A 'bed of nails' made of Platinum wires on a Platinum sheet base, was placed in each of the two Platinum crucibles in the reaction tube. These are designed to overcome the problem of splashing when a sample is dropped from room temperature into a melt in the crucible. Splashing must be avoided at all costs, since the melts react with the SiO_2 tubes and erroneous heats would therefore be measured.

Before the drop the sample was held at the top of the silica tube on a piece of Platinum sheet and its temperature was measured with a mercury thermometer. The dropping device and reaction tube assembly is shown in Fig 18.

The initial experiments consisted of dropping

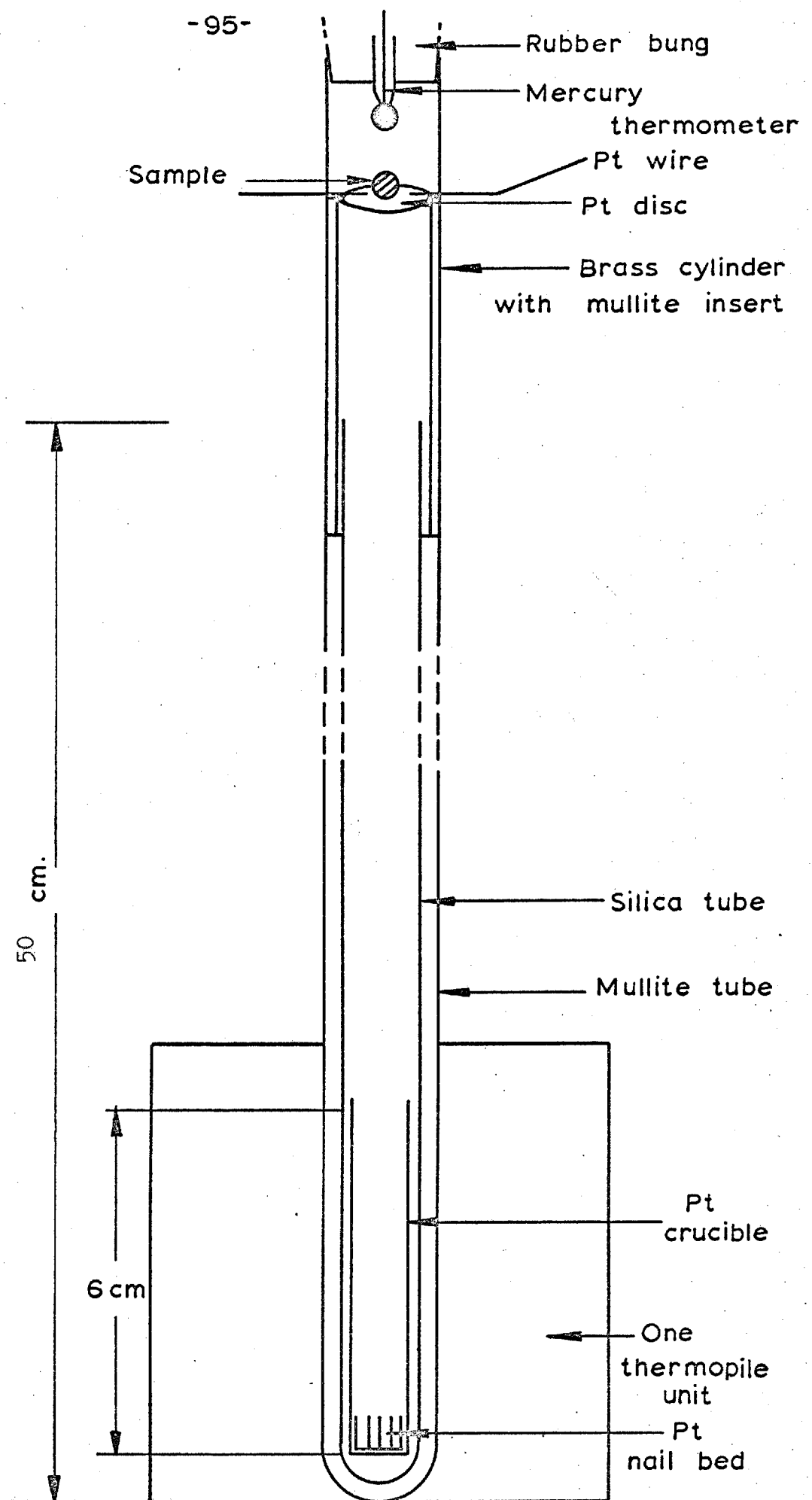


Fig.18 SAMPLE DROPPING DEVICE
AND REACTION TUBE ASSEMBLY

known weights of Platinum into the calorimeter held at different temperatures in order to study the sensitivity.

The heat involved in the drop is directly a measure of the area under the curve 'millivolts versus time' recorded on the chart, see Chapter 3, page 41. In each experiment the area was measured to ± 0.02 centimetres² with an Allbrit planimeter.

It was found that firstly the sensitivity decreases with increasing temperature, but secondly and most important, the calibration depends on the wall thicknesses of the silica tubes used and is not necessarily the same for a drop into the left-hand side compartment as the right-hand side compartment. For this reason it was decided that a calibration drop must be made immediately before or after each experiment. The heat content of Platinum is given by Hattgreen, Orr, Anderson and Kelley (50)

$$\text{as } H^T - H_{298.15} = 5.80T + 0.64 \times 10^{-3}T^2 - 1785 \pm 0.3\%$$

The calibration with Platinum was checked firstly against drops with single crystal alumina and polycrystal alumina, and secondly against an electrical method.

The electrical method consisted of dissipating a known amount of heat by means of Kanthal heating coils and silver leads, which were wound onto two millimetre diameter by two hundred centimetres long

twin bore alumina tubes, and inserted into the reaction tubes of the calorimeter; one was used as a dummy. It is most important that the geometry for each experiment is the same in both sides of the calorimeter. The amount of heat liberated was calculated from $q = \frac{V i t}{J}$. Where, V =volts
 i =amps, t =secs
 J =joules

It was found in these experiments that the use of radiation shields was unnecessary, since raising the shields in order for the sample to drop past, produced a larger error than the small error produced by fluctuation in the radiation heat loss from the two reaction tubes, since the radiation heat loss should be the same from both tubes (if the geometry is identical) to achieve the observed balance.

The base line during these experiments always returned to within ± 0.005 millivolts, and the use of radiation shields could not improve on this figure.

The initial calibration experiments are represented in figure 19, as calories per square centimetre versus temperature. The electrical calibration compares reasonably well with the platinum drop calibration, the difference being five per cent, being due firstly to localized heating at the Kanthal-Silver junctions when the current is passed, because of the difficulty of the Kanthal-Silver contact, and also conduction of heat away along the leads from the heater, since Silver is an excellent thermal conductor.

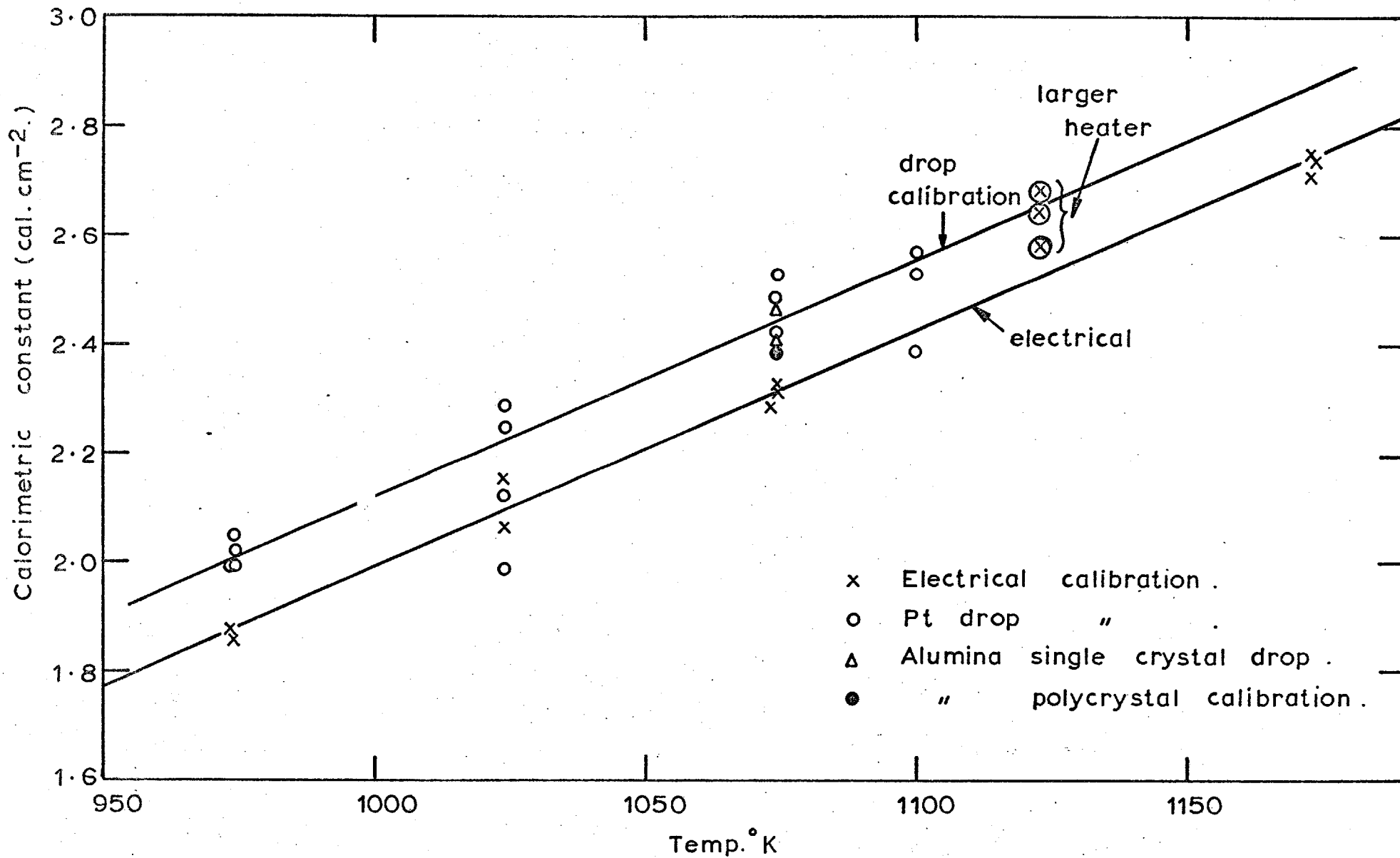


Fig. 19

CALORIMETRIC CONSTANT vs. TEMPERATURE

The alumina drop experiments are in excellent agreement with the platinum drop calibration at 800°C. using the heat content data of alumina (.51)

In these early experiments, the DC signal from the thermopile was amplified to five times magnification with a Leeds and Northrup DC amplifier, and then recorded on a Leeds and Northrup pen recorder using a 0 - 10 millivolt full scale range card. During later experiments, the signal was fed straight into the pen recorder using a 0 - 1 millivolt full scale range card.

The largest error involved in the calorimetry is the comparison of each unknown heat with platinum. The RMS error of several results for each substance is quoted in the following chapters.

Chapter 7.

THE DETERMINATION OF THE LATENT HEAT OF
FUSION OF LEAD OXIDE.

1. Experimental.

The melting point of PbO is given by Rodigina (37) as 897°C.

~~This~~ experiment consisted of dropping accurately weighed spherical PbO samples from room temperature into Platinum crucibles (containing the Platinum nail beds) inside the silica tubes in the calorimeter, which was maintained at various temperatures below and above the melting point of PbO. A few milligrams of Pb_3O_4 was placed in the Platinum crucibles in each experiment before insertion into the calorimeter to insure a slightly oxidising atmosphere in the crucibles at the temperature of operation. Under the operating conditions Pb_3O_4 decomposes to PbO and oxygen above 870°K, as can be seen from the free energy versus temperature plot given in Fig 20 . It is essential to maintain this oxidising atmosphere since lead formed by any reduction would immediately alloy with the Platinum crucibles and terminate the experiment. Before each PbO drop, an accurately weighed sphere of Platinum was dropped into the calorimeter from room temperature, such that the heat effect due to the PbO drop can be directly compared to that of the Platinum, which has a known

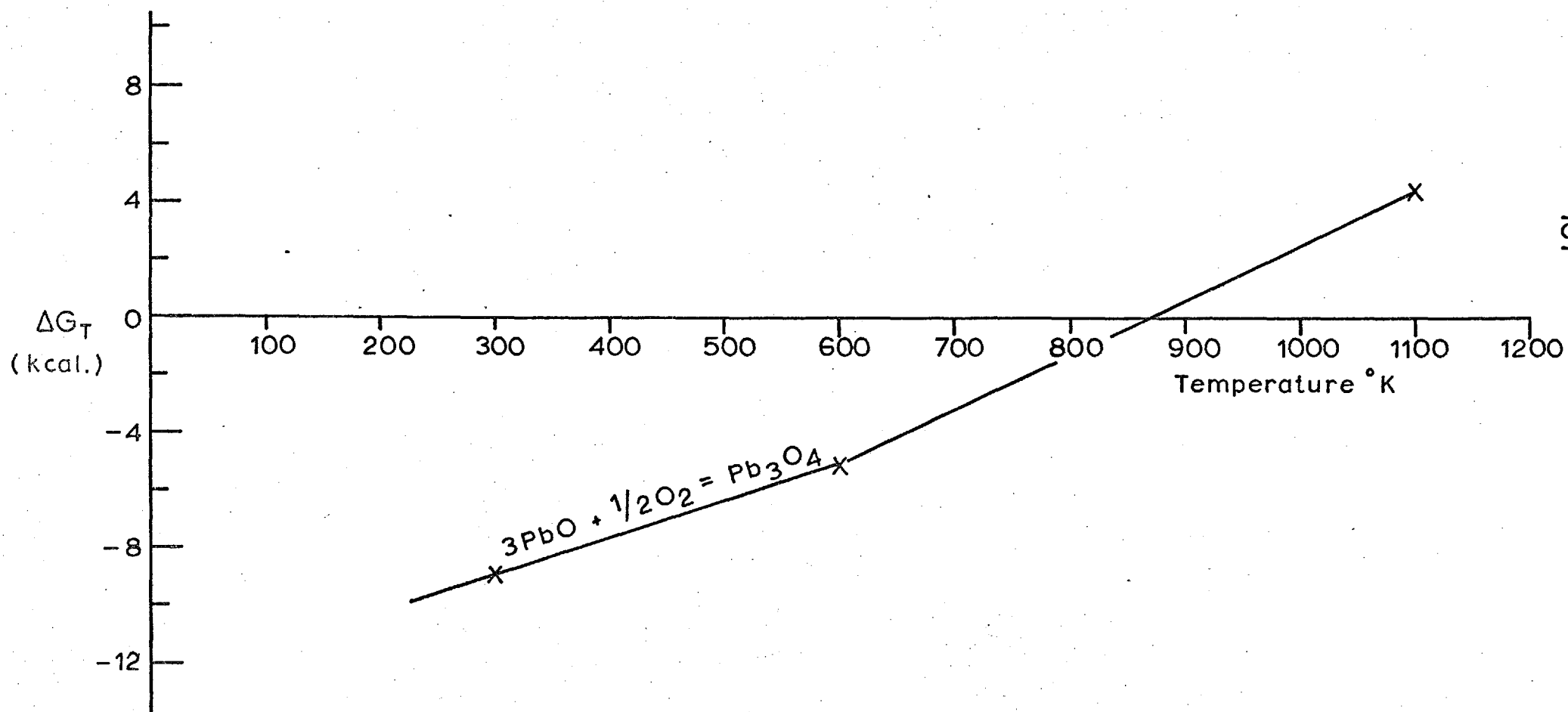


Fig.20 ΔG_T vs. Temperature relationship for $\text{PbO} - \text{Pb}_3\text{O}_4$.

heat content (50), as a measure of the area under the curve ' millivolts versus time ' recorded on the chart recorder.

It was found that for unannealed samples of PbO, the heat measured was in the order of $\frac{1}{2}$ Kcal lower than for samples annealed at 800°C for one hour and then quenched. No difference between the two Xray powder patterns could be determined by the Debye Scherrer powder Xray technique. Although a very small amount of PbO (red) phase could be seen from the Xray analysis, the amount was the same in both cases. Other than this small amount of PbO (red) present, all the lines observed were in accordance with the PbO (yellow) structure, as given in the Fink index, and no other phase or oxide of PbO or Pb could be detected.

It was decided to anneal all the samples for this experiment at 800°C for one hour and then quench, since a degree of sintering was achieved and the samples did not break off or crumble as easily as the unannealed samples. As long as all the samples are pretreated in the same way, this effect will not effect the value of the latent heat of fusion of PbO.

This value of $\frac{1}{2}$ Kcal is a measure of the strain energy in the samples introduced by compression in the production of the spherical samples as described earlier.

2. Results.

Assuming linear relationships between ΔH_{298}^T versus $T^{\circ}K$ over the temperature range studied, then the lines of linear regression for PbO solid and liquid are given by :-

$$\Delta H_{298}^T \text{ PbO solid} = + 0.01561T - 6.8055 \quad \text{Kcals/mole}$$

$$\text{Correlation coefficient} = 0.95294$$

$$\text{R.M.S.} = \pm 0.235 \quad \text{Kcals/mole}$$

$$\Delta H_{298}^T \text{ PbO liquid} = + 0.003980T + 13.150 \quad \text{Kcals/mole}$$

$$\text{Correlation coefficient} = 0.38520$$

$$\text{R.M.S.} = \pm 0.356 \quad \text{Kcals/mole}$$

The results and their lines of regression are plotted in Fig 21. The results are given in Table 11. Taking $897^{\circ}C$ as the melting point of PbO, then

$$\begin{aligned} \Delta H_f &= \Delta H_{298}^T \text{ liquid} - \Delta H_{298}^T \text{ solid at the melting point} \\ &= 6.37 \pm 0.43 \text{ Kcals / mole.} \end{aligned}$$

Also shown in Fig 21 are the results obtained by Rodigina, Gomel'skii and Luginina (37). These results are in excellent agreement with the results obtained in this study.

3. Discussion.

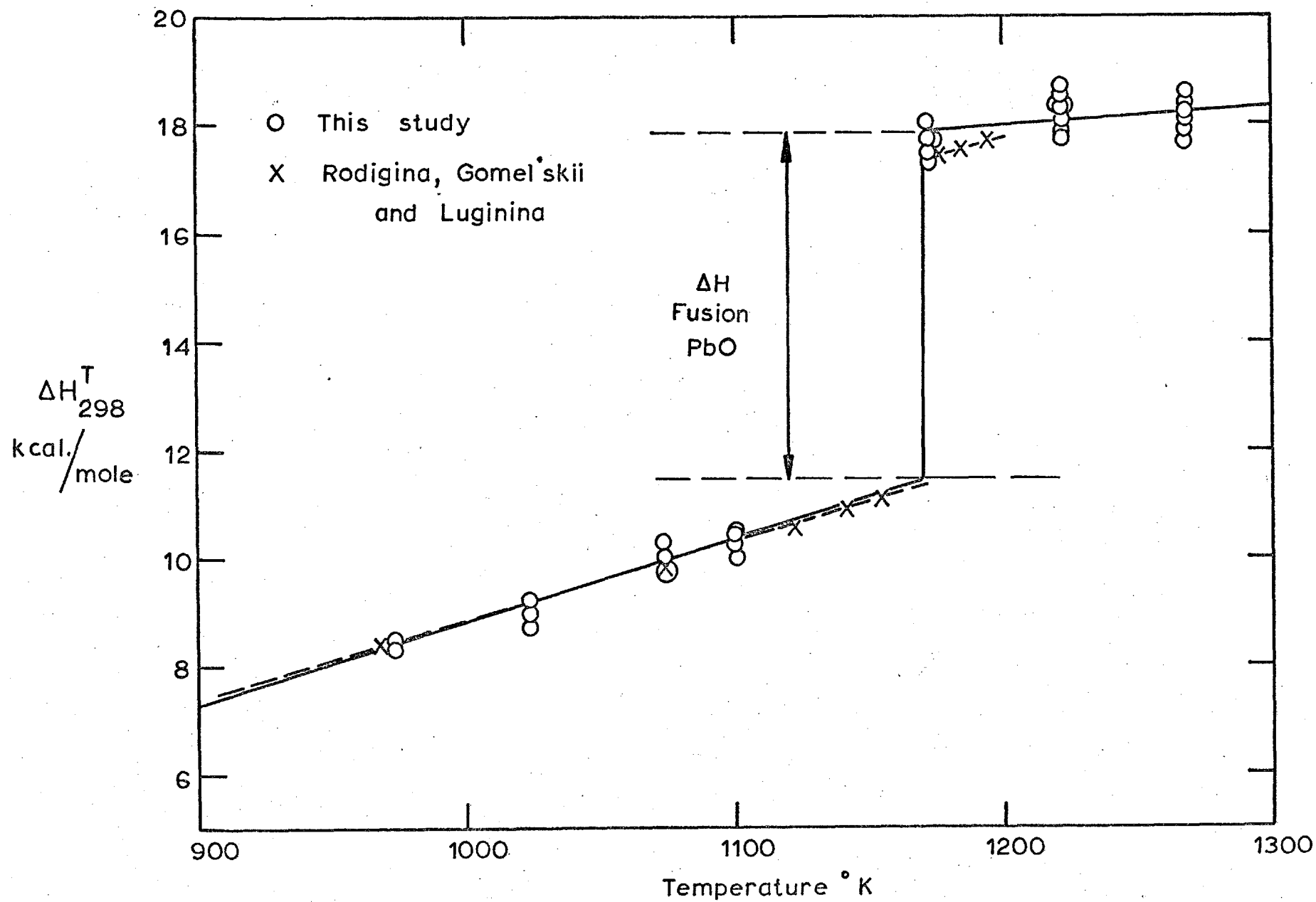
The results of ΔH_{298}^T given by Rodigina, Gomel'skii and Luginina are in most excellent agreement with the results of ΔH_{298}^T measured in this study for both liquid and solid PbO. Rodigina's method consisted of heating the PbO in gold capsules at temperature ' $T^{\circ}K$ ' and then dropping these capsules

TABLE II.

ΔH_{298}^T VERSUS TEMPERATURE FOR PURE PbO (YELLOW)

PbO Solid		PbO Liquid	
Temperature in °K.	ΔH_{298}^T in Kcals/mole	Temperature in °K.	ΔH_{298}^T in Kcals/mole
973	8.344	1172	17.778
	8.569		18.080
	8.460		17.567
	8.511		17.395
			17.706
1023	9.282	1221	18.050
	9.004		17.963
	9.298		18.511
	8.704		18.360
	8.719		18.714
			18.409
			17.768
1073	9.951	1267	17.921
	10.085		17.754
	10.390		18.301
	9.997		18.288
1100	10.068		18.117
	10.350		18.676
	10.486		
	10.550		

Fig. 21 ΔH_{298}^T vs. $T^\circ K$ for PbO (yellow)



into a room temperature calorimeter. The enthalpies were determined by the method of mixtures. The upper temperature limit in Rodigina's experiment is the melting point of the gold capsules, and so the liquidus results obtained were over a very limited temperature range.

The liquidus results obtained by Rodigina etc are within the experimental error of this study, although the consistently lower values obtained by Rodigina can be perhaps explained in terms of the actual stoichiometry of the liquid PbO. Fig 33 given in Chapter II is the phase diagram for Pb-O given by Hansen (52). The difference in stoichiometry of the PbO between the two experiments, arises from the fact that Rodigina held the PbO in an Argon atmosphere to one third atmosphere pressure, and in this study the PbO is held in an atmosphere containing excess oxygen. From the phase diagram the difference in stoichiometry is not very great, but is significant, being of the order of one weight per cent oxygen.

The results for the Latent Heat of fusion of PbO (yellow) 6.37 ± 0.43 Kcals / mole from this study and 6.13 ± 0.1 Kcals / mole from Rodigina are in excellent agreement within the experimental error. From the E.M.F. technique described in Chapter 4, by extrapolation of the solidus and liquidus free energy curves to absolute zero, the

Latent Heat of fusion of PbO was found to be 7 Kcals / mole, ± 1 Kcal / mole would be a reasonable error limit as the result depends on the extrapolation of results measured at approximately 1000°K to 0°K. This is in good agreement with the calorimetrically obtained values. Hofer (53) has recently measured the heat of fusion of PbO and found it to be 3046 cal / mole. This value compared well with the phase diagram calculation of Kelley (54) which produced a value of 2800 cal / mole but is of the order of a half lower than the value found in this study and by Rodigina. Hofer's experiment however, involves changing the calorimeter temperature as part of the experiment through the melting point of PbO, which is an inaccurate procedure, but also the melting point of PbO is very sensitive to its actual stoichiometry which is an important factor in Hofer's experiment, but is excluded in the present study.

Chapter 8.

CALORIMETRIC STUDIES OF $n \text{ PbO} \cdot \text{P}_2\text{O}_5$ MELTS.

1. Introduction.

In the system $\text{PbO} \cdot \text{P}_2\text{O}_5$, it is not feasible to measure heats across the whole composition range, because of the physical and chemical nature of the compound P_2O_5 in its pure state. The phase diagram for $n \text{ PbO} \cdot \text{P}_2\text{O}_5$ is given in Fig 22 .

An intermediate compound of composition $N \text{ PbO} = 0.5$, i.e. $\text{PbO} \cdot \text{P}_2\text{O}_5$ was used as the reference for this experiment. The object of the experiment is to determine the heats of mixing for this system, and this was done by measuring the partial heats of PbO ($\Delta \bar{H}_{\text{PbO}}$) between $N \text{ PbO} = 1$ to $N \text{ PbO} = 0.5$.

Using a Gibbs Duhem type integration, it is possible to determine $\Delta \bar{H}_{\text{P}_2\text{O}_5}$ (the partial heats of P_2O_5) using $\Delta \bar{H}_{\text{P}_2\text{O}_5} = - \int_{N_2=1}^{N_2=N} \frac{N_1}{N_2} d \bar{H}_{\text{PbO}}$

Since the reference however is the equimolar compound $\text{PbO} \cdot \text{P}_2\text{O}_5$, in order to carry out the above integration, it is necessary to know the heat of formation of this compound from its constituent oxides.

The experiment is in two parts:-

Firstly the determination of the heat of formation (ΔH_{Form}) of $\text{PbO} \cdot \text{P}_2\text{O}_5$, and secondly the determination of the partial heats of PbO ($\Delta \bar{H}_{\text{PbO}}$) from pure PbO to $N \text{ PbO} = 0.5$.

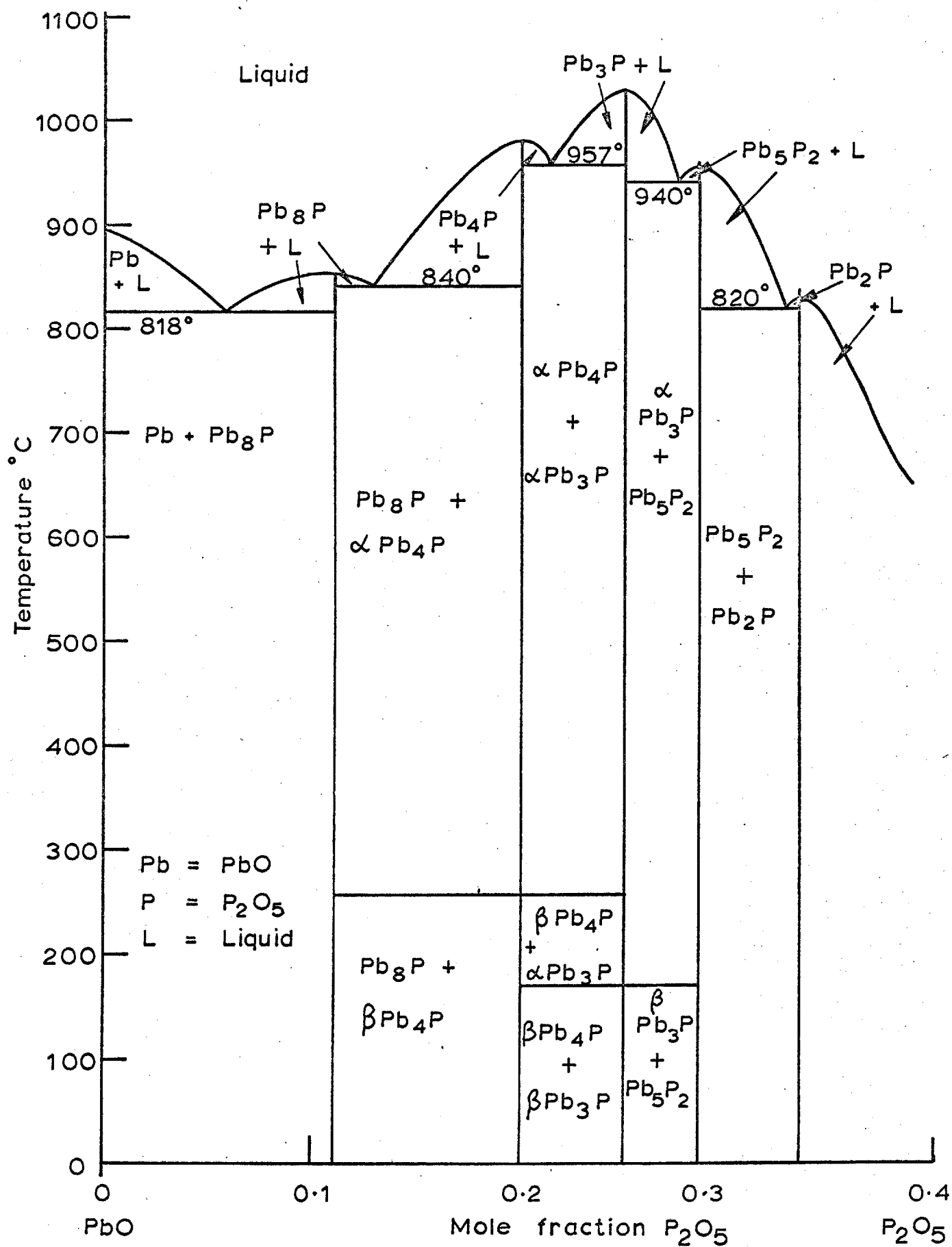
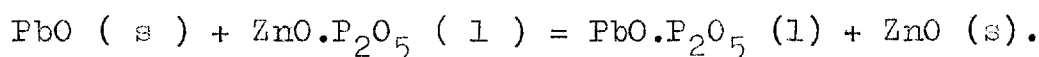


Fig. 22 $\text{PbO} \cdot \text{P}_2\text{O}_5$ PHASE DIAGRAM

2. The Determination of the Heat of Formation

of $\text{PbO.P}_2\text{O}_5$ (N PbO = 0.5).

The heat of formation of $\text{PbO.P}_2\text{O}_5$ was measured indirectly using the exchange reaction :-



The heat of formation was determined by the measurement of the heat of solution of each of the compounds involved in the exchange reaction, in a suitable solvent and straight application of Hess's law of constant heat summation, knowing the heats of formation of PbO , ZnO and $\text{ZnO.P}_2\text{O}_5$.

The solvent used was the melt $9\text{PbO} : 3\text{CdO} : 4\text{B}_2\text{O}_3$ recommended by Kleppa⁽⁴³⁾, and henceforth referred to as 'Kleppa' melt. This melt has a light yellowish appearance and is highly fluid at the temperature of this experiment.

The experiment was divided into two parts. Firstly, accurately weighed samples of each of the compounds were dropped from room temperature into empty platinum crucibles at 800°C in order to determine $\int_{298}^{1073} \text{Cp dT}$ in the case of PbO (s) and ZnO (s) and $\int_{298}^{1073} \text{Cp dT} + \Delta H_f$ in the case of $\text{PbO.P}_2\text{O}_5 \text{ (l)}$ and $\text{ZnO.P}_2\text{O}_5 \text{ (l)}$. The phosphates were dropped as glasses from room temperature. Secondly, accurately weighed samples of PbO and ZnO were dropped from room temperature into the 'Kleppa' melt in platinum crucibles at 800°C such that

2.5×10^{-3} moles of solute were dissolved in five grams of solvent in every case. Accurately weighed samples of $\text{PbO.P}_2\text{O}_5$ and $\text{ZnO.P}_2\text{O}_5$ were dropped from room temperature into the Kleppa melt containing 2.5×10^{-3} moles ZnO and PbO respectively to five grams of melt, also with the same dilution. The composition of the resulting melts after the two phosphate drops should therefore be identical. After quenching the resulting melts on an aluminium block after the experiments, complete homogeneity was observed.

Analysis of the Zinc and Lead phosphate melts.

The $\text{ZnO.P}_2\text{O}_5$ was analysed as $\text{Zn}(\text{C}_{10}\text{H}_6\text{O}_2\text{N})_2 \cdot \text{H}_2\text{O}$, zinc quinaldate as described by Vogel (84). The analysis found $\text{N ZnO} = 0.50$ as was expected.

The $\text{PbO.P}_2\text{O}_5$ analysis was carried out by the analytical services laboratory. The result $\text{N PbO} = 0.5$ was found as expected.

3. Results.

The results obtained are given in Table 12.

Let us consider the exchange reaction in terms of the model:-

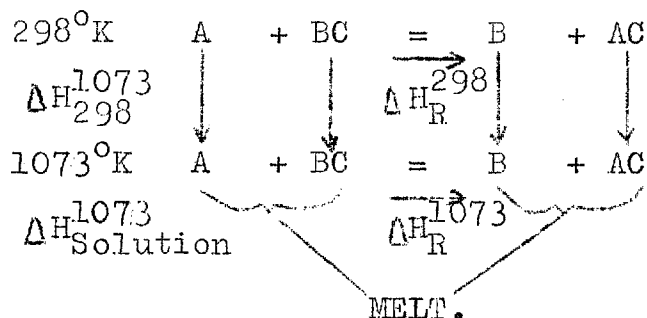


TABLE 12.



in Kleppa solvent at $800 \pm 1^\circ\text{C}$.

Sample	ΔH_{298}^T cals/gram into empty crucible.	$(\Delta H_{298}^T + \Delta H_{\text{Soln}})$ cals/gm. in Kleppa solvent.
PbO	+ 42.899 + 45.185 + 41.095 + 42.104 Mean + 42.821 $\pm$ 1.74	+ 61.47 + 61.60 Mean + 61.54 $\pm$ 0.092
ZnO.P ₂ O ₅	+167.97 +158.63 +166.38 +164.56 Mean +164.39 $\pm$ 4.08	- 96.40 - 83.97 - 70.82 - 86.67 Mean - 84.46 $\pm$ 10.54
PbO.P ₂ O ₅	+128.73 +122.77 +126.09 Mean +125.86 $\pm$ 2.99	- 20.16 - 18.59 Mean - 19.37 $\pm$ 1.10
ZnO	+ 82.96 + 80.03 + 84.22 Mean + 82.40 $\pm$ 2.15	+135.97 +138.84 Mean +137.41 $\pm$ 2.03

Where A = PbO.

B = ZnO.

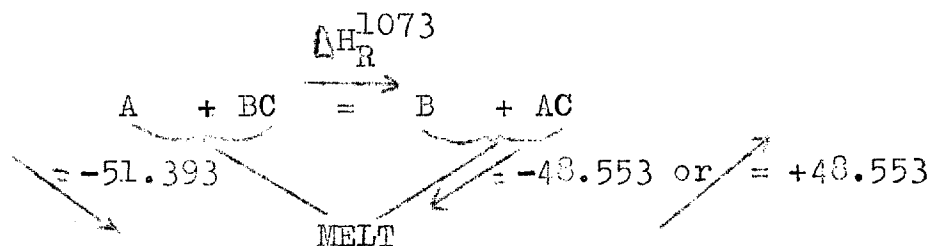
C = P₂O₅.

The first part of the experiment measured the values of ΔH_{298}^{1073} for each of the components in the exchange reaction, and the second part measured the values ($\Delta H_{298}^{1073} + \Delta H_{\text{Solution}}^{1073}$) in 'Kleppa' melt. The difference between the two gives the isothermal heats of solution at 1073°C. Since the experiment was designed such that the resulting melts after the solution of the phosphates (A + BC) and (B + AC) are identical, then by direct application of Hess's law, the heats of reaction at 1073°K and 298°K are known.

From the results:-

Sample.	$\Delta H_{298}^{1073} + \Delta H_{\text{Sol}}^{1073}$ in Kleppa melt. Kcals/ mole.	$\Delta H_{\text{Solution}}^{1073}$ in Kleppa melt. Kcals/ mole.
PbO	$+13.727 \pm 0.021$	$+4.178 \pm 0.388$
ZnO.P ₂ O ₅	-18.861 ± 2.354	-55.571 ± 2.523
	<u>-5.134</u>	<u>-51.393</u>
ZnO	-7.062 ± 0.402	-53.029 ± 1.161
PbO.P ₂ O ₅	$+11.181 \pm 0.165$	$+4.476 \pm 0.241$
	<u>+4.119</u>	<u>-48.553</u>

Thus at 1073°K



i.e. $\Delta H_R^{1073^\circ K} = -2.840 \pm 2.815$ Kcals.

Similarly at 298°K $\Delta H_R^{298} = -9.253 \pm 2.39$ Kcals.

Meadowcroft and Richardson (30) give the heat of formation of $Zn(PO_3)_2$ glass at 35°C as -45.400 ± 2 Kcals/mole. Assuming that the heat of formation at 25°C is the same value within experimental error then at 298°K:- $\Delta H_F^{298} PbO.P_2O_5 = -45.400 - 9.253 \pm 3.11$
 $= -54.65 \pm 3.11$ Kcals/mole.

For the second part of the experiment it is necessary to know $\Delta H_F^{1273} PbO.P_2O_5$ since the heats of solution were measured at 1273°K.

$$\Delta H_F^{1273} = \Delta H_F^{298} + \int_{298}^{1273} \Delta C_p dT$$

	Now $PbO + P_2O_5 = PbO.P_2O_5$	298°K
$\int_{298}^{1273} C_p dT$ in Kcals per mole.	$\begin{array}{c} 18.30 \\ \pm 0.9 \end{array}$ $PbO + P_2O_5$	$\begin{array}{c} 46.87 \\ \pm 1.0 \end{array}$ $= PbO.P_2O_5$
		1273°K

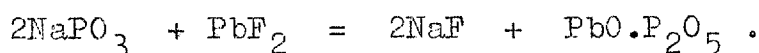
Therefore $\int_{298}^{1273} \Delta C_p dT = -12.26 \pm 2.4$ Kcals/ mole.

The value of $\int_{298}^{1273} C_p dT$ for P_2O_5 was obtained from JANAF (55) and $\Delta H_{Sublimation}$. The value given for PbO includes its heat of fusion.

Thus $\Delta H_{F_{ox}}^{1273} = -54.65 - 12.26 \pm 4.17$
 $= -66.91 \pm 4.17$ Kcals/mole oxides.

Thus $\Delta H_M^{1273} \text{ PbO.P}_2\text{O}_5 = -33.45 \pm 2 \text{ Kcals / mole oxides,}$
 since for the next part of the experiment it is
 necessary to consider one mole of mixture.

An alternative exchange reaction was considered:-



This however was found impracticable since
 PbF_2 has a high vapour pressure even at its melting
 point (2.7 millimetres Hg at its melting point) such
 that the vapour reacted with the silica tube to form
 lead fluorosilicate, which terminated the experiment.

4. Calorimetric determination of ΔH PbO in $\text{PbO.P}_2\text{O}_5$.

A partial heat is defined by the expression :-

$$\Delta H_A = \left(\frac{\partial \Delta H}{\partial N_A} \right)_{P,T,N_B}$$

This means that if one adds a small amount of
 one component (in this case PbO) to a relatively large
 amount of solvent of composition N_B ($\text{PbO.P}_2\text{O}_5 = 1$ to
 0.5) such that the resulting composition of the solvent
 is unchanged, then the heat evolved or absorbed by the
 addition per mole of component added (constant
 temperature and pressure) is the partial heat of that
 component at the composition N_B .

In a typical integral heat of mixing curve given
 in Fig 23 , the partial heat of component A at

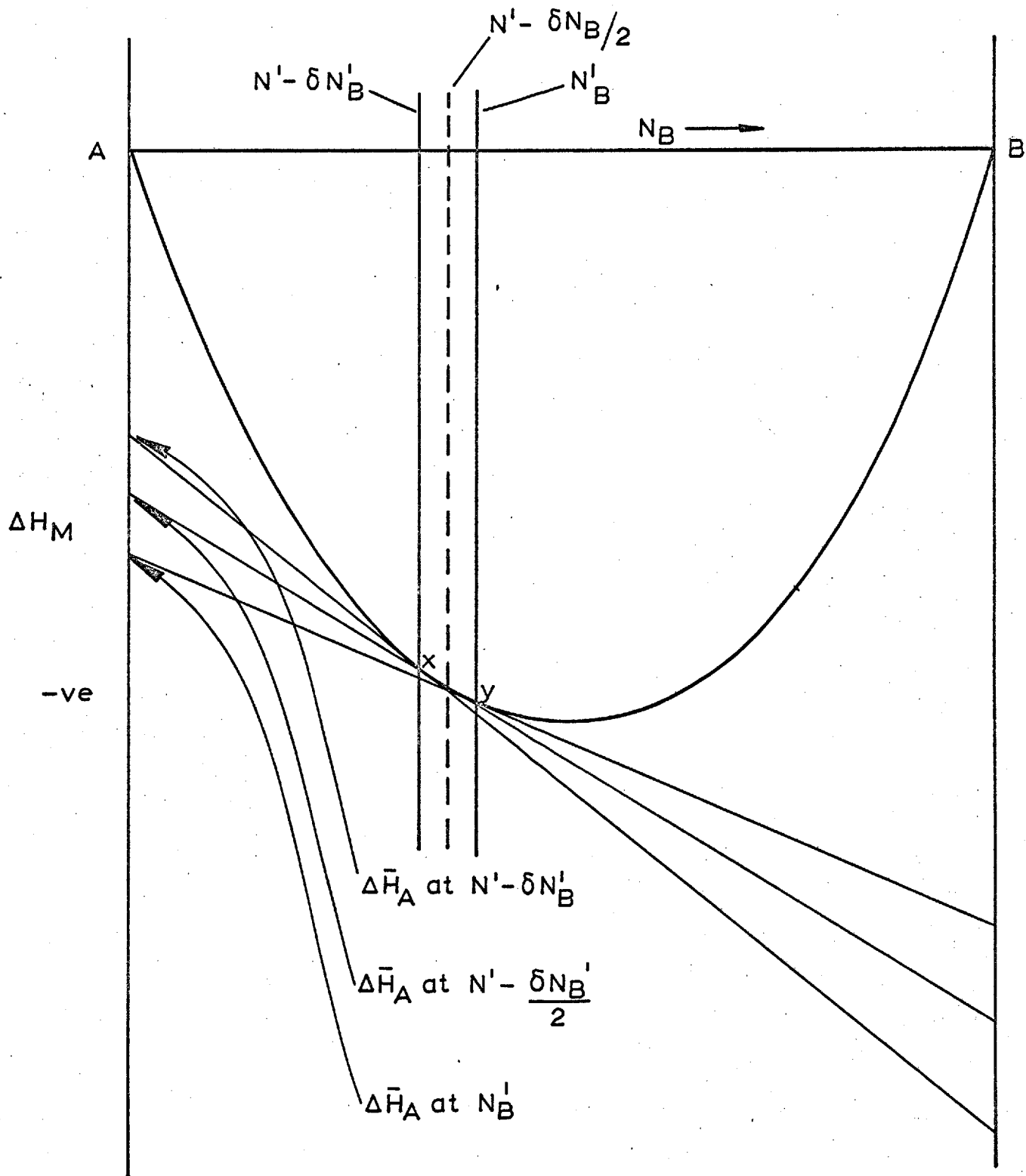


Fig. 23 TYPICAL ΔH_M CURVE .

composition N_B is given by the intercept with the A axis of the tangent to the curve at N_B i.e. ΔH_A as shown (56). If however, the result of the addition changes the composition of the melt by a small amount $-\delta B$ so that the resulting melt has composition $N_B - \delta B$, then the partial heat measured is an average of the partial heats at these two compositions. This represents the intercept with the A axis of the line passing through the ΔH_m curve at composition N_B and $N_B - \delta B$ (points x and y). As long as δB is small compared to one, then this value obtained is the partial heat of A of the composition $N (B - \frac{\delta B}{2})$.

5. Experimental:

Accurately weighed samples of PbO were first dropped from room temperature into platinum crucibles, containing the platinum nail beds at $1000^\circ\text{C} \pm 1^\circ\text{C}$ in the calorimeter. This produced the value of ΔH_{298}^{1273} PbO which includes the latent heat of fusion of PbO, by direct comparison with platinum drops immediately prior to the PbO drop.

Weighed samples of PbO were then dropped from room temperature into known weights of melt of known compositions, such that the composition of the melt before and after the drop was known. (Approx $\frac{1}{2}$ gram

samples were dropped into $\gg 5$ gram melt). The heats evolved were measured as square centimetres and compared with platinum drops immediately after or before each PbO drop, to determine the heat in calories. The melts were maintained at $1000^{\circ}\text{C} \pm 1^{\circ}\text{C}$ in the calorimeter for this experiment.

6. Results:

The results obtained are given in Table 13 and plotted in Fig 24 as ΔH_{PbO} versus N PbO where N PbO is taken as the average composition of the melt before and after the addition.

On the same plot, Sridhar's values of ΔH_{PbO} versus N PbO are shown, as well as the two results obtained earlier in Chapter 5(4) using an EMF technique.

Using the value of $\Delta H_{\text{M}}^{1273} \text{ PbO.P}_{205} = -33.45 \pm 2 \text{ Kcals/mole}$

and application of the Gibbs Duhem integration, then $\Delta H_{\text{P}_{205}}$ versus N PbO can be calculated and is shown in Fig 24 and Table 14

$$\text{Since } \Delta H_{\text{M}} = N_{\text{PbO}} \Delta H_{\text{PbO}} + N_{\text{P}_{205}} \Delta H_{\text{P}_{205}}$$

then ΔH_{M} can be determined and is shown in Fig 26

The heats of formation of crystalline and glass zinc, calcium, lithium and sodium phosphates at room temperature are shown in Fig 27 (30) with the inclusion of the integral heat of mixing of glass PbO.P_{205} at 1000°C from this study.

TABLE 13.

Partial Heats of PbO in a PbO.P₂O₅ Melts at 1000 $\pm$ 1°C.

Composition N PbO	$\Delta\bar{H}$ PbO in Kcals/mole.
0.515	-35.06
0.528	-35.60
0.554	-30.51
0.570	-28.80
0.578	-30.15
0.582	-30.27
0.607	-29.55
0.628	-25.37
0.641	-25.90
0.644	-25.98
0.672	-25.47
0.676	-22.37
0.727	-17.99
0.728	-16.03
0.840	- 3.13
0.843	- 3.07
0.850	- 0.67
0.859	- 0.90

Pure PbO $\Delta\bar{H}_{298}^{1273}$ = 18.30 $\pm$ 0.9 Kcals/mole.

TABLE 14.

Partial Heats of P_2O_5 in n PbO. P_2O_5 Melts obtained from Gibbs Duhem Integration, and hence integral heat of mixing for n PbO. P_2O_5 Melts.

Composition N PbO	$\Delta\bar{H}_{P_2O_5}$ in Kcals/mole	$\Delta\bar{H}_{PbO}$ in Kcals/mole	$\Delta H_m. \pm 2$ Kcals in Kcals/mole.
0.50	- 29.9	-37.0	-33.45
0.55	- 34.3	-33.2	-33.7 $\pm$ 0.2
0.60	- 40.2	-29.3	-33.7 $\pm$ 0.4
0.65	- 46.9	-24.8	-32.5 $\pm$ 0.4
0.70	- 56.1	-20.2	-31.0 $\pm$ 0.5
0.75	- 69.8	-14.8	-28.6 $\pm$ 0.45
0.80	- 90.0	- 9.2	-25.4 $\pm$ 0.8
0.85	-127.7	- 1.8	-20.7 $\pm$ 0.35
0.90	-139.7	- 0.2	-14.2 $\pm$ 0.3
1.0	-141.4	- 0	- 0

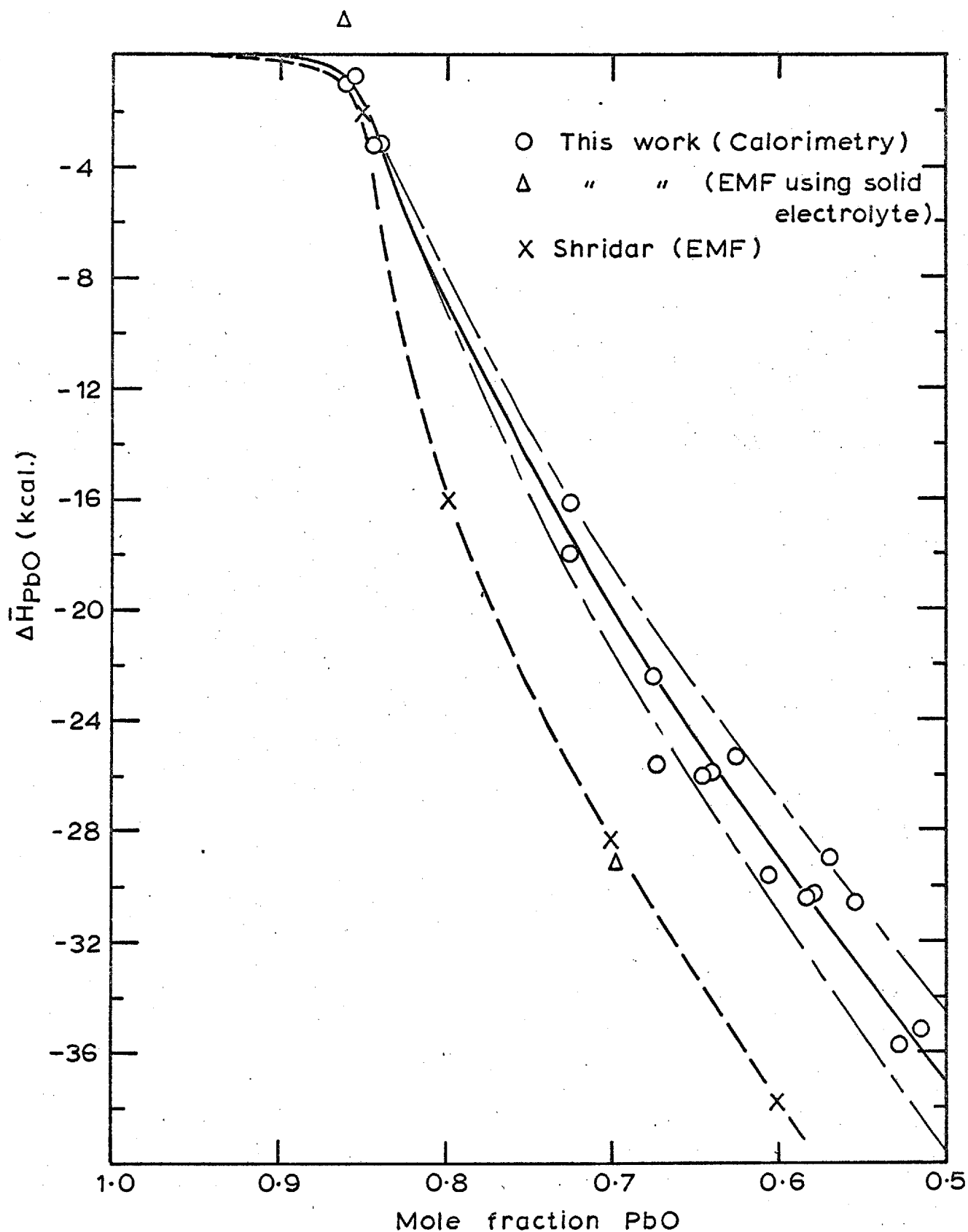


Fig.24 PARTIAL HEAT OF SOLUTION OF PbO IN PbO-P₂O₅ MELT.

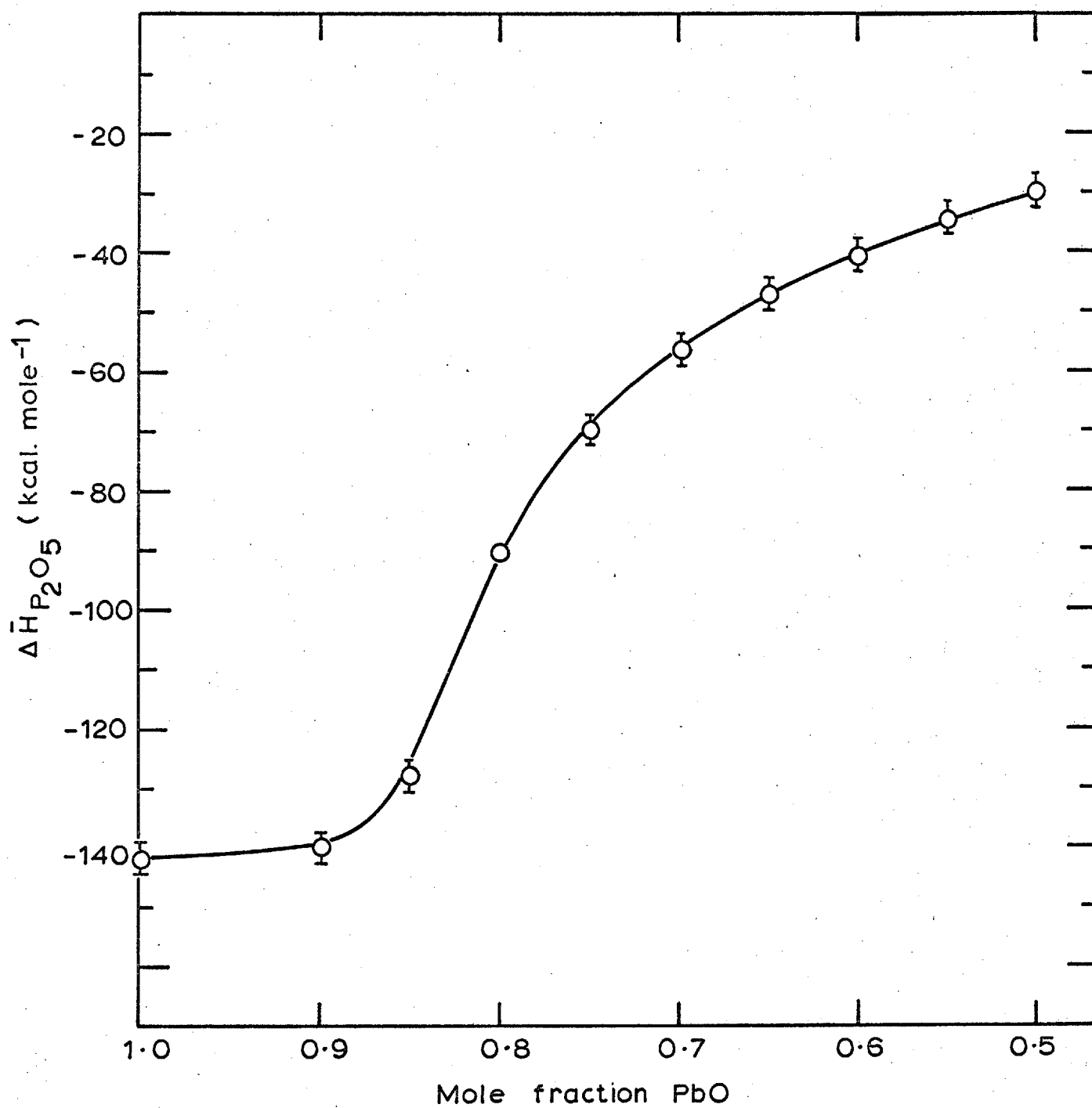


Fig.25 PARTIAL HEAT OF SOLUTION OF P_2O_5 IN $PbO-P_2O_5$

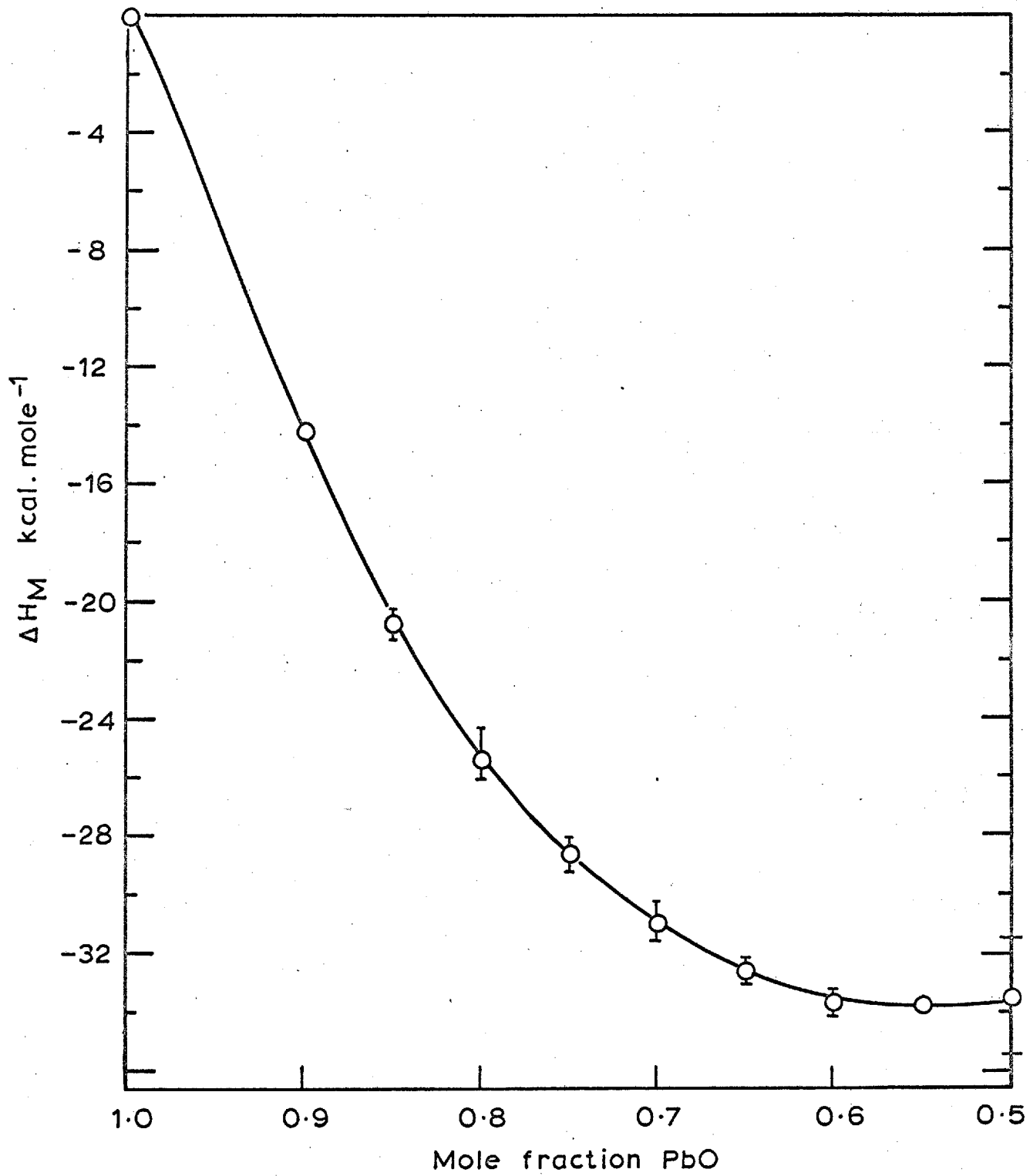


Fig.26 INTEGRAL HEAT OF MIXING OF PbO- $P_2O_5 \pm 2$ kcal.

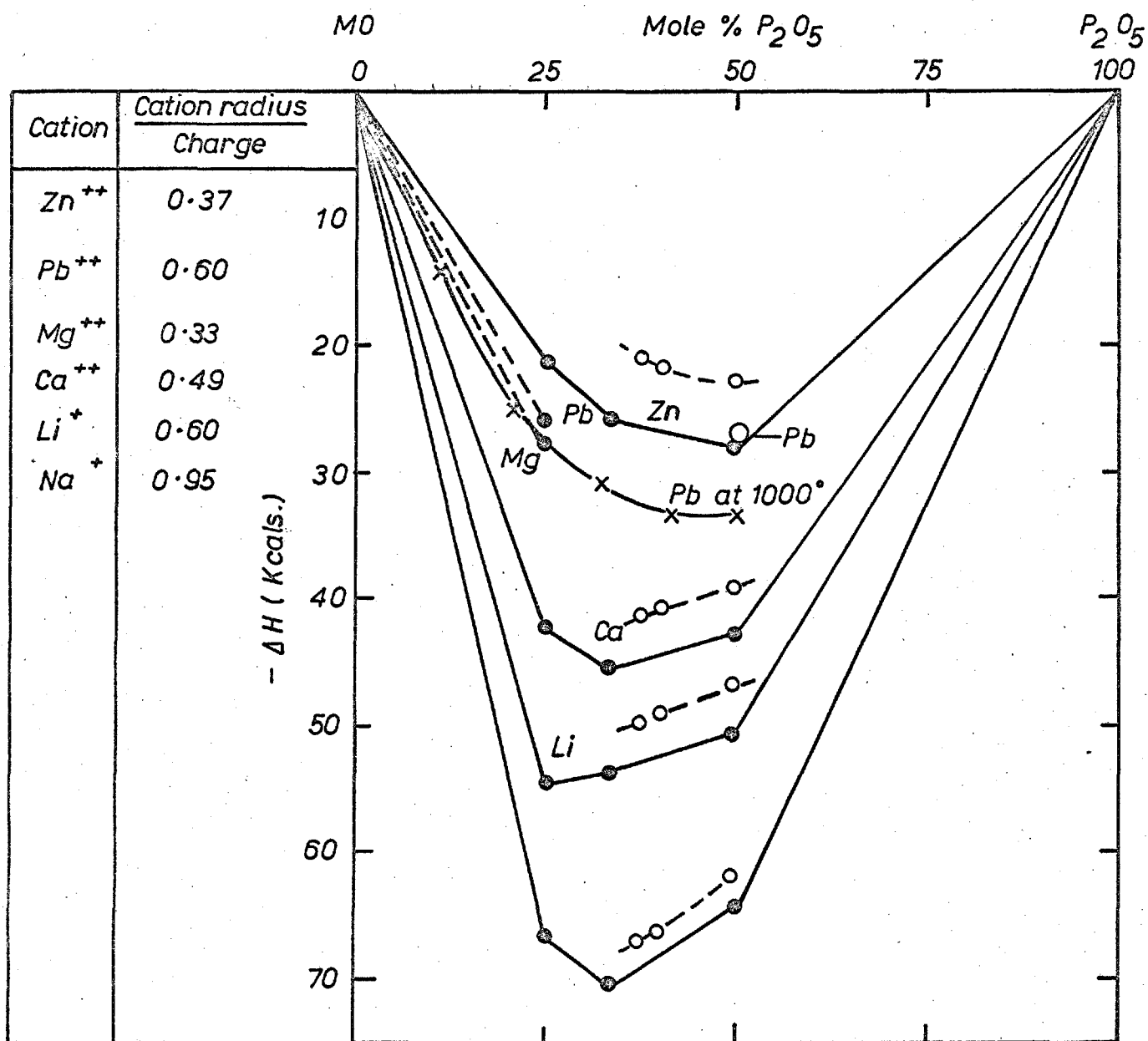


FIG. 27 HEAT OF FORMATION OF CRYSTALLINE PHOSPHATES ● & GLASSES ○ IN Kcals/mole OXIDE ($MO + P_2O_5$) AT 35°C AND HEAT OF FORMATION OF $PbO \cdot P_2O_5$ AT 1000°C

7. Discussion:

The shape of the partial heats of PbO obtained calorimetrically is in fair agreement with the partial heats found by Sridhar and Jeffes (57) and this author using an E M F technique.

It is observed that between mole fraction PbO of 0.9 and pure PbO, the partial heat is approximately zero.

The heat of formation of lead metaphosphate at 1000°C was found to be - 6 Kcals/mole oxide greater than the heat of formation of lead metaphosphate glass at room temperature. Meadowcroft and Richardson (30) give the heats of formation at 35°C of $\text{Zn}(\text{PO}_3)_2$ crystal and glass.

$\text{Zn}(\text{PO}_3)_2$ Crystal $\Delta H = - 56.000$ Kcals/mole oxide.

Glass $\Delta H = - 45.40$ Kcals/mole oxide.

Thus the heat of formation of $\text{Zn}(\text{PO}_3)_2$ crystal at room temperature is -10.6 Kcals/mole oxides then the heat of formation of the glass at the same temperature.

From these observations it might be expected that the heat of formation of lead metaphosphate glass at 1000°C should be approximately equal to the heat of formation of lead metaphosphate crystal at 35°C.

Fig 27 shows the heat of formation of crystalline and glassy phosphates at 35°C and the

heat of formation of $\text{PbO} \cdot \text{P}_2\text{O}_5$ at 1000°C . It can be seen that the heat of formation of lead orthophosphate crystal at 35°C as determined by Pitzer (58) is in excellent agreement with the heat of formation of lead orthophosphate at 1000°C determined in this study, within the approximation.

The errors in the determination of the integral heat of mixing of $\text{PbO} - \text{P}_2\text{O}_5$ are small compared with the error associated with the heat of formation of lead metaphosphate as determined by the exchange reaction. Thus the error in the integral heat curve is correct to ± 2 Kcals/mole.

CHAPTER 9.

CALORIMETRY ON $(\text{Na PO}_3)_n$.

1. Materials:

The Kurrol salt, Maddrell salt (insoluble sodium trimetaphosphate) and the sodium trimetaphosphate were supplied by Albright and Wilson.

Emission spectroscopy showed traces of Al, Au, Be, Bi, Cu, Te, Hg, K, Mn, Mo, Pb, Nb, Pt, Si, Sn, Sr, Ta. In addition Mg of the order $>$ traces in all, and especially in the Kurrol salt. Pb is of the order $>$ traces in the Maddrell salt. Co traces were found in the Kurrol salt only.

The quantitative analysis for phosphorus yielded results of percentage phosphorus:- Maddrell salt 30.60%, sodium trimetaphosphate 30.25%, Kurrol salt 30.65%. All $\pm$ 0.05%. Theoretical percentage phosphorus = 30.38%.

A Debye Scherrer Xray powder pattern was taken of each sample. With reference to the Fink Xray powder pattern index, the 'd' spacings for sodium trimetaphosphate and the Kurrol salt were in good agreement with the pattern given for $(\text{NaPO}_3)_3$, and that of the Maddrell salt with the literature values for Maddrell salt.

It was found that for Maddrell salt 6.5 (+1)% by weight dissolved in three hours in distilled water,

and for Kurrol salt $14(\pm 1)\%$ dissolved in two and a half hours in distilled water, all at room temperature. The anhydrous sodium trimetaphosphate was very soluble in distilled water at room temperature.

(59)

Van Wazer reports that Form II Maddrell salt dissolves at a rate of $1.8 \times 10^{-2}\%$ per hour and Form III more rapidly at 0.34% per hour. The value 6.5% in three hours approximately 2% per hour suggests that the Maddrell salt used contained up to 2% of sodium trimetaphosphate. Van Wazer reports that Kurrol salt dissolves slowly in water at room temperature which was observed in this study.

2. Method of preparation of the sodium metaphosphates.

$(\text{NaPO}_3)_3$ crystalline sodium trimetaphosphate is prepared by heating Analar grade $\text{NaH}_2\text{PO}_4 \cdot 2 \text{H}_2\text{O}$ at 150°C and then at 550°C for one week. Less than 0.5% phosphorus is present as ortho and pyrophosphate.

The preparation of the sodium Kurrol and sodium Maddrell salts is given by Van Wazer (59). The Kurrol salt is usually made by tempering a sodium phosphate melt between $550 - 600^\circ\text{C}$ for about two hours and then rapidly quenching. A small amount of Maddrell

salt can be used to promote crystallization.

The Maddrell salt is usually made by dehydrating the monosodium orthophosphate below 500°C .

NaPO_3 form III is formed by dehydrating at about $260 - 270^{\circ}\text{C}$ and NaPO_3 form II by dehydrating at about $400 - 425^{\circ}\text{C}$.

The phase diagram for $n\text{Na}_2\text{O} - \text{P}_2\text{O}_5$ is given in Fig 28.

The anhydrous sodium trimetaphosphate and the Maddrell salt were prepared for the calorimetric experiment as spheres by the method described in Chapter 6 (2b). The Kurrol salt however, was of an asbestos nature and pieces of suitable size 0.4-0.5 millimetre cube were selected for this experiment.

3. Experimental Procedures

The samples of sodium phosphate were dropped from room temperature into platinum crucibles, containing only the nail beds, at 800°C in the calorimeter as described previously. Each sodium phosphate drop was followed by a platinum drop for calibration purposes.

Forty five minutes in every experiment was allowed to elapse between each drop, to ensure complete thermal equilibrium in the calorimeter.

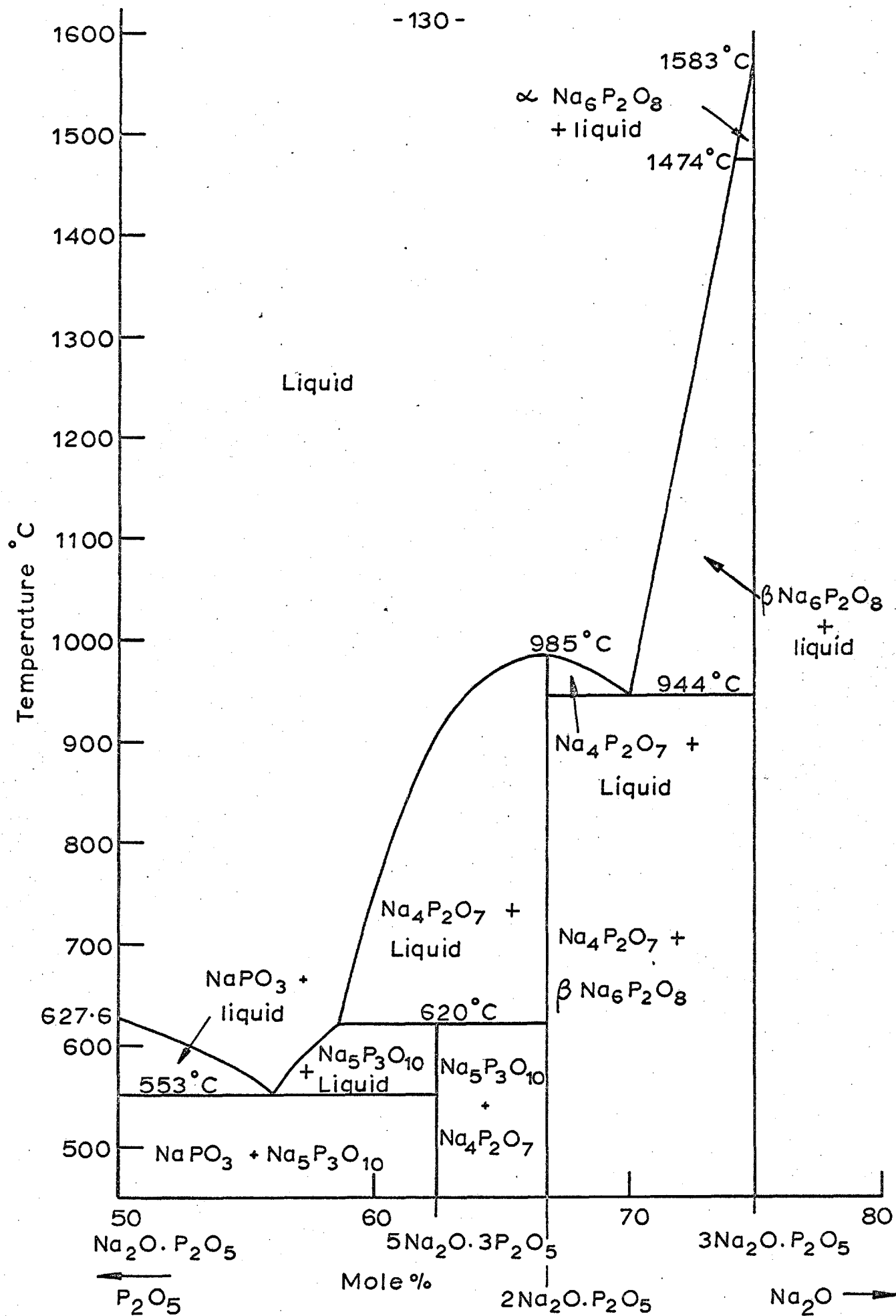


Fig. 28

PHASE DIAGRAM

$\text{Na}_2\text{O} \cdot \text{P}_2\text{O}_5 - 3\text{Na}_2\text{O} \cdot \text{P}_2\text{O}_5$

4. Results:

Table 15.

The following results were obtained from dropping the sodium metaphosphate samples from room temperature into liquid NaPO_3 at 800°C .

Sample	$\Delta H_{\text{RT}}^{800^\circ\text{C}} + \Delta H$ Transformation in cals/gram.
Anhydrous sodium trimetaphosphate	$\left. \begin{array}{l} 237.5 \\ 245.9 \\ 246.0 \end{array} \right\} 243.1 \pm 3.2 \text{ cals/gram.}$
Maddrell Salt	$\left. \begin{array}{l} 295.4 \\ 295.7 \\ 288.8 \end{array} \right\} 293.3 \pm 3.2 \text{ cals/gram.}$
Kurrol Salt	$\left. \begin{array}{l} 271.1 \\ 271.2 \\ 274.4 \end{array} \right\} 272.2 \pm 1.5 \text{ cals/gram.}$

Assuming that $\Delta H_{\text{RT}}^{800^\circ\text{C}}$ is the same for the three forms of sodium metaphosphate, then it follows that:-

1. ΔH Anhydrous $(\text{NaPO}_3)_3 \longrightarrow$ Maddrell Salt.
 $= - 50.2 \pm 4.53 \text{ Cals/ gram.}$
 $= - 5.13 \pm 0.46 \text{ Kcals/ NaPO}_3.$
2. ΔH Anhydrous $(\text{NaPO}_3)_3 \longrightarrow$ Kurrol Salt.
 $= - 29.1 \pm 3.53 \text{ Cals/ gram.}$
 $= - 2.96 \pm 0.36 \text{ Kcals/ NaPO}_3.$

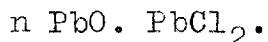
3. ΔH Kurrol Salt $\longrightarrow$ Maddrell Salt.

$$= - 21.1 \pm 3.53 \text{Cals/ gram.}$$

$$= - 2.16 \pm 0.36 \text{Kcals/ NaPO}_3.$$

Chapter 10.

VAPOUR ENTRAINMENT IN THE SYSTEM



1. Apparatus:

The vapour entrainment technique involves passing a known volume of inert carrier gas over a combustion boat containing the melt under examination, in such a way that the gas becomes saturated with the vapour above the melt. The gas laws can then be applied, and the vapour pressure above the melt can be determined.

A longitudinal section of the apparatus is given is Fig 29.

The flushing gas tube was ground at both ends to a B 29 cone, and one end of the reaction tube was ground to a B 19 cone. The flushing gas tube was water cooled at both ends in order to avoid excessive over-heating of the glass sockets, which had to be removed after each experiment. Also the water cooling acted as a condensor in the output end of the tube, and the majority of the PbCl₂ condensed in this section.

The apparatus is so designed that the initial source of argon is channelled along two different routes, through a differential manometer, after the

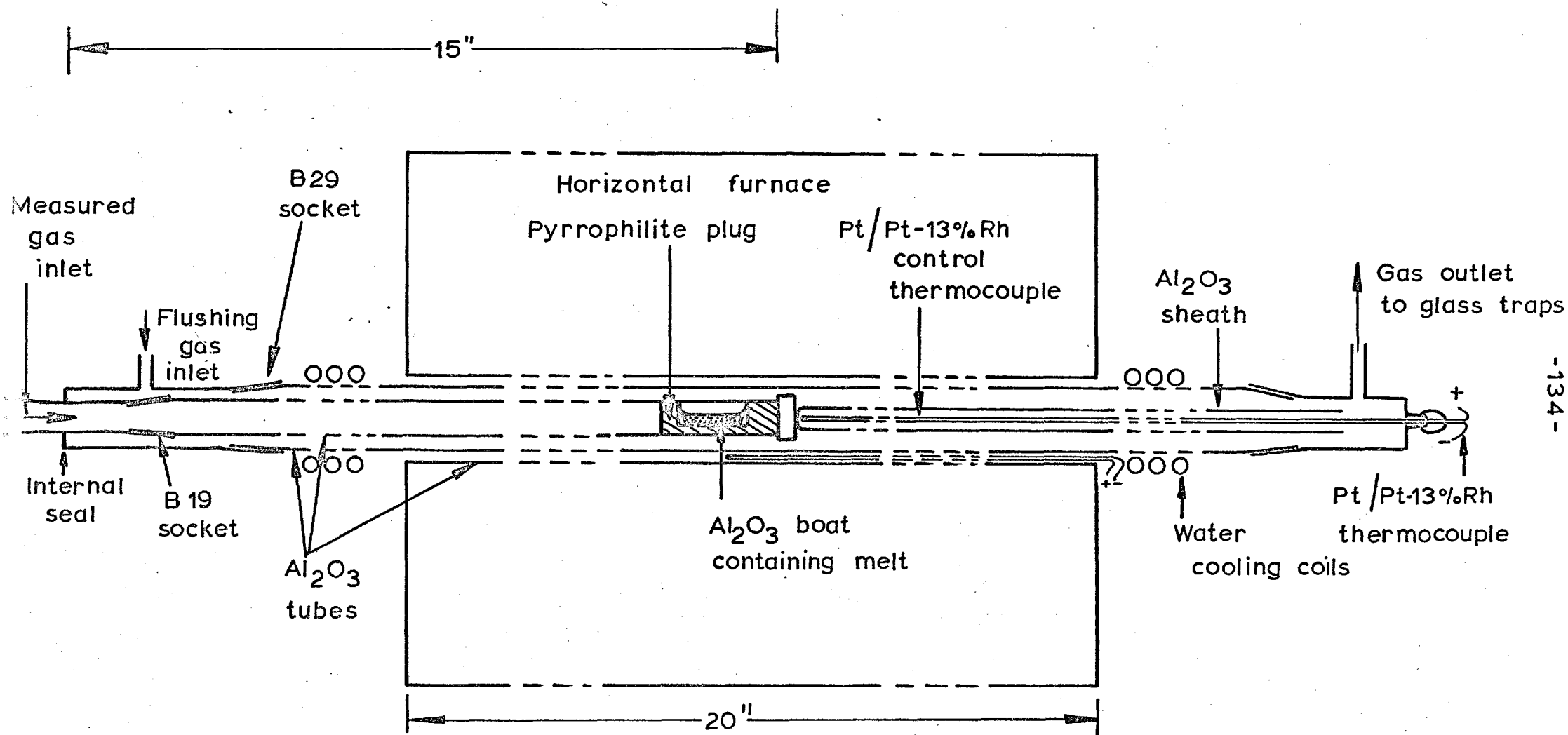


Fig. 29 APPARATUS FOR VAPOUR ENTRAINMENT

purification train (outlined in the previous section). One route then passes through a water displacement volume flow meter, followed by two drying towers containing silica gel and magnesium perchlorate and then into the reaction tube. The other route passes through a flow rate meter and then into the tube containing the reaction tube. The second route is used solely as a flushing gas, such that the vapour carried through the reaction plug passes to the outlet end of the furnace. The differential manometer ensures that the pressure of the flushing gas is less than that of the measured gas flow route.

A two inch long pyrophyllite plug was designed to contain the alumina boats which in turn contain the melts under study. The alumina boats were thirty millimetres long and about six millimetres deep and were a fairly tight fit in the plug, which was in turn a tight fit in the alumina reaction tube. A two millimeter diameter hole was drilled from both ends of the plug into the saturation compartment, for the passage of the gas through the plug.

The gas outlet consisted of a series of kidney shaped glass ware immersed in cold water to ensure that no lead chloride could contaminate the atmosphere.

The furnace was controlled with a 'Transtat'

controller and a platinum/platinum - 13% rhodium thermocouple. The temperature of the plug was also measured with a similar thermocouple.

2. Materials:

Extra pure lead chloride and A.R. yellow lead oxide were used for making the melts $n\text{PbO} \cdot \text{PbCl}_2$ which were contained in recrystallized alumina boats during the experiment.

A plug designed for saturating the carrier gas with the vapour was made of pyrophyllite.

The furnace tube, the reaction tube and the tube for carrying the flushing gas through the furnace were all made from recrystallized alumina tubes.

The furnace tube was doubly wound with Kanthal A. I. wire, and lagged with alumina powder.

The gas inlet device was made from one B 29 and two B19 pyrex sockets.

Pure argon was used as the carrier gas after being passed through a gas train consisting of towers of silica gel, sofnolite, magnesium perchlorate and one copper and one titanium furnace.

3. Experimental:

The melts to be used for this study were firstly prepared by melting together the relevant quantities of PbO and PbCl_2 in a platinum crucible, and then quenching these melts on an aluminium block. The

melts were then ground up and stored in a dessicator ready for use.

Before each experiment the melt to be studied was premelted in an accurately weighed recrystallized alumina boat, and after cooling in a dessicator was weighed to ± 0.0001 grams on a semi micro balance.

The alumina boat was then placed in the plug, which in turn was pushed into the reaction tube, which was held outside the furnace. The flow through the reaction tube was started and the volume registered on the meter was noted. After passing the argon through the reaction tube for three minutes, the tube was then introduced into the furnace and the flushing gas was connected. After thirty minutes the volume registered on the meter was noted as well as the temperature of the flow meter and the plug. After this time the whole length of the plug was at the recorded temperature ($\pm 1^{\circ}\text{C}$). After a further time 't' minutes the volume was again recorded and the reaction tube was removed from the furnace. After a further ten minutes the volume was again recorded. Also for each composition the above procedure was adopted, but after the first thirty minutes the reaction tube was removed from the furnace. The latter procedure is referred to as the zero-time experiment.

After every experiment the alumina boat and contents were accurately reweighed. Following this procedure the weight loss of the contents at the measured temperature as a result of the flow of a known volume of gas can be determined.

The first part of the experiment was to determine the most suitable flow rate for the entraining gas, such that the gas becomes saturated with the vapour at the temperature in question. A flow rate of six to eight millimeters per minute was found to be suitable see Fig 30 and Chapter 2 (2). The results plotted are from zero-time experiments.

Using this range of flow rate the weight loss for pure lead oxide at 630°C was found to be negligible, which was as expected from vapour pressure considerations. The weight loss in the system nPbO.PbCl_2 is then directly attributed to the loss of PbCl_2 to the transporting gas. The vapour pressure above pure PbCl_2 and nPbO.PbCl_2 melts in the composition range $\text{NPbCl}_2 = 0.6$ to 1.0 were measured at 630°C .

The nPbO.PbCl_2 melts were analyzed for chlorine by the method described in Chapter 4 (6). The results of the analysis showed the compositions to be within 0.5% of the intended compositions.

In the initial experiments a graphite plug was

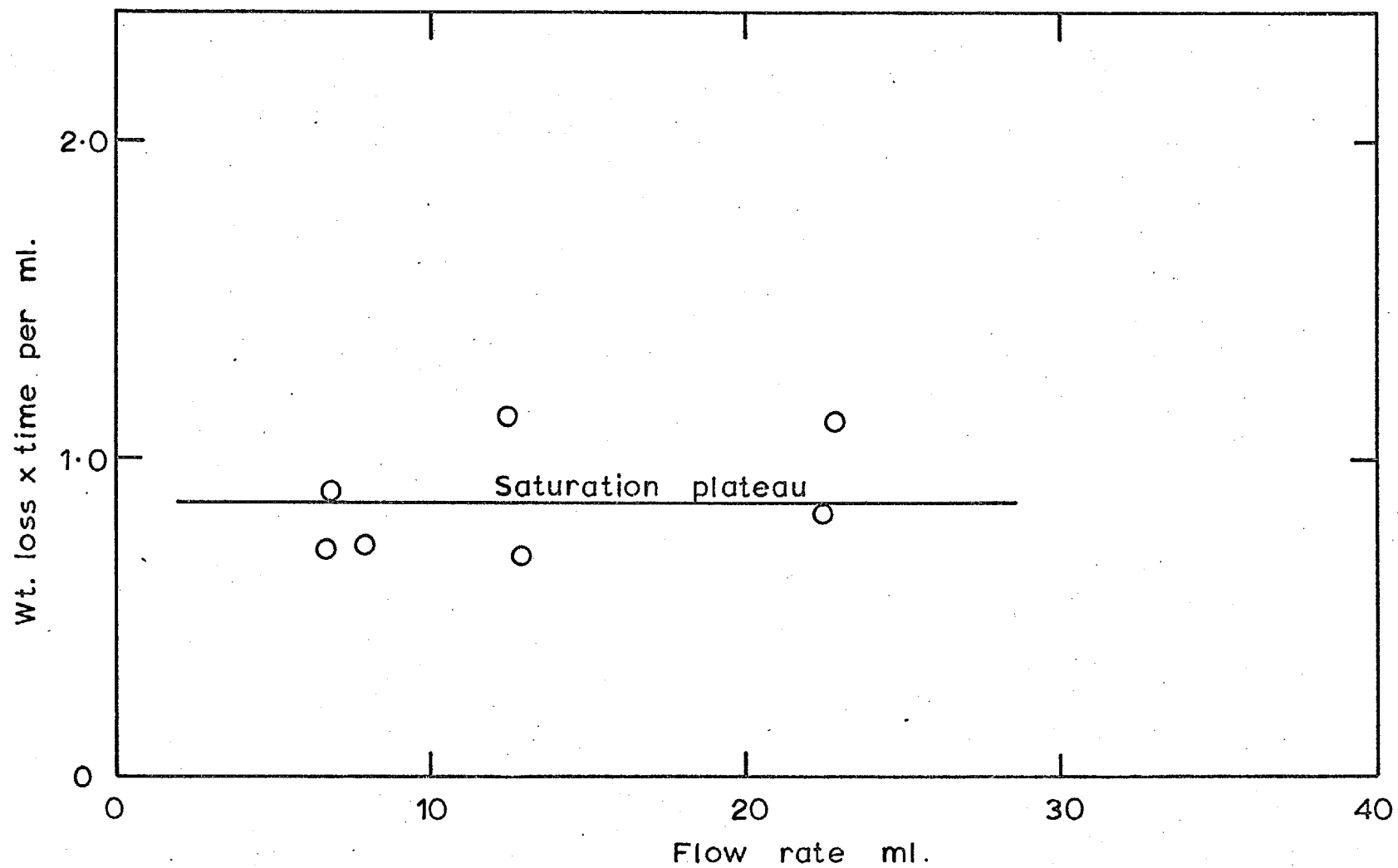


Fig. 30. WT. LOSS IN ONE MINUTE PER MILLILITRE vs FLOWRATE .

used, but this was found to be unsatisfactory because of the adsorption of hydrogen in graphite at room temperature, and at the temperature of the experiment the hydrogen reduced some of the lead oxide in the alumina boat to lead. Also the volume of hydrogen present was significantly high such that the total volume of gas passing over the alumina boat was higher than the metered value.

4. Results:

The total dry volume of gas that has passed over the sample during the experiment must be calculated from the wet volume measured on the volume flowmeter; knowing the saturated vapour pressure of water at the temperature of the meter. This volume is then corrected to N.T.P.

$$V_{\text{Dry}} = V_{\text{Wet}} \times \frac{273}{T_{\text{Water Meter}}} \times \left(\frac{\text{Atmos} - \text{S.V.P.}_{\text{H}_2\text{O}}}{760} \right)$$

in mls.

The volume of Lead Chloride carried away by the gas is also determined and corrected to N.T.P. , symbol V_1 . If the gas is saturated with the vapour, then the gas laws can be applied, $PV = \text{Constant}$.

$$\text{Thus } P_{\text{PbCl}_2} \text{ in atmospheres} = \frac{V_1}{V_1 + V_{\text{Dry}}}$$

The results obtained in this study are given in Table 16 as the partial pressure of PbCl_2 expressed in millimetres of mercury.

Now activity is defined as the ratio of fugacities

of the component in the melt to that of the pure component, which is taken as the ratio of partial pressures in the melt to that of the pure component.

$$\begin{aligned}
 a_{\text{PbCl}_2} &= \frac{f_{\text{PbCl}_2 \text{ in } n \text{ PbO.PbCl}_2}}{f_{\text{Pure PbCl}_2}} && \text{at } T^\circ\text{K} \\
 &= \frac{p_{\text{PbCl}_2 \text{ in } m \text{ PbO.PbCl}_2}}{p_{\text{Pure PbCl}_2}} && \text{at } T^\circ\text{K}.
 \end{aligned}$$

The activities of PbCl_2 are given in Table 17, and shown in Figure 31, which is presented in chapter 11.

The melting point of PbCl_2 is given in 'JANAF' as 768°K and the heat of fusion as 5.7 Kcals/ mole. From the phase diagram for PbO.PbCl_2 given in Fig 32 the activity of PbCl_2 at mole fractions $N_{\text{PbO}} = 0.1$ and $N_{\text{PbO}} = 0.2$ was calculated and is included in . Figure 31 and Table 17.

If one extrapolates the activity-composition plot for PbCl_2 shown in Figure 31 to composition 0.5 N_{PbO} , then a Gibbs Duhem integration can be carried to determine the activity of PbO between pure PbCl_2 and the equimolar composition, using the value for the activity of PbO at $N_{\text{PbO}} = 0.5$ and at 629°C (with reference to liquid PbO standard state) determined from the E M F measurements.

Similarly a Gibbs Duhem integration can be carried out to determine the activity of PbCl_2 between pure PbO and the equimolar composition from the activity-

TABLE 16.

Partial pressure of lead chloride above
 $n\text{PbO} \cdot \text{PbCl}_2$ melts.

Pure PbCl_2	P mm Hg	
	9.243	
	7.003	Mean = 8.151 mm Hg
	9.235	Standard Deviation = ± 1.069
	7.216	= $\pm 13.11\%$
	8.057	
$\text{NPbO} = 0.1$	P mm Hg	
	7.35	Mean = 6.955 mm Hg
	6.56	Standard Deviation = ± 0.56 mm Hg
		= $\pm 8.052\%$
$\text{NPbO} = 0.2$	P mm Hg	
	6.565	
	5.009	
	6.127	Mean = 6.123 mm Hg
	5.875	Standard Deviation = ± 0.765 mm Hg
	7.04	= $\pm 12.49\%$
$\text{NPbO} = 0.3$	P mm Hg	
	4.593	
	4.193	
	3.094	
	3.894	Mean = 3.854 mm Hg
	3.425	Standard Deviation = ± 0.535 mm Hg
	3.928	= $\pm 13.88\%$

TABLE 16. continued.

NPbO = 0.4		P mm Hg	
	3.105	Mean = 2.929 mm Hg	
	2.616	Standard Deviation = ± 0.272 mm Hg	
	3.066	= $\pm 9.29\%$	

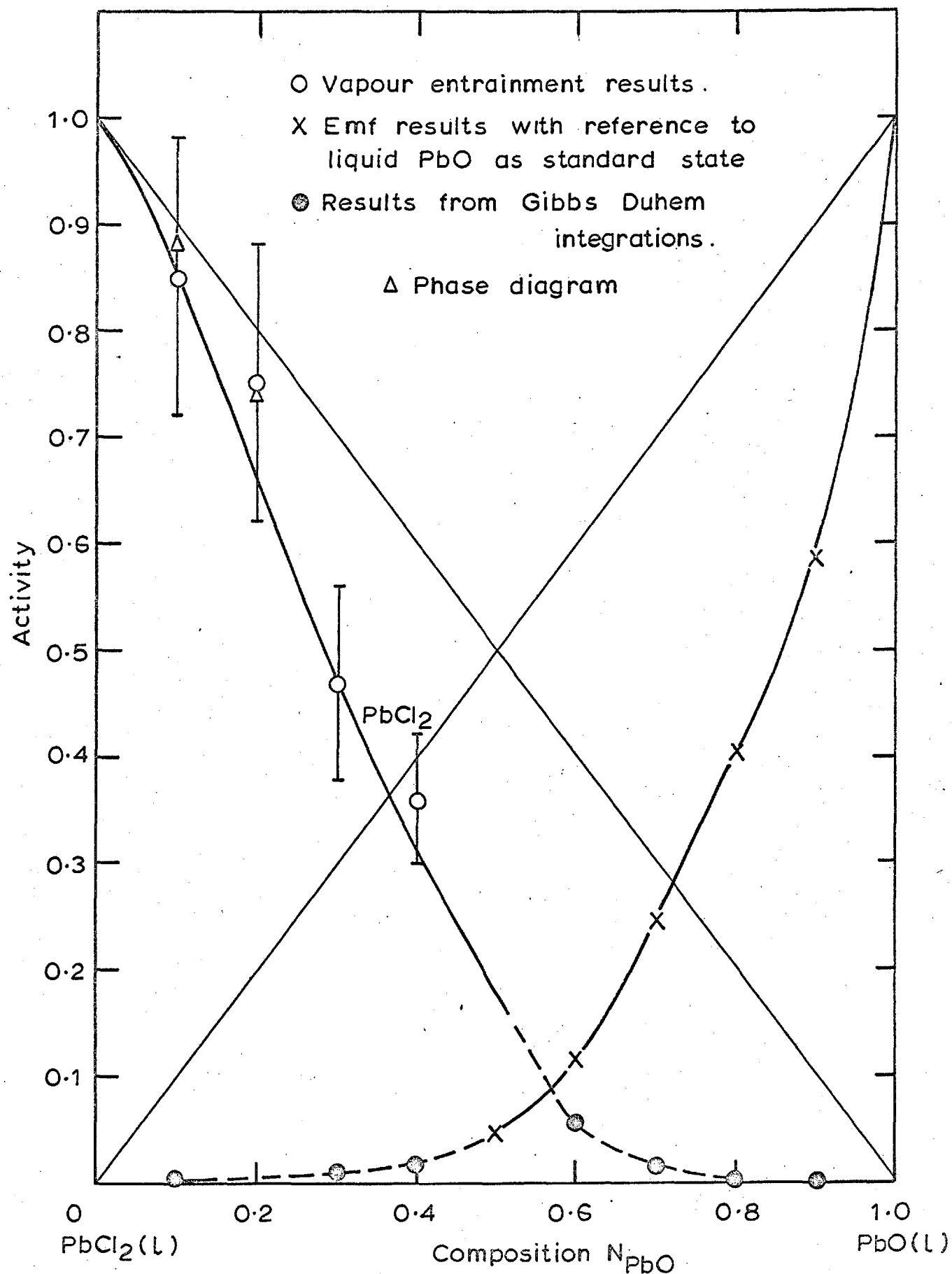


Fig. 31 ACTIVITY OF PbCl₂ & PbO AT 629 °C IN PbO.PbCl₂ MELTS

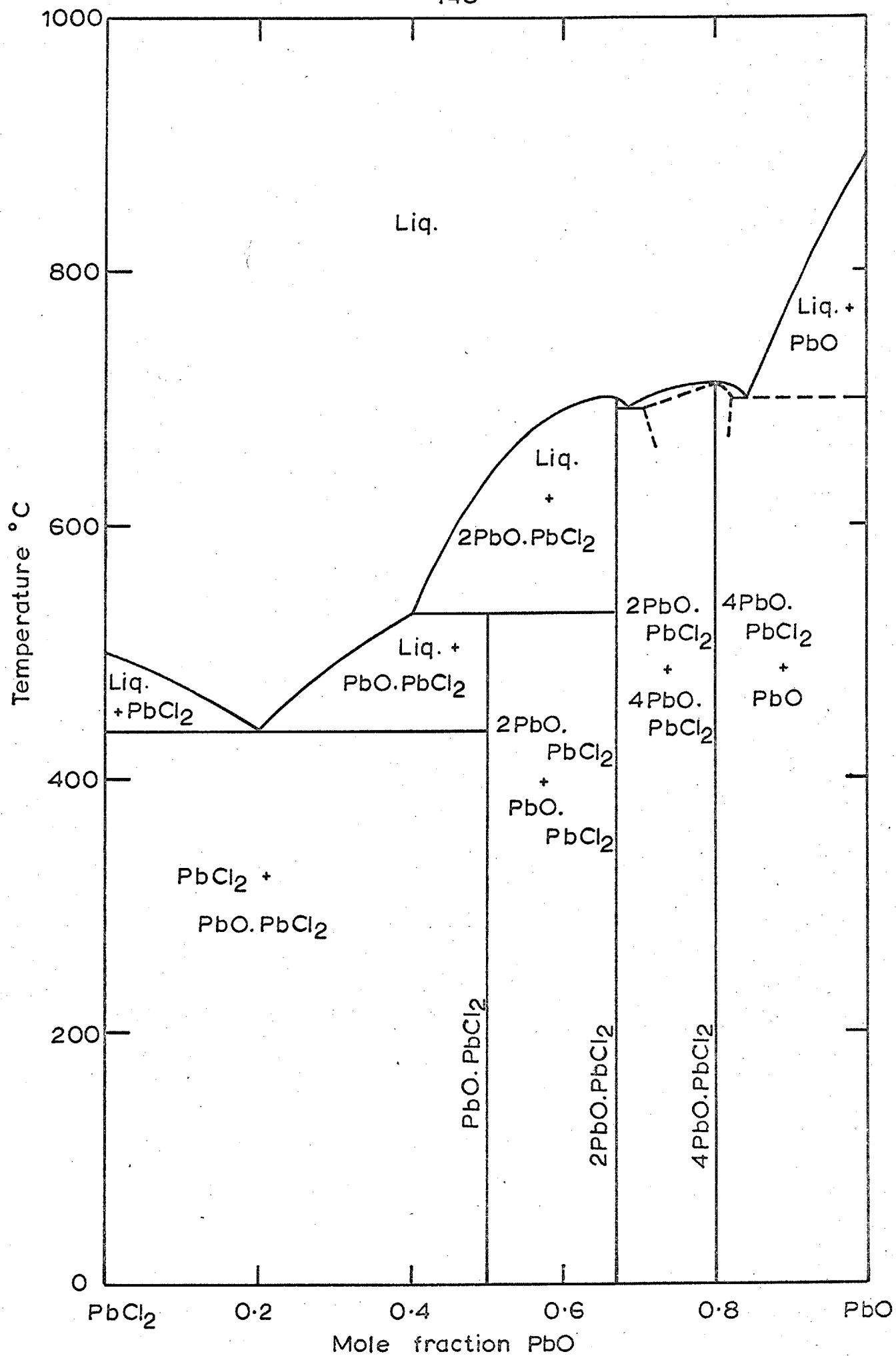


Fig. 32

$\text{PbO} \cdot \text{PbCl}_2$ PHASE DIAGRAM

composition curve for PbO at 629°C , (with reference to liquid PbO) determined from the E M F measurements. The results are also given in Table 17 and shown in Fig 31 . The partial free energies and integral free energy of mixing for $n \text{ PbO.PbCl}_2$ at 629°C is also given in Table 17 . The integral free energy curve is plotted in Fig 48 , see chapter II.

5. Discussion:

The greatest care was required when handling the reaction assembly to avoid any spillage of the melt from the alumina boat, as obviously this would invalidate the experiment, and is the largest source of error in this experiment. In order to minimise this spillage, the powdered samples were premelted into the alumina boats such that the boats were approximately one third full with the melts. Before the experiment the boats were visually examined to ensure that there were no traces of the melts on the outside or top. The 'zero-time' experiment is obviously a source of error because the correction applied for the heating up and cooling down times is dependant on the temperature versus time characteristic in the furnace. As a cold reaction tube is introduced into the hot furnace, then the furnace cools initially

TABLE 17.

The activities, partial free energies of PbO and PbCl₂, and the integral free energy of mixing for the system nPbO.PbCl₂ at 629°C.

Composition n PbO.	a _{PbO}	a _{PbCl₂}	ΔḠ _{PbO}	ΔḠ _{PbCl₂}	ΔḠ _M
0.9	0.5876 (E.M.F)	0.0003 (G.D)	-0.953	-14.54	-2.3117
0.8	0.4083 (E.M.F)	0.0029 (G.D)	-1.605	-10.47	-3.378
0.7	0.2469 (E.M.F)	0.0141 (G.D)	-2.507	-7.637	-4.046
0.6	0.1157 (E.M.F)	0.0572 (G.D)	-3.865	-5.728	-4.3702
0.5	0.0465 (E.M.F)	0.19 (E)	-5.500	-2.976	-4.2380
0.4	0.0198 (G.D)	0.36 (V.E)	-7.027	-1.831	-3.9094
0.3	0.0116 (G.D)	0.47 (V.E)	-7.981	-1.353	-3.3414
0.2	0.0028 (G.D)	0.75 (V.E)	-10.53	-0.515	-2.5180
0.1	0.0013 (G.D)	0.85 (V.E)	-11.923	-0.291	-1.4542

(E.M.F) ... E.M.F. technique results with reference
to liquid PbO.

(V.E) ... Vapour entrainment results.

(G.D) ... Results obtained from Gibbs Duhem integration.

(E) ... Extrapolated result from vapour entrainment
results.

n PbO = 0.1 Phase diagram a_{PbCl₂} = 0.882

n PbO = 0.2 Phase diagram a_{PbCl₂} = 0.7413

and has to heat up again to the controlling temperature. The error in the measured total volume of gas saturated with the vapour is small compared with that from the previous two sources, except that there is a danger that some of the gas could escape underneath the plug if the plug is not pressed tightly into the reaction tube. The R. M. S. error in the vapour pressure measurements was found to be about ten per cent, which is unfortunately large.

The value found in this study for the vapour pressure of PbCl_2 at 629°C , 8.15 mm Hg assumes that the vapour is monomeric PbCl_2 . As was previously discussed in Chapter 2 (2), the vapour could contain dimer and higher polymers of lead chloride.

Barton and Bloom (26) have used a boiling point method for the determination of vapour pressures of molten salts and at 629°C ., they obtain a value of 6.25 mm Hg. If one assumes that the vapour consists of monomer and dimer only then the experimental value obtained in this study suggests that 30% of the vapour is dimer. A knowledge of the molecular weight of the lead chloride vapour is not necessary for the boiling point method.

It seems unlikely that any complexes such as $\text{Pb}_2\text{O Cl}_2$ will be present in the vapour because of the large difference in vapour pressures between PbO and PbCl_2 . It would however be interesting to

run a Mass Spectrograph on this system to study the vapour species above PbO-PbCl_2 . Bloom and Hastie (27) carried out a mass spectral study on the system $\text{PbCl}_2\text{-PbBr}_2$. The vapour was found to contain only the species PbCl_2 , PbBr_2 and PbClBr . In this study if one assumes that the proportion of any other species to monomer in the vapour remains constant with changing composition of the melt, then the actual composition of the vapour is irrelevant in the calculation of activities.

The error in the activity results from the vapour entrainment experiments are about $\pm 14\%$ and from the E M F experiments are about 5%. The error in the temperature in both experiments is about $\pm 1^\circ\text{C}$, is the error in ΔG_{PbCl_2} from the vapour entrainment is about ± 350 cals and in ΔG_{PbO} from the E M F experiments ± 130 cals. The assumptions in the Gibbs Duhem integrations are additional errors with the result that the total error in ΔG_M is approximately ± 400 cals.

PART C

GENERAL DISCUSSION.

In chapter 11, the thermodynamics of pure PbO and the PbO melts n PbO.SiO₂, n PbO.P₂O₅ and n PbO.PbCl₂ are discussed in turn. The thermodynamics of n PbO.SiO₂ and n PbO.P₂O₅ melts are considered in the light of various structural theories, which have been outlined in section A. The thermodynamics of n PbO.PbCl₂ melts however are treated more with an emphasis on polarisation and compared with the data on n PbO.PbF₂ melts obtained by Sridhar.

In chapter 12, the thermodynamical data available on the sodium phosphates are discussed in terms of ring-chain equilibria which occur in the phosphates, the silicates and the borates.

Chapter 11. THERMODYNAMICS OF SOME PbO MELTS

1. Thermodynamics of pure PbO.

The phase diagram for the system Pb - PbO is given in Fig 33 . It is observed from this diagram that this system consists of a monotectic with a melting point of approximately 850°C. The relevance of this phase diagram to the present study lies in the fact that the cell used contains the melt in contact with liquid lead, with the result that the observed melting point of lead oxide in contact with liquid lead should be approximately 850°C instead of 897°C which is the melting point of pure lead oxide. (37) It was possible to measure the E M F versus temperature relationship at temperatures below the freezing point of the melts in this cell, since a solid electrolyte is involved in the cell design, and the results for pure lead oxide are shown in Fig 8 as the lines of linear regression, see Chapter 5. Similarly Charrette and Flengas (21) and Jacob (23) measured the E M F versus temperature relationship for pure lead oxide above and below its melting point, using cells containing solid electrolytes, and their results are shown in Fig 8 . Sridhar (4) however used an oxygen electrode which involved bubbling oxygen gas through the surface of the melt and as a result could only measure the E M F versus temperature relationship at temperatures above the freezing point

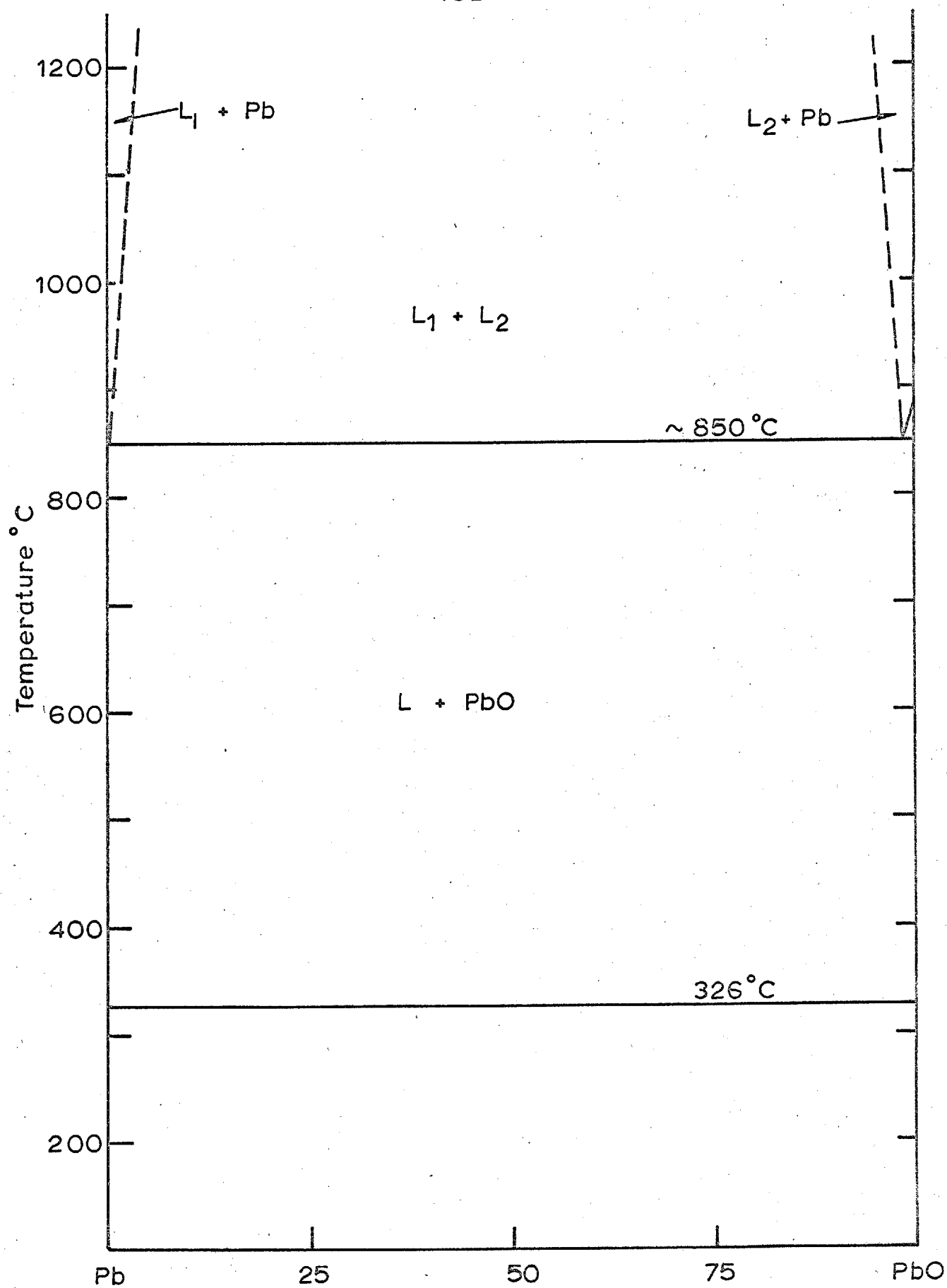


Fig. 33.

PHASE DIAGRAM Pb - PbO

of the melt. Sridhar's results for pure lead oxide are also shown in Fig 8 . In Fig 8 it can be seen that the results for pure PbO from this study, from Jacob, and Charette and Flengas are in fair agreement with each other and the extrapolated values from Alcock and Belford using the value for ΔH_f PbO determined in this study. However these results are about 30 millivolts larger than those obtained by Sridhar⁽⁴⁾, which suggests that the electronic conductivity of pure PbO liquid is not negligible as was assumed in the treatment of the results from Sridhar's cell, but in the order of 4 to 6%. Secondly, it is of interest to note that the apparent melting point of PbO in contact with liquid lead measured in this study is 865°C, and from Jacob is 858°C, which is in agreement with the approximate monotectic temperature discussed previously. Charette and Flengas show this value to be 875°C.

The free energy of formation of liquid PbO obtained in the present study is given by the equation

$$\Delta G_T^\circ = + 16.403T - 44,149 (\pm 300) \text{ cal/mole PbO}$$

and is plotted in Fig 34 as a function of temperature. Also plotted in Fig 34 are the results obtained by Sridhar⁽⁴⁾, Richardson and Webb⁽¹⁵⁾, Matsushita and Goto⁽²⁰⁾; Elliot and Gleiser⁽⁶⁰⁾, Alcock and Belford⁽⁴⁹⁾, (extrapolated), Charette and Flengas⁽²¹⁾, Jacob⁽²³⁾ and ΔG° from recent

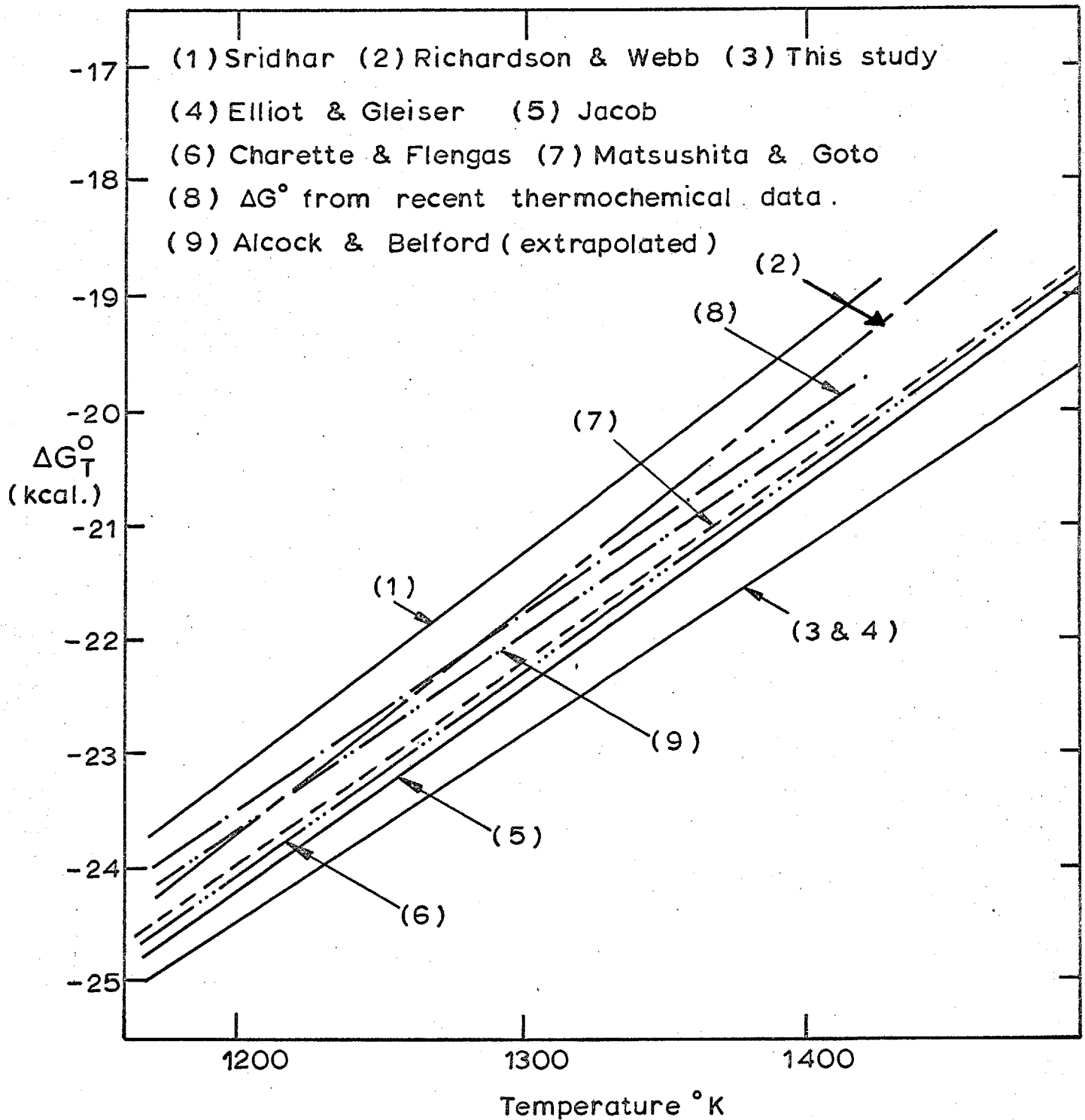


Fig. 34. FREE ENERGIES OF FORMATION OF LIQUID PbO

thermochemical data^(4).

The work of Matsushita and Goto has been corrected for the Ni/NiO reference electrode using the standard free energy change of the reaction $2\text{Ni} + \text{O}_2 = 2\text{NiO}$ as given by Steele^(61). The free energy of formation of liquid PbO from the work of Matsushita and Goto after correction is:-

$$\Delta G_T^{\circ} = +18.10T - 45,736 \text{ cal/mole PbO.}$$

From Charette and Flengas' work:-

$$\Delta G_T^{\circ} = + 17.96 T - 45,560 \text{ cal/mole PbO.}$$

From Jacobs work:-

$$\Delta G_T^{\circ} = + 17.903 T - 45,652 \text{ cal/mole.}$$

From Sridhar's work:-

$$\Delta G_T^{\circ} = + 18.90 T - 45,830 \text{ cal/mole PbO.}$$

The free energy of formation of liquid PbO determined in this present study is in excellent agreement with the values compiled by Elliot and Gleiser^(60) but differ from the other works by about $\frac{1}{2}$ kcal. Sridhar's value differs from the other works by about 1 Kcal in the opposite direction, which again suggests an electronic transport number of 0.04 in pure liquid PbO.

The free energy of formation of solid PbO determined in the present study is given by the equation:-

$$\Delta G_T^{\circ} = + 22.633 T - 51,241 \text{ cal/mole PbO.}$$

From the third law of thermodynamics $\Delta G = \Delta H$ when $T=0^{\circ}\text{K}$.

This difference between the free energy of formation of the liquid and the solid extrapolated to 0°K yields $\Delta H_{\text{fusion PbO}} = 7.19$ Kcals. The calorimetric result was 6.37 ± 0.4 Kcals/mole. Jacob (23) gives the free energy of formation of PbO solid:-

$$\Delta G_T^0 = + 23.635 T - 52,127 \text{ cal/mole PbO}$$

which yields a value of $\Delta H_{\text{fusion PbO}} = 6.47$ Kcals/mole. Alcock and Belford (49) have determined the free energy of formation of PbO solid with the result:-

$$\Delta G_T^0 = + 23.627T - 52165 \text{ cal/mole PbO.}$$

These three equations for the free energy of formation of solid PbO are in good agreement with one another. It is difficult at the present time to distinguish between the equations for the free energy of liquid PbO without a further study by a different technique.

2. Thermodynamics of nPbO. SiO₂ Melts.

It was proposed in the last section that the fault with the treatment of results obtained using Sridhar's cell, was the assumption that the contribution due to electronic conductivity in the melts was zero.

However as one increases the silica content in lead silicate melts, one would expect this contribution to approach zero since large silicate ions are formed with the result that the activation energy for the

transfer of electrons from one cation site to another should increase as the size of the silicate matrix increases. If this is the case one would expect that the plot of E M F versus composition from this study should approach the same plot obtained by Sridhar, since the only difference between the two cells is the introduction of a solid electrolyte to ensure that the transport number of oxygen ions is unity. This relationship is shown in Fig 35 together with the results obtained by Charette and Flengas (21). Fig 35 shows that the results from the present study and those of Sridhar fit this explanation, but the results from Charette and Flengas differ. In Fig 36 the activity of PbO in $n\text{PbO} \cdot \text{SiO}_2$ melts as obtained from this study, from Matsushita and Goto (20), from Charette and Flengas (21), from Sridhar and Jeffes (48) and from Richardson and Webb (15) are given.

The results from the present study appear to be in good agreement with those obtained by Matsushita and Goto, who also used an iron electrode in the liquid lead and a solid electrolyte, across the whole composition range. In the lead rich compositions these results also agree with Charette and Flengas but are greater than those obtained by Sridhar and Richardson and Webb, although the results of Charette and Flengas show a slight positive deviation from Raoultian ideality in this region. However as the

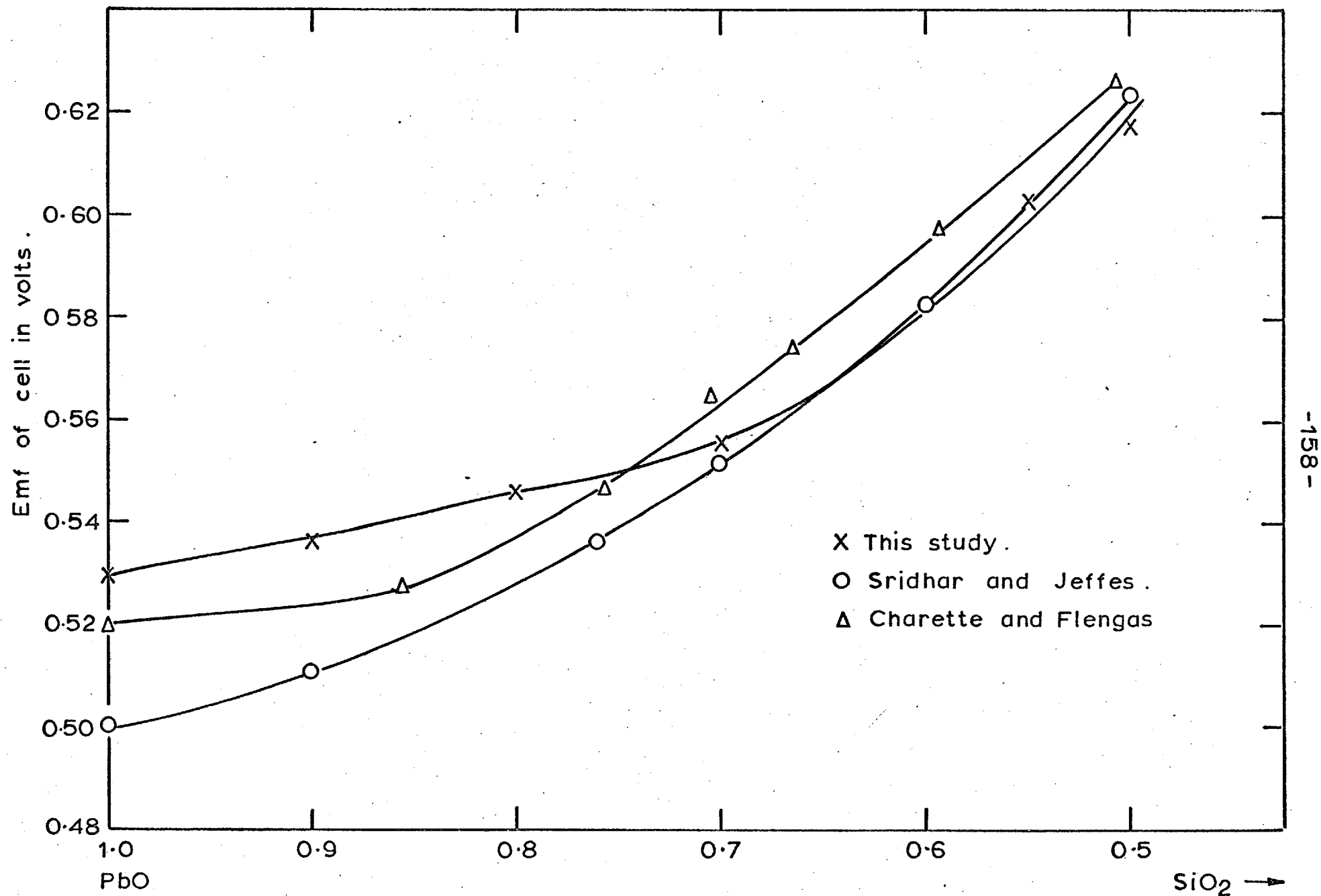


Fig. 35 EMF OF CELL CONTAINING n PbO.SiO₂ MELTS vs. COMPOSITION AT 1200°K

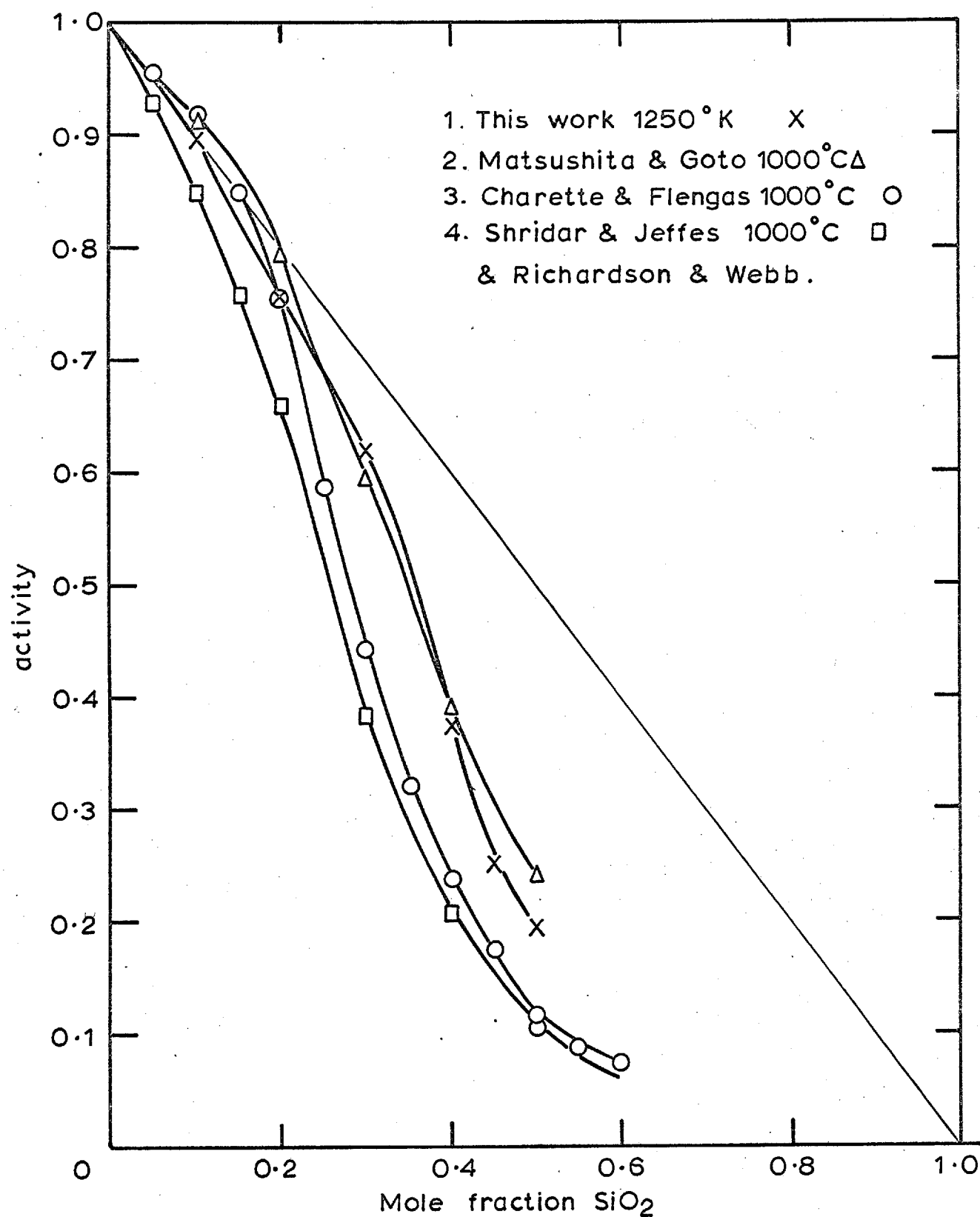


Fig. 36 ACTIVITY OF PbO IN nPbO-SiO₂ MELTS

silica content of the melt is increased the activities of Charette and Flengas approach those of Richardson and Webb and are smaller than those found in the present study. It seems likely that the difference between the results obtained in this study and those of Charette and Flengas result from the design of the cells that they used. It is interesting that in this study and that of Matsushita and Goto an iron electrode has been used to make the contact with the liquid lead, whereas Charette and Flengas have used an Iridium wire which passes through the melt into the liquid lead to make the contact. Without a further investigation into this system using another technique, it does not seem possible at ~~the~~ present time to show which is the correct activity plot.

The phase diagram for $\text{PbO} \cdot \text{SiO}_2$ is given in Fig 37. If one uses the values for the latent heat of fusion of PbO determined in the present study and the temperature of fusion of 897°C as reported by Rodigina (37), then the activities can be calculated from the phase diagram. If one can assume regular solution behaviour for the liquid, then the activity at any temperature in the liquid can be related to the activity at the liquidus using the equation:-

$T_1 \ln Y_1 = T_2 \ln Y_2$, where Y is the activity coefficient.

The activities calculated from the phase diagram

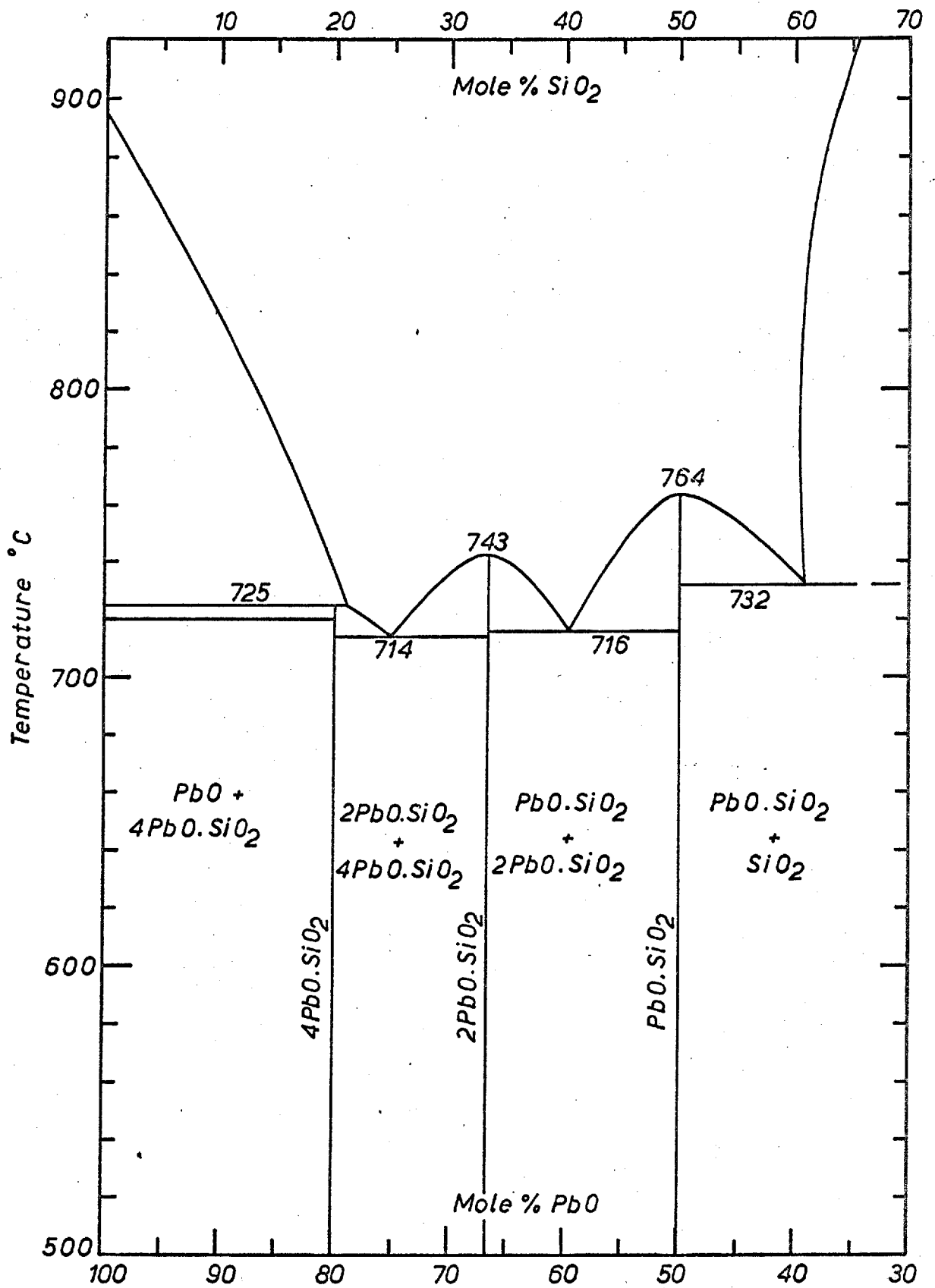


FIG.37 PbO-SiO₂ PHASE DIAGRAM

at the liquidus and at 1000°C are given in the following table together with the experimental results at 1000°C. Table 18.

Composition N_{PbO}	a_{PbO} From phase diagram	a_{PbO} experimental This study.	a_{PbO} Charcotte and Flengas
0.95	0.914 @ 860°C	0.95	0.955
0.90	0.842 @ 828°C	0.90	0.92
0.85	0.748 @ 785°C	0.83	0.85
0.80	0.646 @ 736°C	0.77	0.77

The phase diagram activities are slightly lower than the experimental values from this study, from Charcotte and Flengas and from Matsushita and Goto. This suggests that the silica in fact starts to polymerise at lower silica contents, by such a reaction as $2SiO_4^{4-} \rightleftharpoons Si_2O_7^{6-} + O^{2-}$, than has previously been suggested. The experimental activities in the range pure PbO to $N_{PbO} = 0.7$ can be compared with the activities calculated from the Temkin model if one assumes that the only ionic species present are Pb^{2+} , O^{2-} and SiO_4^{4-} . From the Temkin model:-

$$a_{PbO} = N_{M^{2+}} \cdot N_{O^{2-}}, \text{ but since } N_{M^{2+}} = 1, \text{ then}$$

$$a_{PbO} = N_{O^{2-}} = \frac{n_{O^{2-}}}{m_{O^{2-}} + m_{SiO_4^{4-}}}$$

$$\text{For example at } N_{PbO} = 0.9, \quad m_{Pb^{2+}} = 0.9$$

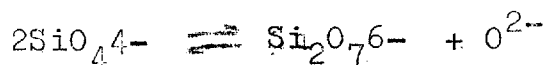
$$m_{SiO_2} = 0.1$$

$$\text{But } SiO_2 + 2O^{2-} \rightarrow SiO_4^{4-}, \text{ therefore } m_{SiO_4^{4-}} = 0.1$$

$$\text{and } m_{O^{2-}} = 0.9 - 0.2 = 0.7$$

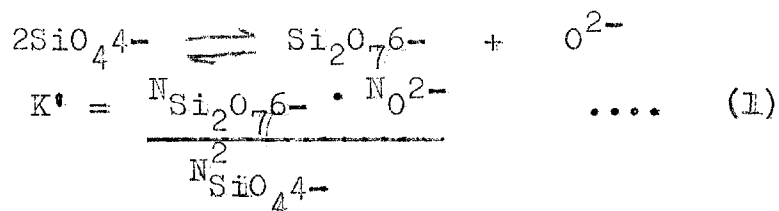
$$\text{Therefore } a_{PbO} = \frac{0.7}{0.7 + 0.1} = 0.875$$

The result is shown in Fig 38 together with the experimental activities from the present study, and those of Richardson and Webb. The deviation of the activity of PbO from this study from the Temkin model begins at lower silica contents than was supposed from the experimental activity of PbO determined by Richardson and Webb⁽¹⁵⁾. Consideration of the activities of PbO determined by Charette and Flengas⁽²¹⁾, and Matsushita and Goto⁽²⁰⁾ also show deviations from Temkin at low silicate concentrations. It has been supposed that the deviation is due to a polymerisation reaction of the type:-



Flood and Knapp⁽¹⁶⁾, as described in Part A divided the lead silicate system into three composition ranges, and suggested polymeric species which forced agreement with the observed activities.

In the composition range $N_{\text{PbO}} = 0.8$ to $N_{\text{PbO}} = 0.6$, a possible polymerisation reaction is



At the stoichiometric orthosilicate composition the observed activity of PbO is in the order of 0.5, compared with 0.33 from the results of Richardson and Webb, and thus if this was the only polymerisation reaction at this composition, all the silica would be

present as $N_{\text{Si}_2\text{O}_7^{6-}}$ and the equilibrium constant would tend to infinity. Flood and Knapp proposed an alternative equilibrium:-

$$3\text{SiO}_4^{4-} \rightleftharpoons 3\text{O}^{2-} + (\text{SiO}_3)_3^{6-}$$

$$K = \frac{N_{\text{O}^{2-}}^3 \cdot N_{(\text{SiO}_3)_3^{6-}}}{N_{\text{SiO}_4^{4-}}^3} \dots\dots (2)$$

Using Richardson and Webb's activity data, they evaluated K at the orthosilicate composition to be 0.0225 at 1000°C. Using the present activity data at 1000°C, the value of K becomes 1.599. If a mixture is composed of n_{Pb} moles PbO and n_{Si} moles SiO₂, then a silica balance results in the equation:-

$$n_{\text{SiO}_4^{4-}} + 3n_{(\text{SiO}_3)_3^{6-}} = n_{\text{SiO}_2}^0 \dots\dots (3)$$

and an oxygen balance gives:-

$$2n_{\text{SiO}_4^{4-}} + 3n_{(\text{SiO}_3)_3^{6-}} + n_{\text{O}^{2-}} = n_{\text{PbO}}^0 \dots\dots (4)$$

From equations (2), (3) and (4) the mole fractions of

$N_{\text{SiO}_4^{4-}}$, $N_{(\text{SiO}_3)_3^{6-}}$ and $N_{\text{O}^{2-}}$ can be determined.

The result is shown in the following table with K = 1.599 at 1000°C:-

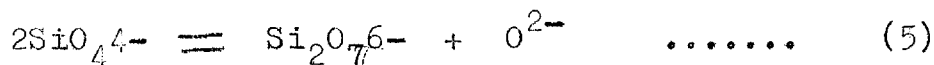
Table 19.

N_{PbO}	$N_{\text{SiO}_4^{4-}}$	$N_{(\text{SiO}_3)_3^{6-}}$	$N_{\text{O}^{2-}}$	a_{PbO} experimental
0.8	0.208	0.037	0.75	0.755
0.667	0.267	0.183	0.55	0.55
0.6	0.243	0.351	0.405	0.385

The theoretical activities are in good agreement with the experimental values using K = 1.599 at 1000°C for the equilibrium given in equation (3), in the same way as this equilibrium can be made to fit the result

of Richardson and Webb^(15) using a value of 0.0225 for K. It is unlikely however that only four ionic species are present in these melts, if the silicates are considered as being analogous to the phosphates, then the present knowledge of the structure of the phosphate systems would indicate a large variety of anions are present.

Masson^(62) has considered the equilibrium:-



with the equilibrium constant:-

$$K_{11} = \frac{N_2 \cdot N_{\text{O}^{2-}}}{N_1^2} \quad \dots\dots (6)$$

The result from the Temkin equation is:-

$$a_{\text{MO}} = N_{\text{M}^{2+}} \cdot N_{\text{O}^{2-}} = N_{\text{O}^{2-}} \quad \text{for a binary system.}$$

Substituting for N_1 and N_2 in equation (6) from the two theories discussed in Chapter 1, then for the Flory distribution:-

$$\frac{a_{\text{MO}}}{1 - a_{\text{MO}}} = \frac{K_{11} (1 - \alpha)^2}{2\alpha (1 - 2\alpha)}$$

For the Masson distribution:-

$$\frac{a_{\text{MO}}}{1 - a_{\text{MO}}} = \frac{K_{11} (1 - \frac{2\alpha}{3})}{2\alpha}$$

Where α is the fraction of functional groups that have condensed. Masson^(62) has related α to the mole fraction of SiO_2 by the equation:-

$$\alpha = \frac{1 - (1 - a_{\text{MO}}) \left(\frac{1}{N_{\text{SiO}_2}} - 2 \right)}{2}$$

If $k_{11} = 0.196$, then Masson's theory^(19) fits the average of the results obtained by Richardson and Webb^(15) and Charette and Flengas^(21) throughout the whole composition range, whereas Flory's theory^(17) begins to deviate at mole fractions of PbO less than 0.75, and approach infinity at $N_{\text{PbO}} = 0.3$.

The activity curves from the Masson distribution when $k_{11} = 0.42$ and $k_{11} = 0.55$ are shown in Fig 38 together with the activity curve calculated from the Flory distribution when $k_{11} = 0.55$. These activity curves for $k_{11} = 0.42$ and $k_{11} = 0.55$ tend to the experimental results obtained in this study.

It seems likely from the consideration of the results obtained in this study and the molecular size distribution theories, that the equilibrium constant k_{11} is about twice as large as that postulated by Masson on the basis of the results obtained by Richardson and Webb^(15).

The partial heats of PbO in $n\text{PbO} \cdot \text{SiO}_2$ melts obtained in this study are shown in Fig 39 together with the results obtained calorimetrically by Kleppa^(7). Also shown in Fig 39 are the partial heats of PbO in this system obtained by Richardson and Webb^(15), Matsushita and Goto^(20) and Charette and Flengas^(21).

In the silica rich composition range $N_{\text{PbO}} < 0.7$ excellent agreement is observed between the present study and calorimetry, although the partial heats

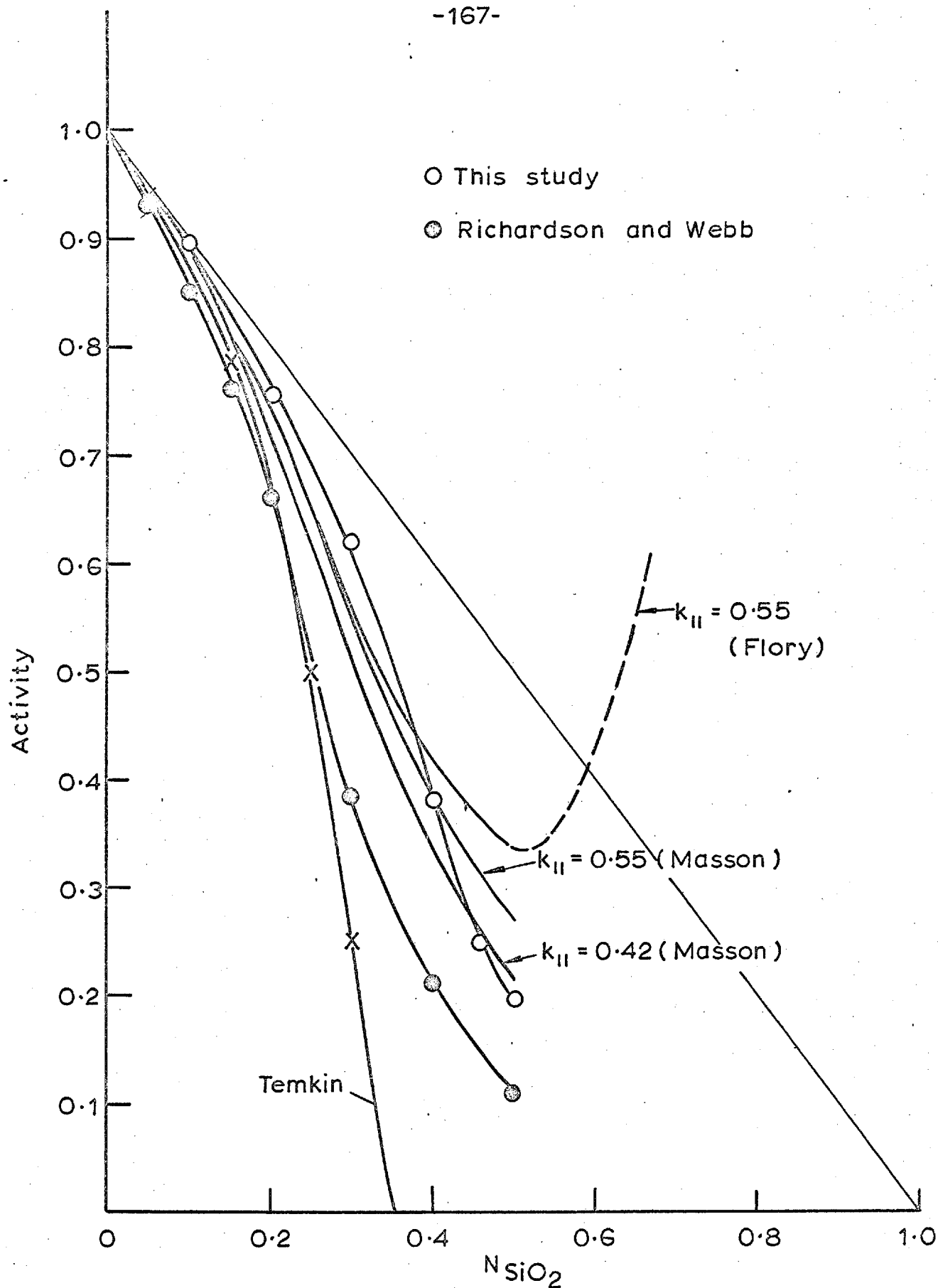
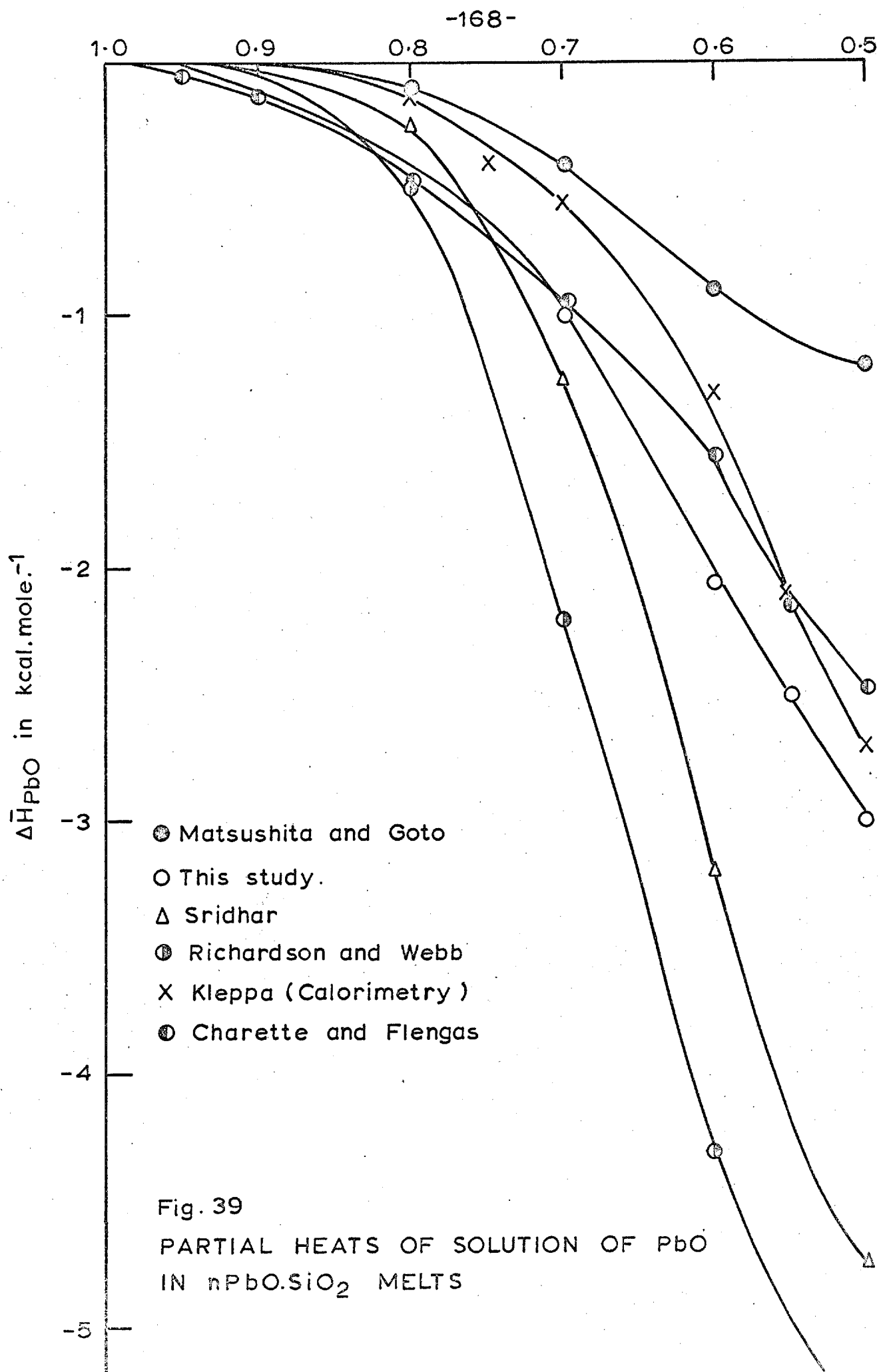


Fig.38. ACTIVITY OF PbO IN $nPbO.SiO_2$, FOR COMPARISON WITH THE MASSON AND FLORY DISTRIBUTIONS, AND THE TEMKIN MODEL



observed at the lead rich compositions were smaller from the calorimetric experiments. The accuracy of partial heats from E M F measurements however should not be relied upon if calorimetric heats are available.

It is observed that the partial heats are small in the region pure PbO to $N_{\text{PbO}} = 0.8$, which is fairly consistent with the view of Flood and Knapp⁽¹⁶⁾ that the only silicate anion present is SiO_4^{4-} , although it has been suggested earlier that polymerisation may start at larger PbO mole fractions. Kleppa⁽⁷⁾ has pointed out that the sharpest dependence on composition is exhibited by the partial heat curves (ΔH_{PbO}) at approximately $N_{\text{PbO}} = 0.65$, which corresponds to the composition at which the reaction $2\text{O}^{2-} + \text{SiO}_2 = \text{SiO}_4^{4-}$ would be complete. However, he has found no evidence of any other simple silicate ions such as $(\text{SiO}_3)_3^{6-}$ which casts doubt on attempts to consider these melts as ideal mixtures of two anionic species as considered by Flood and Knapp⁽¹⁶⁾ and discussed previously.

The integral heats of mixing from this study and from the calorimetry experiments performed by Kleppa⁽⁷⁾ are shown in Fig 40. The two studies compare well with experimental error. The integral entropies of mixing obtained from the combination of the integral free energies and the heats from this

study and secondly from the combination of the calorimetric heats with the free energy data from this study are shown in Fig 40. Also shown in Fig 40 are the entropies of mixing obtained from the combination of the calorimetric heats with the integral free energies obtained by Charette and Flengas^(21) and by Richardson and Webb^(15)

If one considers random mixing of PbO and Pb_2SiO_4 ($N \text{ PbO} > 0.66$), then if the only silicate species were SiO_4^{4-} the entropy of mixing curve should exhibit a cusp at $N \text{ PbO} = 0.66$. If however the SiO_4^{4-} undergoes a polymerisation reaction of the type $2\text{SiO}_4^{4-} = \text{O}^{2-} + \text{Si}_2\text{O}_7^{6-}$ then $K \neq 0$ as in the first case but has some finite value. As K increases, the magnitude of this cusp decreases. The integral entropies of mixing using this model for $K = 10^{-6}$ and $K = 10^{-3}$ as well as $K = 0$, as estimated by Kleppa^(7) are also shown in Fig 40. The other extreme is the ideal entropy of mixing curve which considers random mixing of SiO_2 and PbO and this is also shown in Fig 40. The results from the present study clearly support the former model and are in fairly close agreement with the entropies obtained by Charette and Flengas^(21). Both sets of results exhibit a small cusp at approximately $N \text{ PbO} = 0.6$ which would fit this model when $K > 0$. It is difficult to interpret these

entropy results more quantitatively, since the magnitudes of the non configurational contributions are not known. Also the effect of the idealised model of random mixing of PbO and SiO_2 on the model which considers random mixing of PbO and Pb_2SiO_4 is uncertain.

Darken⁽⁶³⁾ has pointed out that it is useful to consider the entire composition range of a binary system in three regions. Namely two terminal regions and the central region. Darken has in general considered simple metallic solutions and has observed two useful features in these systems. Firstly he observed in the terminal regions that the second derivative of the molal excess free energy with respect to atom fraction was constant, and this he called the excess stability function. Secondly in the central region he observed that the excess stability function varies with composition, exhibiting maxima at compositions corresponding to intermetallic compounds. If one considers an actual solution containing A and B, and then divides this solution into two portions, if the solution were ideal one would expect the change in excess free energy accompanying the transfer of a small amount of A from one portion to the other and a small amount of B in the opposite direction, to be zero. If however one considers a solution containing sodium chloride then the change in excess free energy associated with the transfer of

sodium ions to chlorine sites and *viceversa* is large. On this reasoning Darken pointed out that the excess free energy change should be large in the vicinity of a compound. He has defined the stability as the second differential of molal free energy with respect to composition, since this was found to be proportional to the free energy change for a process in which a solution is broken down into two solutions such that the difference in composition between the two solutions is very small.

Now $\bar{G}_2 = G + (1 - N_2) \frac{dG}{dN_2}$, where $\bar{G}_2$ is the chemical potential of component 2, and G is the molal free energy.

$$\text{Now stability} = \frac{d^2G}{dN_2^2} = \frac{1}{(1-N_2)} \cdot \frac{d\bar{G}_2}{dN_2} = -2 \frac{d\bar{G}_2}{d(1-N_2)^2}$$

$$\begin{aligned} \text{Similarly excess stability} &= \frac{d^2G^{XS}}{dN_2^2} \\ &= \frac{1}{1-N_2} \cdot \frac{d\bar{G}_2^{XS}}{dN_2} = -2 \frac{d\bar{G}_2^{XS}}{d(1-N_2)^2} \end{aligned}$$

$$\text{But } d\bar{G}_2 = 2.303 RT \, d \log_{10} a_2$$

$$\text{Therefore stability} = -4.605 RT \frac{d \log a_2}{d(1-N_2)^2}$$

$$\text{Also } d\bar{G}_2^{XS} = 2.303 RT \, d \log_{10} Y_2$$

$$\text{Therefore excess stability} = -4.605 RT \frac{d \log Y_2}{d(1-N_2)^2} .$$

The excess stability calculated from the activity results from the present study, from Sridhar and from Charotte and Flengas (21) are shown in Fig 41 .

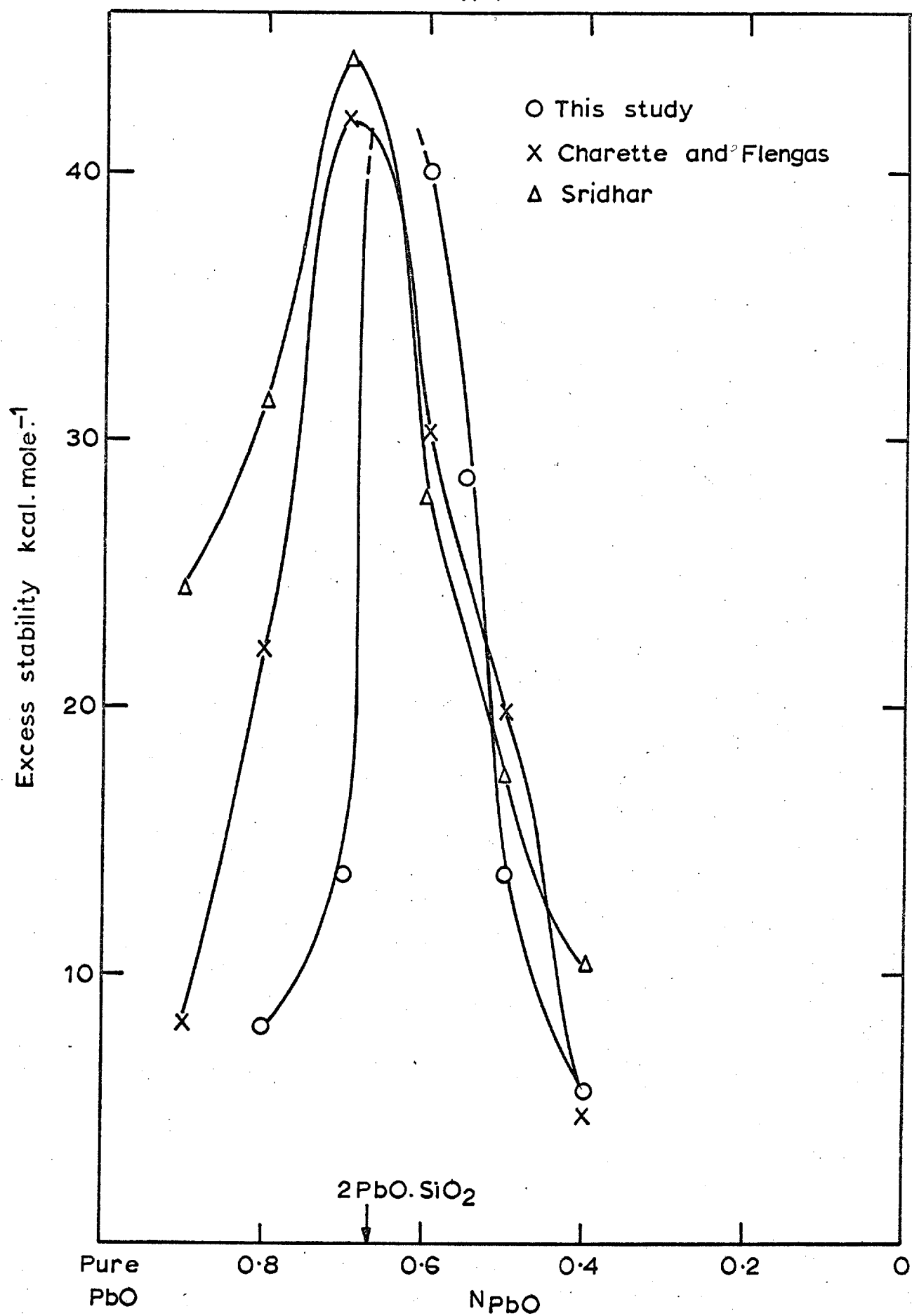


Fig. 41. EXCESS STABILITY OF LIQUID PbO.SiO₂ AT 1000°C

All these curves show a maximum at about $N \text{ PbO} = 0.66$ which is the composition corresponding to $2\text{PbO} \cdot \text{SiO}_2$. Since the excess stability at this composition is so large, no other maxima were observed at any other compositions corresponding to the other compounds such as $\text{PbO} \cdot \text{SiO}_2$.

Darken⁽⁶³⁾ has calculated the stability functions for the systems $\text{CaO} \cdot \text{SiO}_2$ from the data of Darken⁽⁶⁴⁾ and Kay and Taylor⁽⁶⁵⁾ and $\text{FeO} - \text{SiO}_2$ from the data of Schuhmann and Ensio⁽⁶⁶⁾. These are shown in Fig 42. The largest maxima in all these silicates systems appears to correspond to the compound $2\text{MO} \cdot \text{SiO}_2$ in the solid state. In the melts at this composition it has been supposed that the largest change in structure with respect to composition takes place with the formation of higher silicate ionic species.

Carbo Nover⁽⁶⁷⁾ studied the tin silicate melts and in Fig 42 the excess stability function calculated from his activity results is presented. Again the maximum stability is observed at the composition $2\text{SnO} \cdot \text{SiO}_2$ although the only compound that was observed by Carbo Nover in this system was a metastable compound $\text{SnO} \cdot \text{SiO}_2$. It would be interesting to determine whether a compound $2\text{SnO} \cdot \text{SiO}_2$ is present in the binary. Unfortunately Carbo Nover and Williamson⁽⁶⁸⁾ have only studied the crystallisation

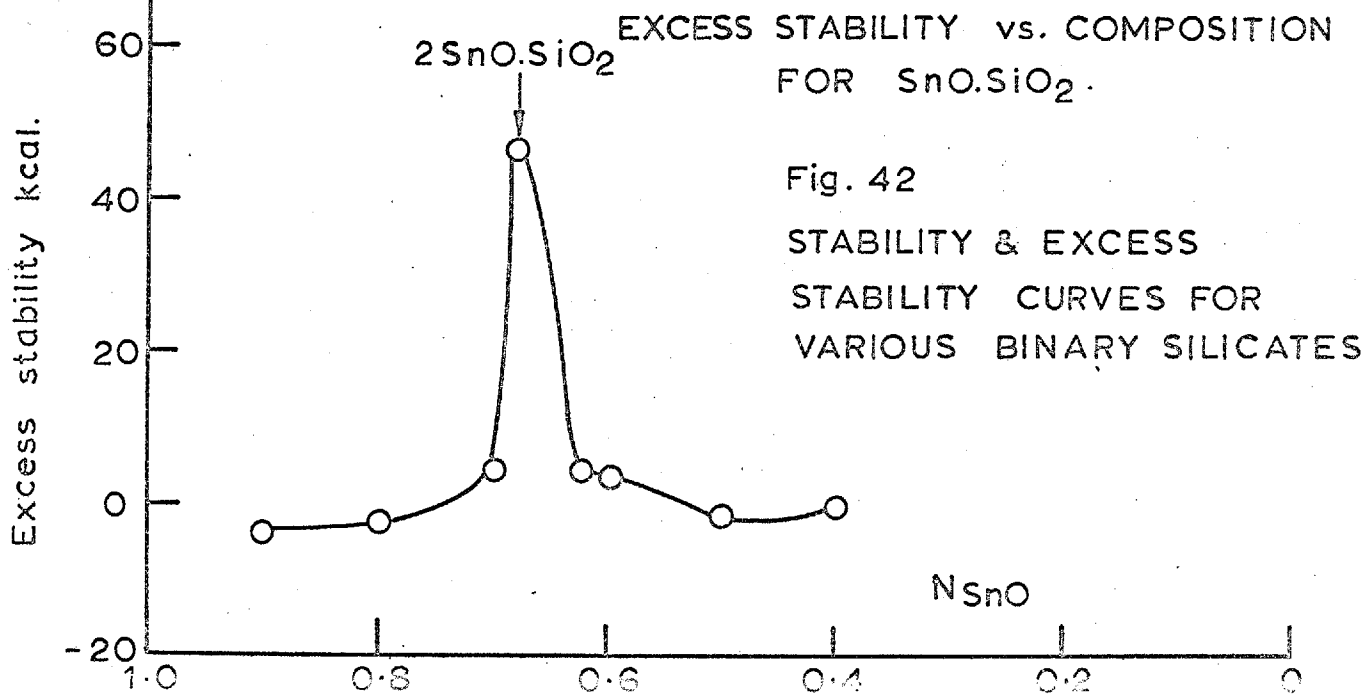
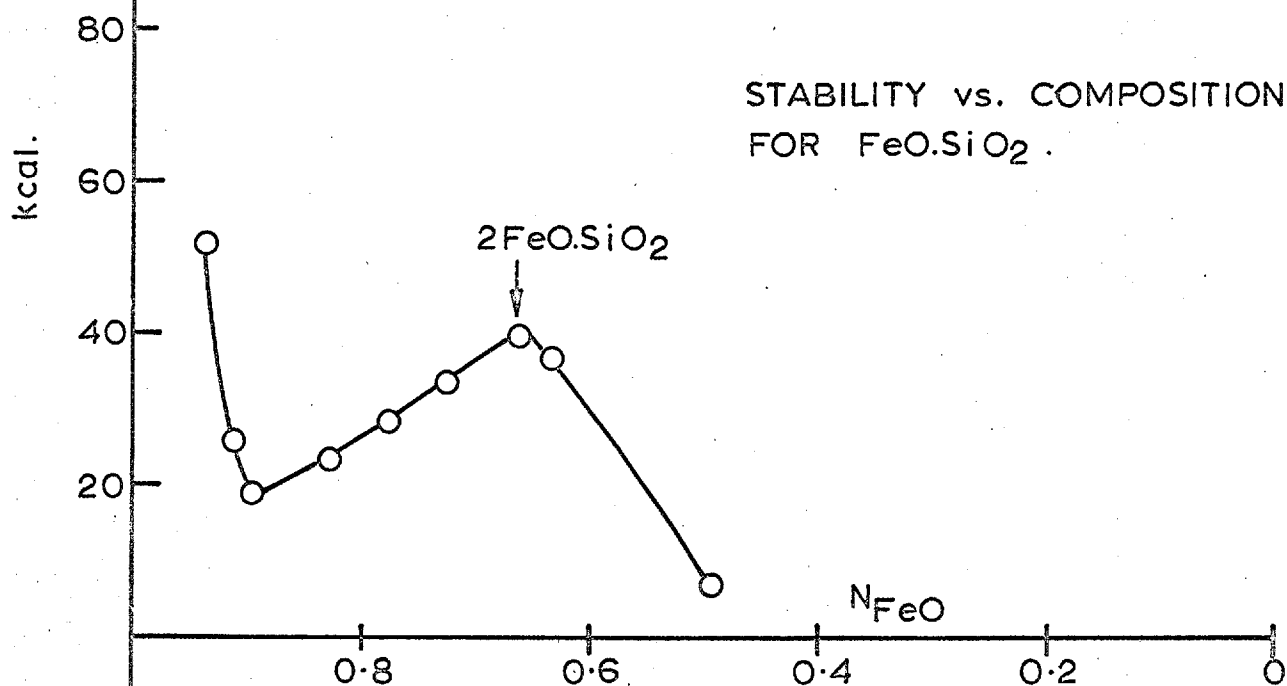
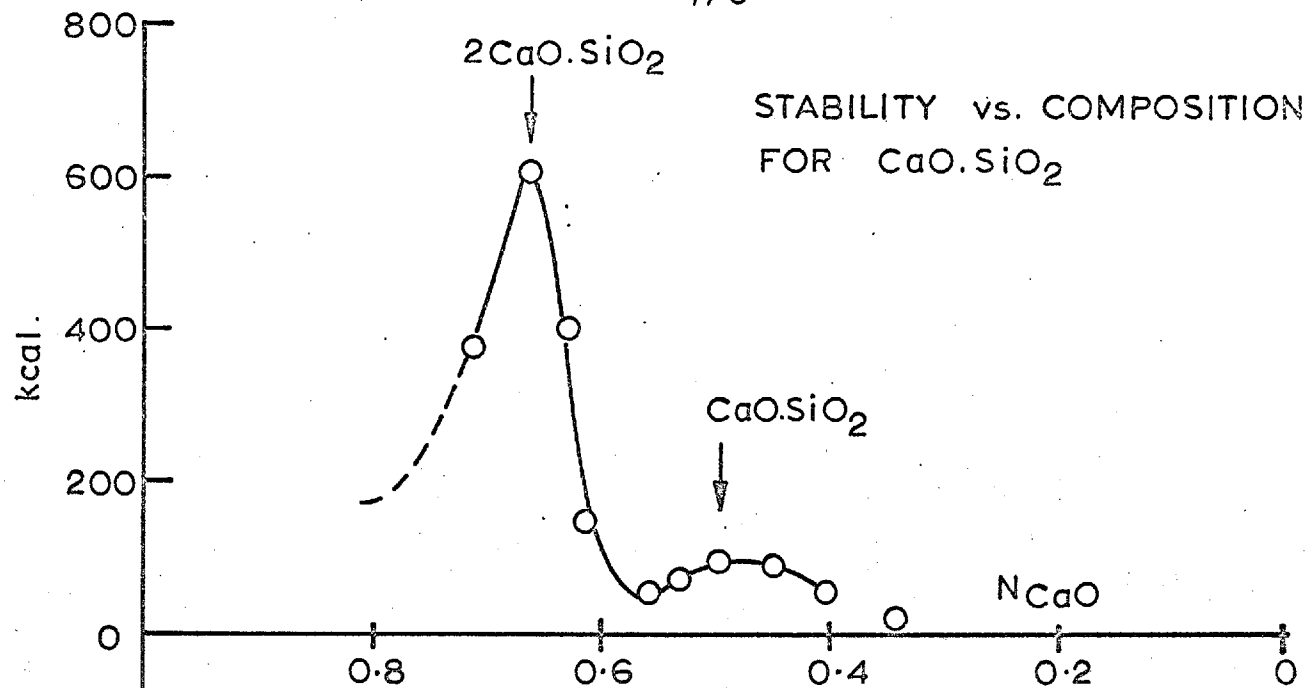


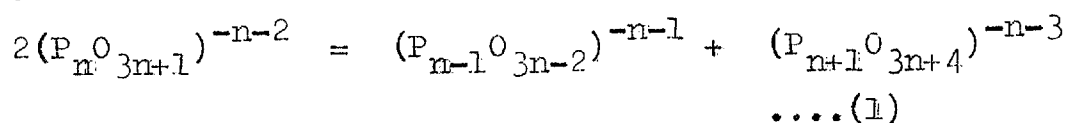
Fig. 42

STABILITY & EXCESS
STABILITY CURVES FOR
VARIOUS BINARY SILICATES

of glasses in this system in the composition range $N \text{ SnO} = 0.2778$ to $N \text{ SnO} = 0.5840$, and they give no indication as to whether a glass can be formed when $N \text{ SnO} = 0.66$.

3. Thermodynamics of $n \text{ PbO} \cdot \text{P}_2\text{O}_5$ melts.

Only two compositions were studied with the modified cell in the lead phosphate system, because of the excellent agreement in the present study with the activity results in this system determined by Sridhar⁽⁴⁾. A similar approach to the lead silicate system can also be applied to the lead phosphate system. Sridhar and Jeffes⁽⁵⁷⁾ have firstly considered a Temkin model based on the ions Pb^{2+} , O^{2-} and PO_4^{3-} , but found that the experimental activities deviated from this model from a composition corresponding to $N \text{ PbO} = 0.98$. They have then considered a Temkin model in terms of PO_5^{5-} ions and PO_6^{7-} ions as the only phosphate ions present. The PO_5^{5-} forced the best agreement with the experimental activities to a composition corresponding to $N \text{ PbO} = 0.85$. If PO_5^{5-} exists, then it seems likely that as the phosphate concentration is increased then a reaction of the type $\text{PO}_5^{5-} \rightarrow \text{PO}_4^{3-} + \text{O}^{2-}$ occurs. The PO_4^{3-} then undergoes a polymerisation reaction of the type:-

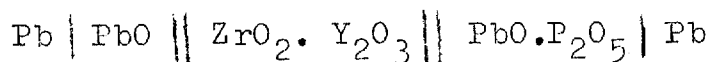


suggested by Meadowcroft and Richardson.⁽²⁾ The partial heats of PbO in n PbO.P₂O₅ melts determined calorimetrically in this study, indicate that the largest change in partial heat (ΔH_{PbO}) with composition occurs at about N PbO = 0.85, which is in accordance with this model, see Fig 24.

In the lead borate system, which has been studied by Sridhar⁽⁴⁾, the borate ion BO₄⁵⁻ was found to fit the activity results better than BO₃³⁻ using a Temkin approach. Thus one could expect a similar reaction to that suggested for the phosphates in which a reaction of the type :- BO₄⁵⁻ → BO₃³⁻ + O²⁻ may occur, and then polymerisation of the BO₃³⁻ ions as before. Kleppa⁽⁸⁾ has observed a sharp dependence of the partial heat of PbO in n PbO.B₂O₃ melts on composition, in the composition range N PbO = 0.84 to 0.8, which may indicate the start of these reactions. The partial heat curve versus composition for PbO in n PbO.P₂O₅ melts determined in the present study, is similar in shape to those determined by Kleppa in the n PbO.SiO₂⁽⁷⁾ and the n PbO.B₂O₃⁽⁸⁾ systems, which suggest that polymerisation of the anions is of the same form in these three systems. It has been suggested earlier in the discussion on the lead silicate system that the polymerisation reaction of the type shown in equation (1) above begins at compositions which are richer in lead than the orthosilicate composition,

and thus it seems likely that the polymerisation takes the same form in the phosphate and borate systems.

In Fig 43 the integral heat of mixing curve for $\text{PbO.P}_2\text{O}_5$ is given together with the free energy of mixing curves from Sridhar⁽⁴⁾ and Cox⁽⁶⁹⁾. From the combination of the integral enthalpies with the integral free energies from the two studies, the entropies of mixing can be determined and are shown in Fig 44. It appears that the integral entropies obtained using the estimated free energy curve of Sridhar are more incorrect than those obtained from Cox's work, since the entropies calculated in this way tend to be completely negative in the first case and negative and positive in the latter case. Since however the integral heats and free energies are large with correspondingly large errors, in the lead phosphate system, and the non configurational contribution to the entropy is unknown, it is not surprising that the entropy data calculated in this way are meaningless. Also the free energy of mixing curve determined by Sridhar was based on the phosphorus pressure being one atmosphere at $N_{\text{PbO}} = 0.55$, and Cox's work was carried out in the solid state $500^\circ\text{C} - 700^\circ\text{C}$ using the E M F cell represented by:-



The present enthalpy measurements suggest that the integral free energy of mixing curve should be just

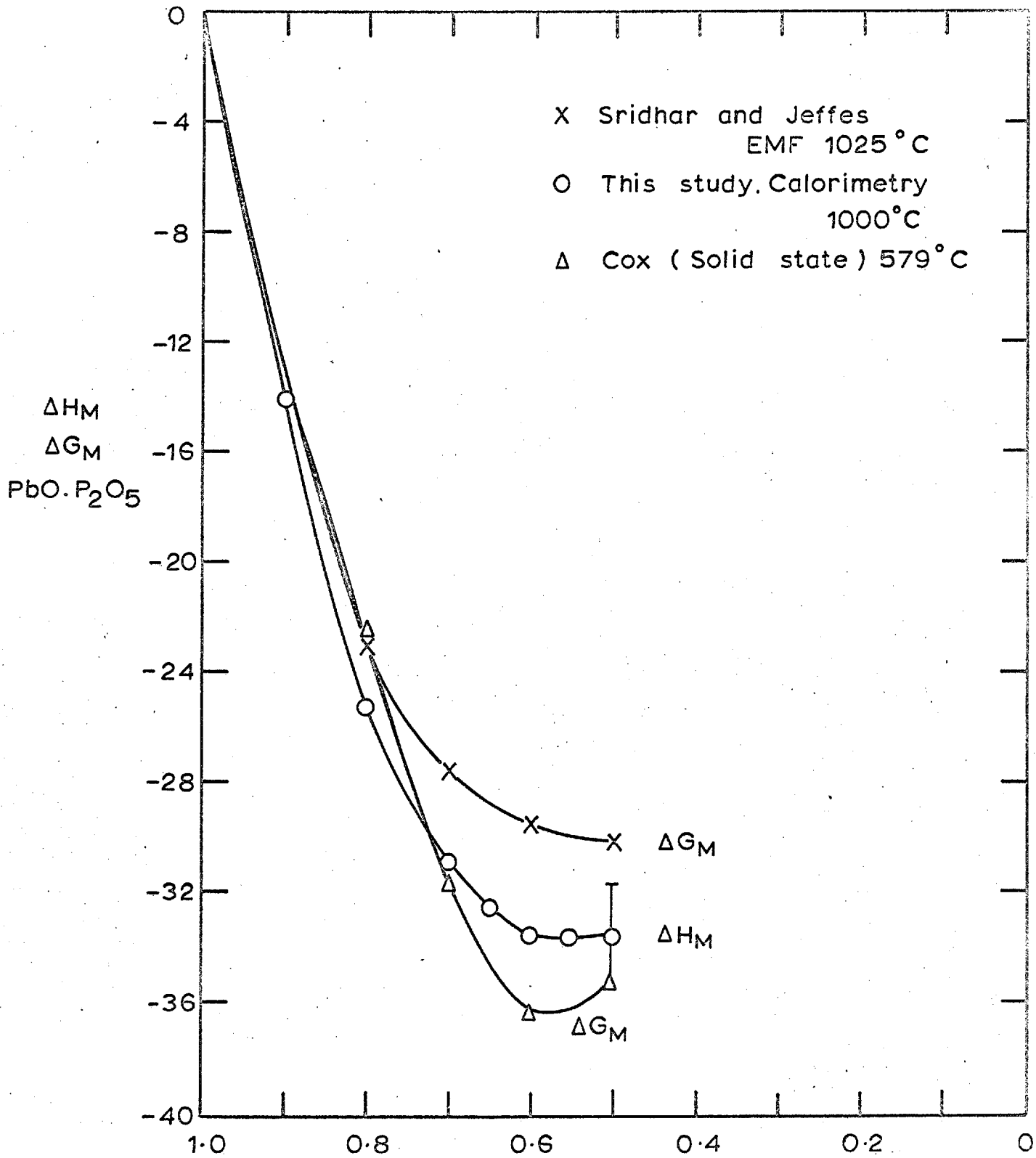
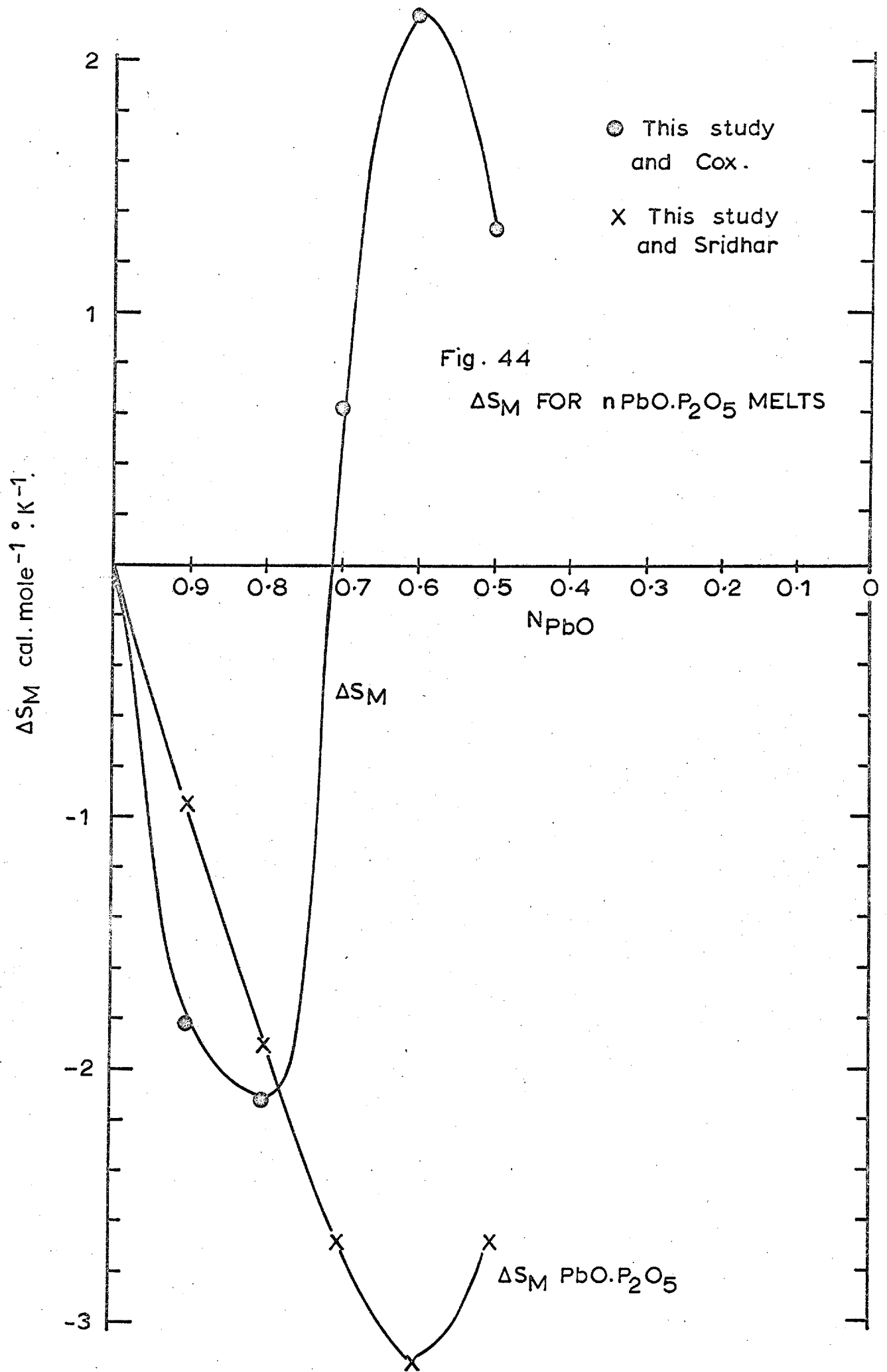


Fig.43 ΔG_M AND ΔH_M CURVES FOR $nPbO \cdot P_2O_5$ MELTS



slightly more negative than presented by Cox purely on the consideration of entropies.

The excess stability function for the $n \text{ PbO} \cdot \text{P}_2\text{O}_5$ system, which was discussed in the last section, is shown in Fig 45 versus composition. A maximum corresponding to $N \text{ PbO} = 0.8$ is observed. This composition corresponds to the compound $4\text{PbO} \cdot \text{P}_2\text{O}_5$. This maximum indicates a rapid change in constitution of the melts at this composition which could result from a reaction represented by the equation:-

$\text{PO}_5^{5-} \rightarrow \text{PO}_4^{3-} + \text{O}^{2-}$, and/or polymerisation of the PO_4^{3-} ions.

Sridhar (4) among other workers has considered the effect of different cations on the heats of formation of their respective phosphates, see Fig 27. He has shown that the breadth of the distribution of the phosphate ions is directly related to these heats of formation curves. This can be better understood if one considers the systems :- phosphoric acid, lead phosphate and calcium phosphate. If one can consider that the heats of solution of the cations in these melts are comparable, then the first ionisation energies given by Pauling (70) are a measure of the ionisation potentials of the cations. Thus it is clear that the ionisation potential decreases from calcium to lead to hydrogen. If one now considers a linear phosphate chain containing initially three phosphorus atoms, then this may

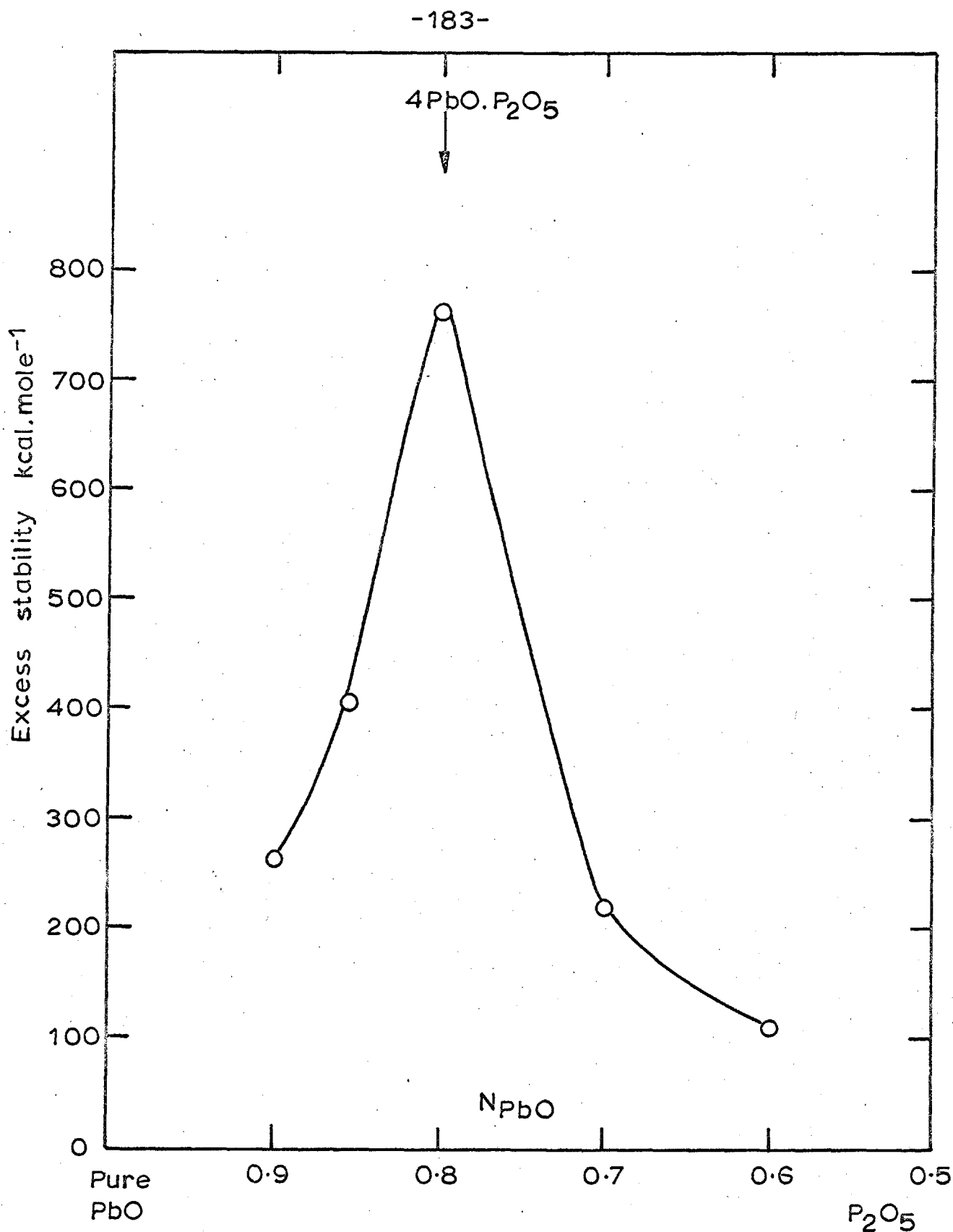
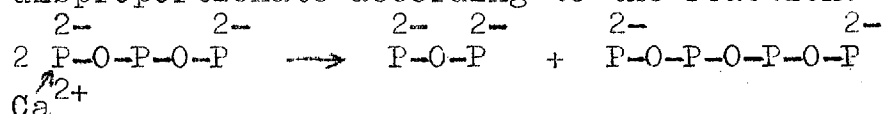


Fig. 45 EXCESS STABILITY vs. COMPOSITION FOR $n\text{PbO.P}_2\text{O}_5$ MELTS AT 1075°C .

disproportionate according to the reaction:-



If a cation with a larger ionisation is brought up to this phosphate chain, it will induce greater polarisation on the phosphate chain, with the result that the repulsion between the opposite ends of the chain is greater. Thus the above reaction will require a larger free energy than a similar reaction in which the phosphate ion is unpolarised. This in turn will be responsible for the diminished distribution in the presense of a highly polarising cation. The heat of formation of lead phosphate is smaller than that of calcium phosphate, as can be seen in Fig 27 .

It is observed that the heat of mixing increases from silicate to borate to phosphate with a common cation. In an instance, where lead is the common cation and considering the equimolar composition, the following heats of mixing have been determined:-

$\text{PbO} \cdot \text{SiO}_2$	Results from Kleppa ^(7)	$\Delta H_M = -1.95 \text{Kcals}$
$\text{PbO} \cdot \text{B}_2\text{O}_3$	Results from Kleppa ^(8)	$\Delta H_M = -6.7 \text{Kcals}$
$\text{PbO} \cdot \text{P}_2\text{O}_5$	Results from this study	$\Delta H_M = -33.45 \text{Kcals}$

It is apparent from a consideration of the electronegativities of silicon, boron, phosphorus and oxygen that that the phosphorus oxygen bond is more covalent than the boron oxygen bond which in turn is more covalent than the silicon oxygen bond. Thus one

would expect larger heats of mixing and smaller distributions in the phosphates compared to the silicates, since more energy is required to break a phosphorus oxygen bond than a silicon oxygen bond.

4. Thermodynamics of $n \text{ PbO} \cdot \text{PbCl}_2$ melts.

The activities of PbO in $n \text{ PbO} \cdot \text{PbCl}_2$ melts at 1200°K determined in this study are shown in Fig 46 together with the activities of PbO in $n \text{ PbO} \cdot \text{PbF}_2$ melts which were determined by Sridhar⁽⁴⁾. If one assumes that these melts are simple ionic solutions containing Pb^{2+} , O^{2-} and Cl^- ions, then the activities according to the Temkin model⁽¹⁰⁾ and the Flood, Forland and Grjotheim's model⁽¹¹⁾ discussed briefly in Part A can be determined.

According to the Temkin model in $\text{PbO} \cdot \text{PbCl}_2$ melts,

$$a_{\text{PbO}} = N_{\text{Pb}^{2+}} \cdot N_{\text{O}^{2-}} = N_{\text{O}^{2-}} \quad \text{since } N_{\text{Pb}^{2+}} = 1$$

$$N_{\text{O}^{2-}} = \frac{n_{\text{O}^{2-}}}{n_{\text{O}^{2-}} + n_{\text{F}^-}}$$

$$\text{Similarly } a_{\text{PbCl}_2} = N_{\text{Cl}^-}^2 = \left[\frac{n_{\text{Cl}^-}}{n_{\text{Cl}^-} + n_{\text{O}^{2-}}} \right]^2$$

The result from the Flood, Forland and Grjotheim model gives:-

$$a_{\text{PbO}} = N_{\text{O}^{2-}}' = \frac{2n_{\text{O}^{2-}}}{2n_{\text{O}^{2-}} + n_{\text{F}^-}}$$

$$\text{and } a_{\text{PbCl}_2} = N_{\text{F}^-}' = \frac{n_{\text{F}^-}}{2n_{\text{O}^{2-}} + n_{\text{F}^-}}$$

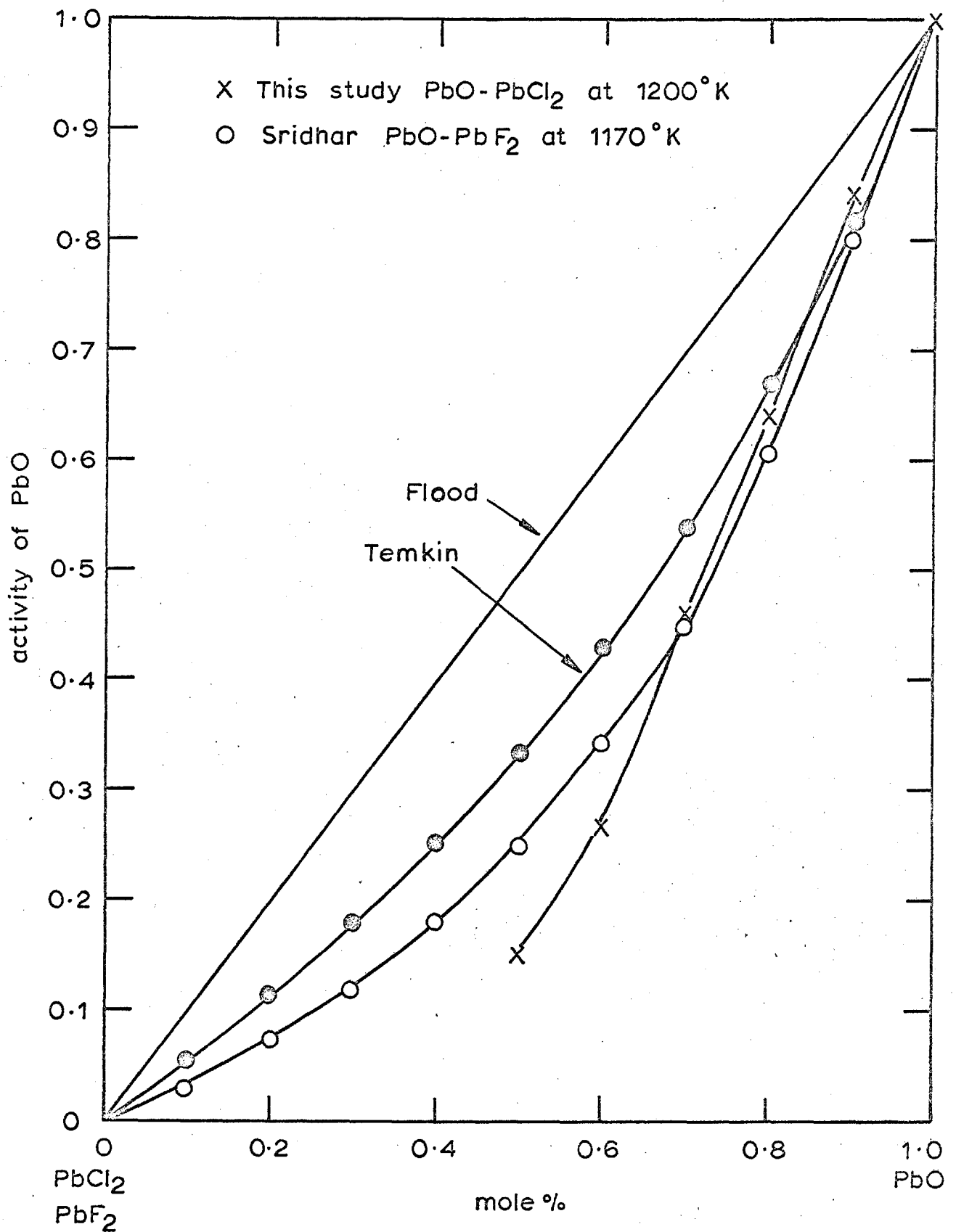


Fig. 46 ACTIVITY OF PbO IN $n\text{PbO.PbCl}_2$ & $n\text{PbO.PbF}_2$ MELTS

The activities of PbO calculated from these two models are shown in Fig 46 . It is apparent that the experimental results are in better agreement with the Temkin model than the Flood, Forland and Grjotheim model.

It has been suggested earlier that the electronic conductivity of pure PbO is not zero as was presumed by Sridhar^(4) but is of the order of 4 to 6%. It seems likely in the light of previous discussion that in a system such as n PbO.PbF₂, that as the concentration of the PbF₂ is increased the melt should become completely ionic in nature. On this reasoning it is probable that the activities of PbO in n PbO.PbF₂ melts should be slightly greater than those given by Sridhar, and are more likely to be in closer agreement with the Temkin model and with the present results for a_{PbO} in the PbO.PbCl₂ system at PbO rich compositions. Thus the deviation of the activity of PbO at the equimolar composition may be larger than suggested from Fig 46 .

The phase diagram was determined by Rudolf Ruer^(71) in 1906 and the compounds PbO.PbCl₂, 2PbO.PbCl₂ and 4PbO.PbCl₂ were suggested, although the PbO liquidus was not altogether clear. Using this liquidus, the activities of PbO can be calculated, using the value of ΔH_f determined in the present study and the melting point of PbO given by Rodigina^(37). These activities are shown in the following table:-

TABLE 20.

Composition N _{PbO}	Temperature liquidus	1. a _{PbO} phase diagram	a _{PbO} exp	Exp. liquidus temperature
0.95	844°C	0.88	0.92	860°C
0.90	780°C	0.74	0.84	822°C
0.866	736°C	0.64	0.78	793°C

The experimental PbO liquidus temperature can be calculated from the experimental results and are also shown in the table above. The experimental results do suggest that the PbO liquidus is not as steep as suggested by the 1906 phase diagram.

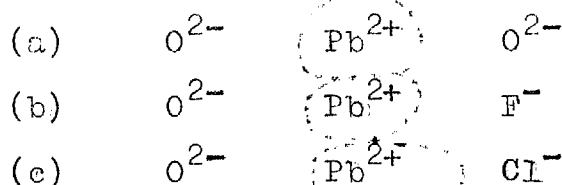
It is evident that the deviation from the Temkin model is very much greater in the case of the n PbO.PbCl₂ melts than for the n PbO.PbF₂ melts, the deviation being more marked as the mole fraction of PbO decreases. This deviation may be explained in terms of the polarising power of the anions.

Consider the three cases:-

(a) Firstly the case where two oxygen anions are the nearest neighbours to a Pb²⁺ ion.

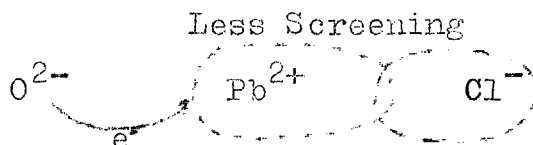
(b) Secondly when the nearest neighbours to a Pb²⁺ cation are an oxygen ion and a fluoride ion.

(c) Thirdly, when these nearest neighbours are an oxygen ion and a chloride ion.



$\frac{e}{r}$
$\frac{2}{1.4} = 0.7$
$\frac{1}{1.36}$
$\frac{1}{1.81}$

The polarising power of an anion is proportional to $\frac{e}{r}$, where r is the ionic radius. The polarising power of oxygen ions is greater than that of fluoride ions, which in turn is greater than that of chloride ions. In the first case one could consider the electron cloud surrounding the lead ion as being completely symmetrical, since the polarising power and hence the effective 'push' of the two oxygen ions on the electron cloud is exactly equal. However in the second case the polarising power of the fluoride ions is slightly smaller than that of the oxygen ions, in other words the effective push by the oxygen ions on the electron cloud surrounding the Pb^{2+} ion is greater than that exerted by the fluoride ion. In the third case this effect is even more marked, with the result that the electron cloud surrounding the lead cation will be distorted well over towards the chloride anion.



The result is that there is less screening around the nucleus, which in turn causes electron flow from the oxygen atom towards the lead, and increases the covalency of the lead oxygen bond. Thus it seems reasonable that the nature of the lead oxygen bond is more covalent in the presence of chloride ions than in the presence of fluoride ions, which will result in the lowering of the oxygen ion activity in the former

case. Since the Temkin model gives $a_{\text{PbO}} = N_{\text{O}^{2-}}$, then this effect explains the experimental result.

It appears from plots of $RT \ln Y_{\text{O}^{2-}}$ versus $N_{\text{O}^{2-}}$ (Temkin), and $RT \ln Y_{\text{O}^{2-}}$ versus $N_{\text{O}^{2-}}$ (Flood), shown in Fig 47, that these $n \text{ PbO} \cdot \text{PbCl}_2$ melts do not exhibit regular solution behaviour, since for a regular solution $RT \ln Y_{\text{O}^{2-}} = k N_{\text{F}}^2$, where k is temperature invariant. When $N_{\text{F}} = 0$, then $RT \ln Y_{\text{O}^{2-}} = 0$, which must fix one point. The deviation from regular solution behaviour is much larger using the Temkin model than the Flood model. The inference is that the entropy of mixing is not ideal. This is not very surprising on consideration of the interactions that have been discussed.

The activity of PbCl_2 determined by the vapour entrainment technique at 629°C is shown in Fig 31, Chap 10 together with the activity of PbO with reference to liquid PbO at 629°C from the E.M.F. technique. By extrapolating a_{PbCl_2} to $N \text{ PbO} = 0.5$, the activity curves for the two components have been completed using a Gibbs Duhem integration. The activity of PbCl_2 from the phase diagram can be calculated using the values for the latent heat of fusion and the temperature of fusion of pure PbCl_2 given by Blanc and Petit⁽⁷²⁾ $\Delta H_{\text{fusion}} = 5.7 \text{ Kcals/mole}$, melting point $\text{PbCl}_2 = 768^\circ\text{K}$.

The results are shown in the following table:-

Fig. 47 ⁻¹⁹¹⁻ $RT \ln Y_{O_2}$ vs. N_F^2 - at 1100°K & 1200°K (Temkin)

$RT \ln Y'_{O_2}$ vs. N_F^{2-} " " " " (Flood)

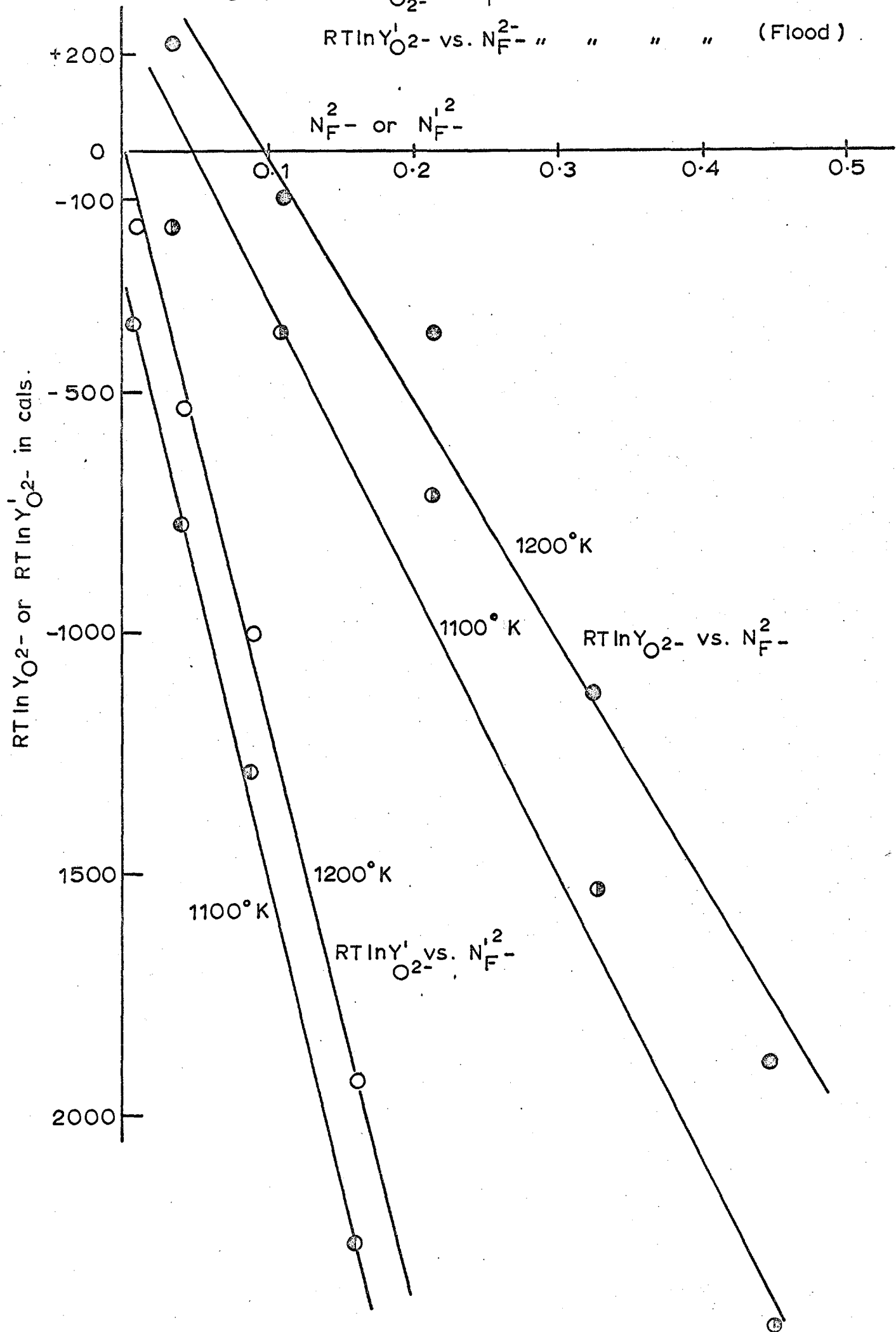


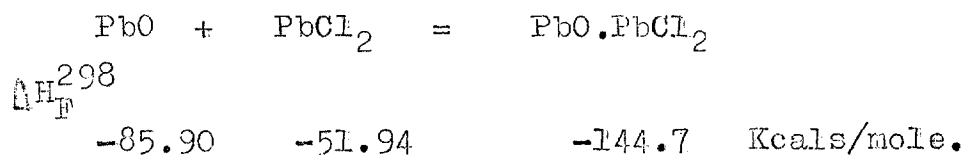
TABLE 21.

Composition N PbCl ₂	Temperature of liquidus	^a PbCl ₂ phase diagram	^a PbCl ₂ experimental
0.9	470°C	0.882	0.85±0.13
0.8	438°C	0.741	0.75±0.13

These phase diagram activities are in good agreement with the experiment although no conclusions as to the validity of the PbCl₂ liquidus can be drawn because of the relatively large error in the values of the experimental activities. After calculation of the partial free energies, the integral free energy of mixing was determined from the equation:-

$$\Delta G_M = N_1 \Delta G_1 + N_2 \Delta G_2 \quad \text{and is shown in Fig 48 .}$$

The temperature dependence on the activity of PbCl₂ was not determined because the accuracy of the activity measurements did not merit such experiments. However the heat of formation of PbO.PbCl₂ (N PbO= 0.5) is given in the National Bureau of Standards 1952 as well as the heats of formation of PbO and PbCl₂, all values given being at 298°K .



$$\text{Therefore } \Delta H_{\text{Reaction}}^{298} = - 6.86 \text{ Kcals/mole.}$$

$$(\Delta H_M \text{ at } 298^\circ\text{K} = -3.43 \text{ Kcals/ mole oxides.})$$

The values ΔH_{298}^{902} for PbO and PbO.PbCl₂ were measured in the calorimeter by the drop method. The value ΔH_{298}^{902} for PbCl₂ was taken from the JANAF tables.

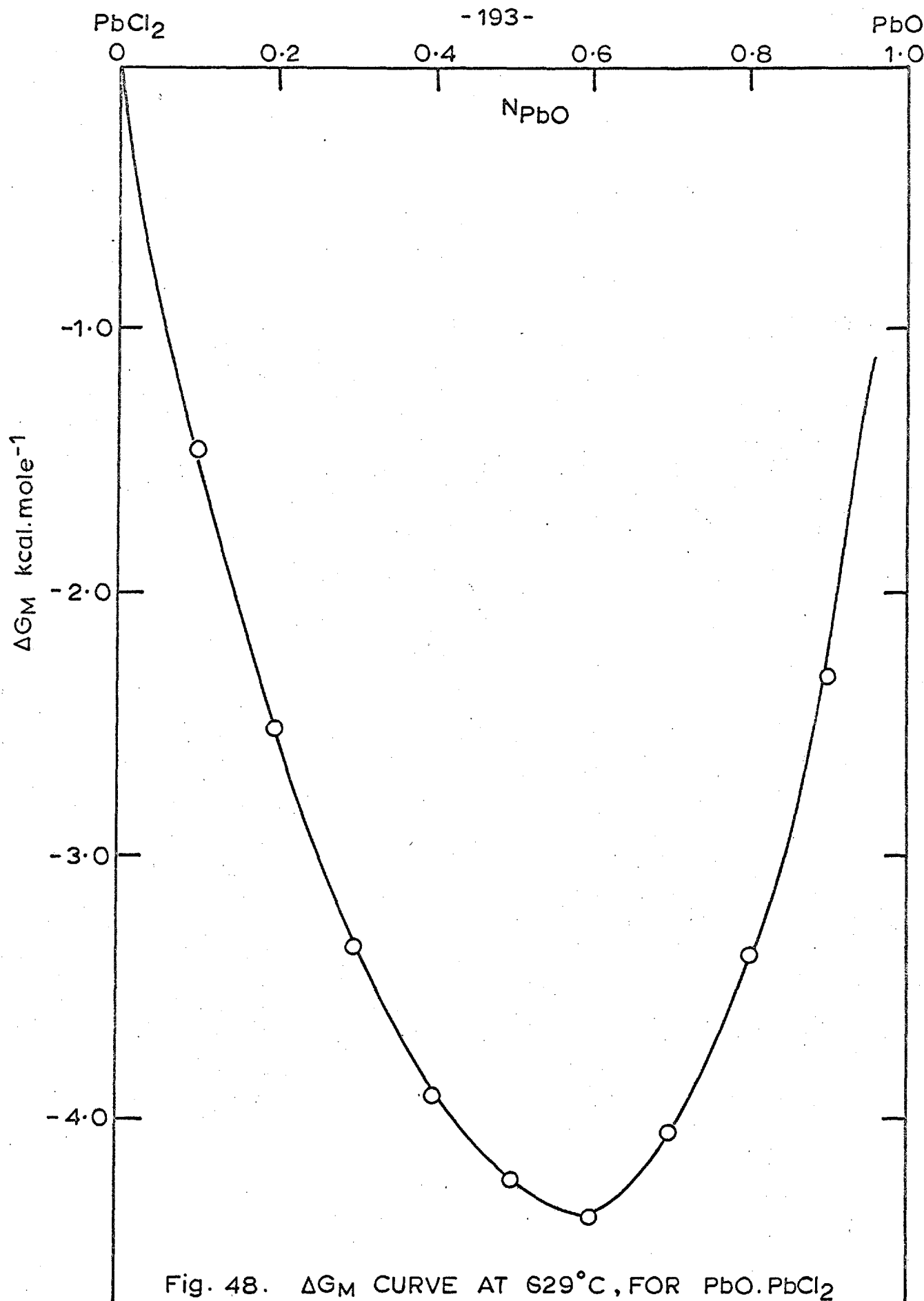
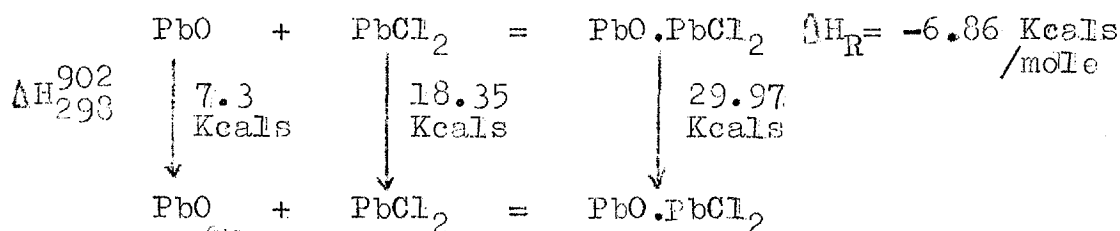


Fig. 48. ΔG_M CURVE AT 629°C, FOR PbO.PbCl₂ MELTS, WITH REFERENCE TO LIQUID PbCl₂ & LIQUID PbO.



$$\Delta H_{298}^{902} = \int_{298}^{902} C_p dT$$

Therefore $\int_{298}^{902} C_p dT = + 4.32 \text{ Kcals/mole with reference to solid PbO}$

$= - 2.05 \text{ Kcals/mole with reference to liquid PbO}$

Therefore $\Delta H_{\text{Reaction}}$ at $902^\circ\text{K} = - 8.91 \text{ Kcals/mole}$
(ref liquid liquid PbO)

Therefore $\Delta H_{\text{Mixing}} = - 4.455 \text{ Kcals/ mole oxides.}$

The partial heats of PbO were determined in the E.M.F. experiment, Table 10 , Chapter 5 (5).

Using the equation $\Delta H_M = N_1 \Delta \bar{H}_1 + N_2 \Delta \bar{H}_2$, and a Gibbs Duhem integration:-

$$\Delta \bar{H}_2 = - \int_{N_1=1}^{N_1=N_1} \frac{N_1}{N_2} d\Delta \bar{H}_1$$

$\Delta \bar{H}_2$ was calculated over the composition range in which $\Delta \bar{H}_{\text{PbO}}$ was measured; where subscript 2 in this case signifies PbCl_2 .

The resulting integral heat of mixing curve is shown in Fig 49, together with ΔH_M of PbO.PbF_2 as determined by Sridhar (4) at 1170°K . A comparison of this integral heat curve with the integral free energy curve shown in Fig 48 results in the integral entropy of mixing curve which is shown in Fig 49 .

Unfortunately no firm conclusions can be drawn from this curve, except that it does suggest an error in the ΔH_M curve of at least 1 Kcal, since it is to be

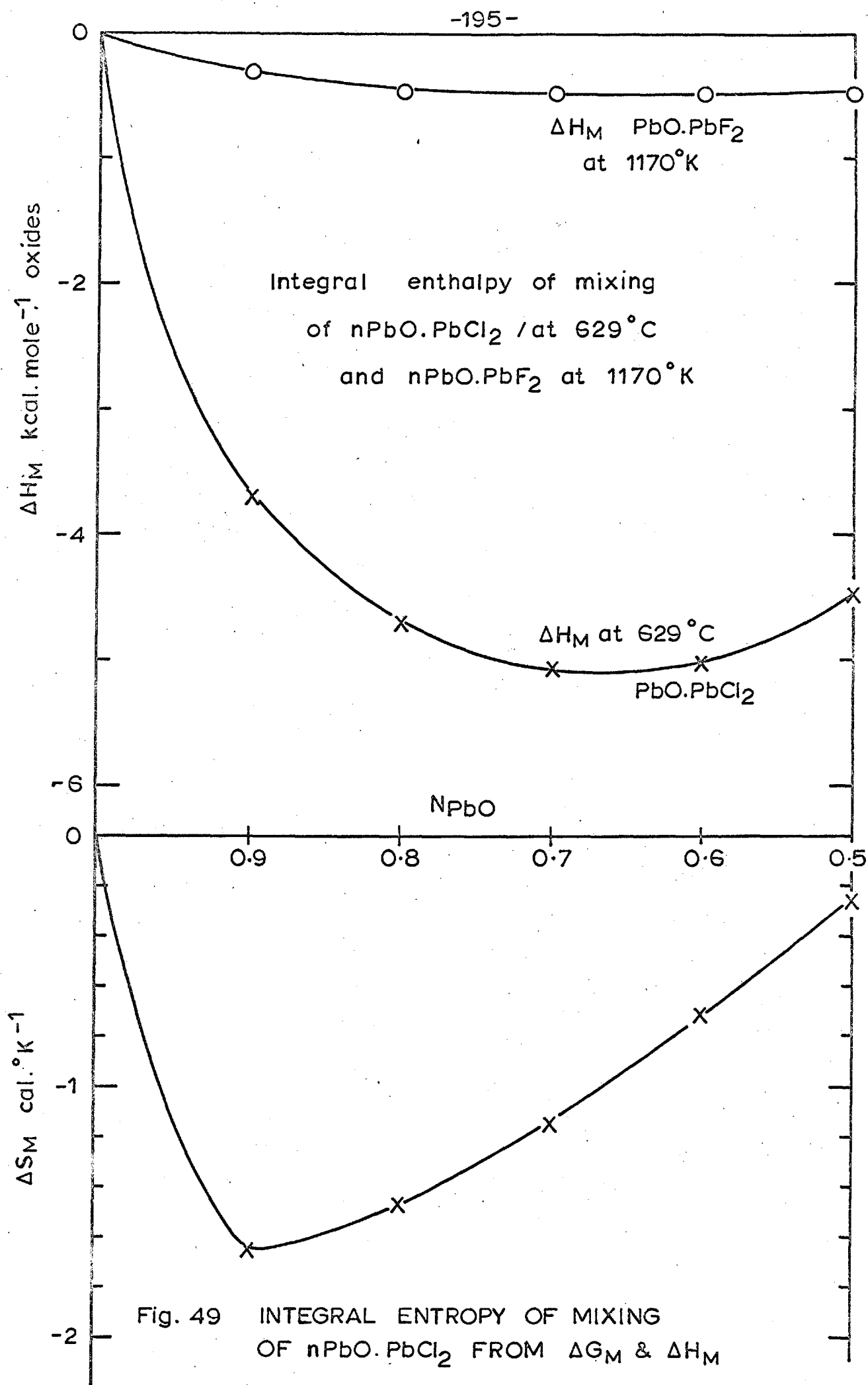


Fig. 49 INTEGRAL ENTROPY OF MIXING OF nPbO.PbCl₂ FROM ΔG_M & ΔH_M

expected that ΔS_M should be positive. This error is not surprising on consideration of the method undergone to calculate ΔH_M . It would be an excellent idea to measure ΔH_M more directly at the temperature 902°K in the calorimeter in the near future.

Lumsden^(73) has considered the heats of mixing of two molten alkali-metal halides with a common anion in terms of the interionic distances, the London dispersion forces and the polarisation energy.

Sridhar^(4) has considered this approach in his discussion on $PbO.PbF_2$ melts in which a common cation is surrounded by anions of different valencies. The non polar London forces acting between the ions is an energy which is proportional to $\frac{1}{r^6}$ where r is the distance between the centres of the ions. In fact $E = -C_L \times \frac{1}{r^6}$, and C_L is the London constant. This is the attractive force between nearest neighbours and is only important at very small values of r . Sridhar however has pointed out that the London force contribution cannot be calculated at present because of the lack of data on the London constants for O^{2-} & F^{2-} . However his consideration of the $PbO.PbF_2$ melts indicates that the contribution to the heat of mixing from London forces is small.

The heat of mixing has been given by Lumsden^(73) as:- $\Delta H = k \frac{xy}{x+y}$, where x and y are the number of moles of PbO and $PbCl_2$ respectively, and $k = k_P + k_L$.

$$E_{\text{London}} = k_L \frac{xy}{(x+y)}$$

$$\text{and } E_{\text{Polarisation}} = k_P \frac{xy}{(x+y)}$$

For the PbO.PbF_2 system, Sridhar has derived the expression:-

$$K_p = -8Ne^2 \left[\frac{1}{r_{\text{Pb-O}}^2} + \frac{1}{r_{\text{Pb-F}}^2} \right]^2$$

($= \frac{\alpha F^2}{2}$, where α is the polarisability of Pb^{2+} given by Frank to be $4.34 \text{ \AA}^3$, and F is the electric field.)

This expression was derived by assuming that the $\text{O}^{2-} \text{ Pb}^{2+} \text{ O}^{2-}$ polarisation is similar to $\text{X}^+ \text{ Z}^- \text{ Y}^+$ in the systems considered by Lumsden. Using $r_{\text{Pb-O}} = 2.49 \text{ \AA}$ and $r_{\text{Pb-F}} = 2.57 \text{ \AA}$, then $k_p = 0.259 \text{ Kcals/mole}$

and not 1.1 Kcals/mole as quoted by Sridhar.

Using $r_{\text{Pb-Cl}} = 3.01 \text{ \AA}$, then k_p from this expression becomes 6.89 Kcals/mole. It is important to note that these values of k_p are very dependent on the value of $r_{\text{Pb-O}}$ which is uncertain. The difference between these two values of k_p goes a long way to explaining the difference observed between the heats of mixing of $n \text{ PbO.PbF}_2$ melts and $m \text{ PbO.PbCl}_2$ melts.

Kleppa and McCarty⁽⁷⁴⁾ have considered the thermochemistry of some charge-unsymmetrical binary fused halide systems basically in terms of the competition between the two cations for the common anion. They have confirmed the statement of Davis⁽⁷⁵⁾ that the interaction parameter $\lambda = \frac{H_M}{X(1-X)}$

(where X is the mole fraction), in a family of related systems to the first approximation is linearly dependant on the parameter $\delta_{12} = \frac{(d_1 - d_2)}{d_1 d_2}$, where d_1 and d_2 are the interionic distances of the relevant salts. They have also shown that λ tends to zero as δ_{12} tends to zero.

This would appear to be a useful correlation for the present systems and the result is shown in Fig 50 . The origin can be considered as the third point. It would be an interesting exercise to measure the heats of mixing in this system, in n $\text{PbO} \cdot \text{PbF}_2$, $\text{PbO} \cdot \text{PbBr}_2$ and $\text{PbO} \cdot \text{PbI}_2$ calorimetrically to determine whether this correlation is valid in such systems.

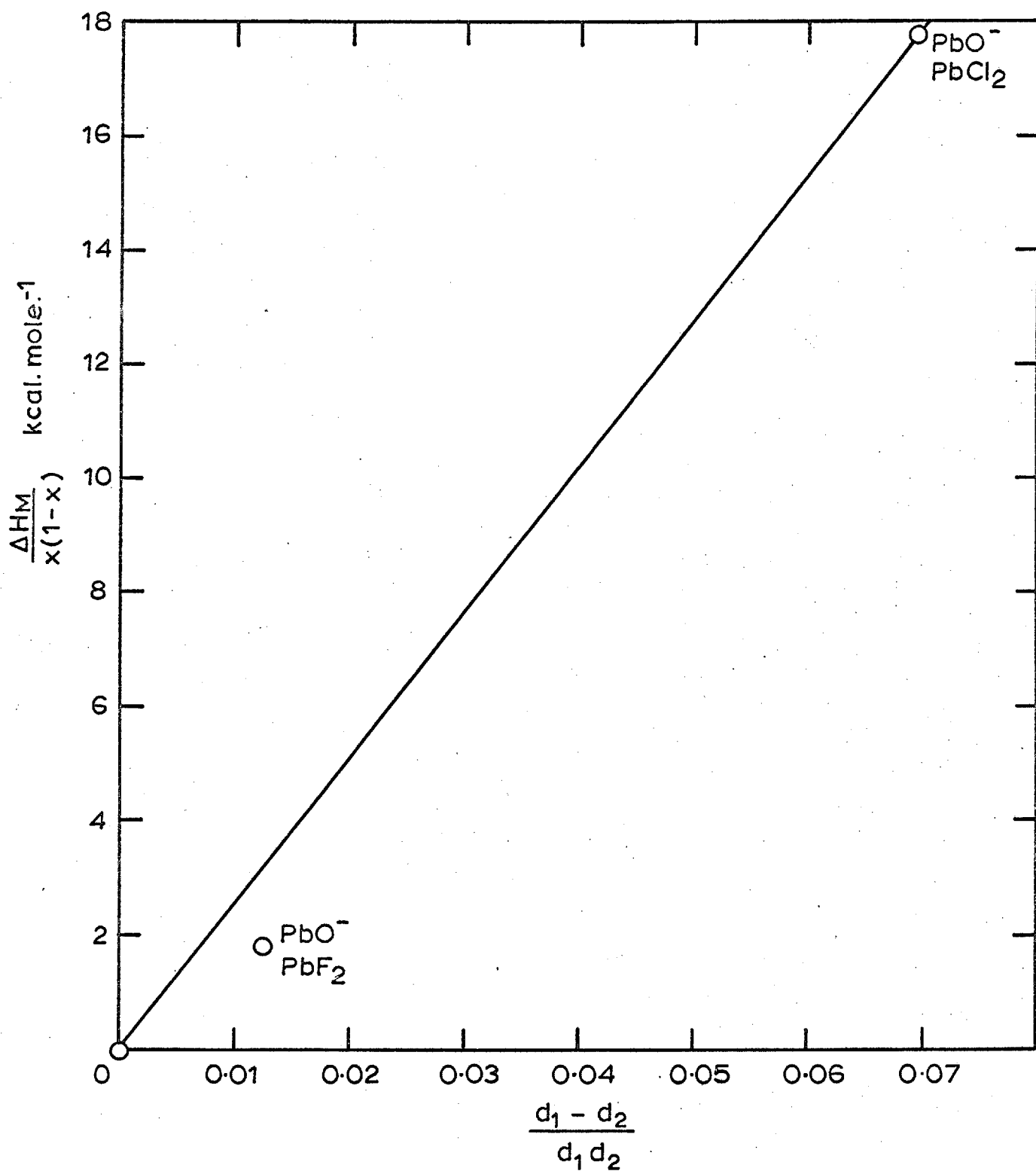
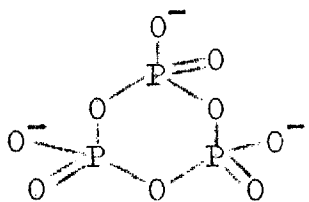


Fig. 50 $\frac{\Delta H_M}{x(1-x)}$ AT $x = 0.5$, vs. $\frac{d_1 - d_2}{d_1 d_2}$.

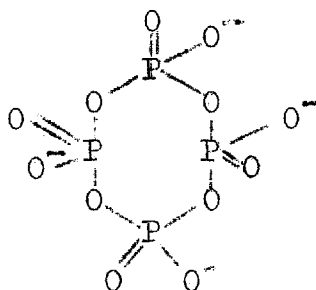
Chapter 12.

RING-CHAIN EQUILIBRIA IN THE SODIUM METAPHOSPHATES.

The structures of the phosphate systems are all based on the fundamental PO_4^{3-} tetrahedron. The two simple ring metaphosphates which are of interest to this study are the trimetaphosphate ring and the tetrametaphosphate ring. In two dimensions these structures may be represented as follows:-



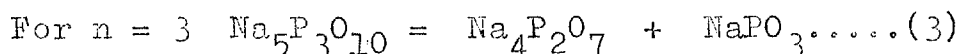
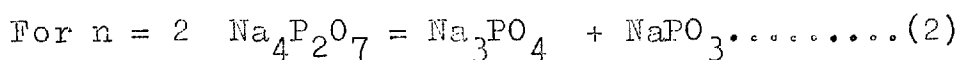
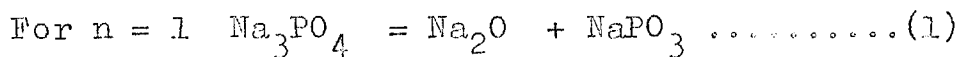
Trimetaphosphate ring.



Tetrametaphosphate ring.

The alternative to the ring structure is the chain structure which for a univalent cation is represented by the formula $\text{M}_{n+2}\text{P}_n\text{O}_{3n+1}$ where n is an integer.

It is of interest to consider the thermodynamics associated with removing an NaPO_3 group from a ring or a chain. In order to do this consider the following equations:-



The entropy data which have been measured by Andon, Cournell, Martin and Mash (76) for the sodium phosphates

TABLE 22.

Compound	S_{298}° cals/deg/mole	ΔH_f^{298} Kcals/mole
$(\text{NaPO}_3)_3$	68.47	-878.6
$(\text{NaPO}_3)_4$	-	-1169.4
$\text{Na}_4\text{P}_2\text{O}_7$	64.60	-763.7
$\text{Na}_5\text{P}_3\text{O}_{10}$ I	91.25	-1056.5
II	87.37	-1059.1
Na_3PO_4	41.54	-459.7
Na_2O	17.0	-100.7

are given in Table 22 together with the heats of formation recently measured by Irving (31-34). The data for Na_2O has been taken from the tables of Kubaschewski, Evans and Alcock (28).

If one considers equation (1), then the entropy associated with the removal of an NaPO_3 group from a chain is $41.54 - 17.0 = 24.54 \text{ cal/}^\circ\text{K}$ (77) where $n = 1$

Similarly when $n = 2$ $S_{298}^0 \text{ NaPO}_3 = 23.10 \text{ cal/}^\circ\text{K}$

$n = 3$ $S_{298}^0 \text{ NaPO}_3 = 22.77 \text{ cal/}^\circ\text{K}$

The entropy associated with each NaPO_3 group in the trimetaring structure is $\frac{68.47}{3} = 22.82 \text{ cal/}^\circ\text{K}$.

A similar calculation can be performed with the heats of formation.

When $n = 1$ the heat of formation per NaPO_3 group
 $= -359.0 \text{ Kcals/mole.}$

When $n = 2$ the heat of formation per NaPO_3 group
 $= -304.0 \text{ Kcals/mole}$

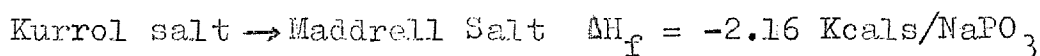
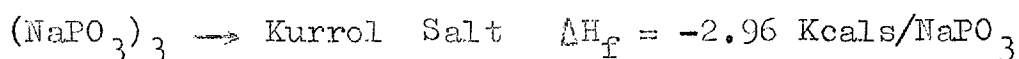
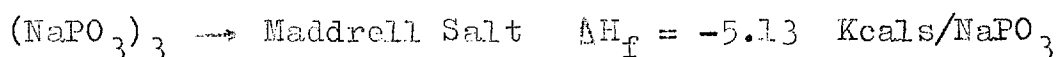
When $n = 3$ the heat of formation per NaPO_3 group
 $= -295.4 \text{ Kcals/mole.}$

If one considers the ring structures, then the heat of formation per NaPO_3 unit in the trimetaring
 $= -292.9 \text{ Kcals/mole}$ and in the tetrametaring
 $= -292.3 \text{ Kcals/mole.}$ The error in the latter calculations being approximately 0.5 Kcals/mole.

It has been well established (59) that as the average chain length increases there is a tendency for

rings to form. When n , the average chain length = 4 there are no rings present, but as $n \rightarrow \infty$ the percentage of P_2O_5 present as rings is about 8%. This tendency to form rings now becomes more apparent in the light of the thermodynamical data, since as the chain length increases the entropy and the heat of formation of each $NaPO_3$ unit in a chain structure tends towards that of each $NaPO_3$ unit in the ring structures. In order to summarise, it can be said that the heats of formation and S_{298}^0 data per $NaPO_3$ unit in a long chain are similar to those with the ring structure.

In the present study the heats of formation of sodium Kurrol salt and sodium Maddrell salt have been measured with reference to sodium trimetaphosphates. The result is given by the equations:-



Both the Maddrell and Kurrol Salts are infinitely long chains of sodium metaphosphate. An Xray structure study has been carried out (78) on sodium Maddrell salt and it was found to consist of long $O-P-O-P-O$ chains made up of interconnected PO_4^{3-} groups, the pattern of the chain repeating itself every three units. Although the structure of the sodium Kurrol salt has not been studied extensively, an Xray study was carried out on the rubidium Kurrol salt. This structure

consisted of two spiralling continuous O-P-O-P-O chains interlinked with one another. The spirals of the two chains being in opposite directions around the screw axis of the crystal. A Debye Scherrer Xray powder pattern which was taken in the present study for the Kurrol Salt exhibited all the 'd' spacings expected for a cyclic trimetastructure and a few other weaker lines. This result suggests that in fact the Kurrol salt is formed by the stacking of cyclic groups, and then the breaking of the necessary bonds, with the formation of new bonds, to form the double chain intertwined structure.

These structures are comparable with infinite chain silicates, which are based on the SiO_4 tetrahedron. The silicate structures however are slightly more complex because there are four reactive groups per silica atom present in the case of the silicates, whereas there are only three reactive groups per phosphorus atom in the phosphates. The infinitely long single chains which are well known (79) are the pyroxenes, and these include enstatite Mg SiO_3 . Also amphiboles such as tremolite $\text{CaMg}_3 (\text{SiO}_3)_4$ which are infinite double chains, are known. In the case of the borates however only the infinite single chains e.g. CaB_2O_4 are known, which is possibly because boron can have three or four coordination.

It is apparent from the present study that the driving force involved in converting cyclic trimetaphosphate to Kurrol salt is small, which explains the difficulty reported by Albright and Wilson^(80) in the preparation of the Kurrol salt. This is not surprising if it is as easy to form ring structures as it is to form infinite chains.

The Kurrol salt is a quenched metastable structure and to form Maddrell salt, which is the stable form at room temperature, it is necessary to separate the two chains present in the Kurrol salt, by breaking the relevant links and straightening out the chains. The heat of transition for this process was found to be $-2.16 \text{ Kcals/NaPO}_3$.

In the calcium silicate system, two infinite chain structures exist, namely pseudo wollastonite which appears to be analogous in nature to the Kurrol salt, and wollastonite which is an infinite straight chain analogous to the Maddrell salt. Kubaschewski^(28) gives the heat of transition of pseudo wollastonite to wollastonite at 1190°C as -1.3 Kcals which is an interesting comparison with the value found in this study for the transition Kurrol salt to Maddrell salt.

Chapter 13.

CONCLUSIONS.

The necessity for using a suitable solid electrolyte has become apparent, since pure PbO (liquid) appears to exhibit about 4% electronic conductivity. The results obtained from the cell used in this study support the value for the latent heat of fusion $\Delta H_f \text{ PbO} = 6.37 \pm 0.4 \text{ Kcals/mole}$ which was determined calorimetrically, and finally disperses any shadow of doubt on the value for the latent heat of fusion of lead oxide.

A study of the lead silicate system by this author and various other workers, indicates positive deviations from the Temkin model at compositions richer in PbO than the orthosilicate composition, when the only ions present are presumed to be O^{2-} , Pb^{2+} and SiO_4^{4-} . This result suggests that polymerisation of the silicate ions begins at richer PbO compositions than has previously been postulated. If the only ions which are present in the composition range $N \text{ PbO} = 0.8$ to $N \text{ PbO} = 0.6$, are SiO_4^{4-} and $(\text{SiO}_3)_3^{6-}$ as postulated by Flood and Knapp⁽¹⁶⁾, then the value of the equilibrium constant K of 1.599 fits the present data as well as the value $K = 0.0225$ fits the data obtained by Richardson and Webb⁽¹⁵⁾. It is unlikely however that these are the only silicate species present in this composition range.

Masson's molecular size distribution theory fits the activity data for PbO in n PbO.SiO₂ melts reasonably well along the whole composition range with a value of k_{11} between 0.42 and 0.55, whereas a value of $k_{11} = 0.196$ fits Richardson and Webb's activity data quite well. The activities of PbO calculated from the Flory distribution are in fairly good agreement with the experimental data with the same equilibrium constants in the lead rich compositions, but as the silica concentration is increased, a_{PbO} calculated from the Flory distribution tends to infinity.

The enthalpy data derived in the present study for the lead silicate system appears to be in fairly good agreement with the calorimetric heats measured by Kleppa⁽⁷⁾. The resulting entropy data determined by the combination of ΔG_M and ΔH_M tends to fit the model of random mixing of PbO and Pb₂SiO₄ in which SiO₄⁴⁻ undergoes a polymerisation reaction of the type:- $2\text{SiO}_4^{4-} = \text{O}^{2-} + \text{Si}_2\text{O}_7^{6-}$, rather than the model of random mixing of PbO and SiO₂.

Darken's excess stability function supports the view that the largest change in structure takes place at approximately the orthosilicate composition in the lead silicate system as well as the n CaO.SiO₂, n FeO.SiO₂ and n SnO.SiO₂ systems. This composition in the lead, calcium and iron silicate systems corresponds to the compound 2MO.SiO₂, and thus it is

suggested that the compound $2\text{SnO} \cdot \text{SiO}_2$ should exist, even if it is only metastable.

The enthalpy data and excess stability function determined in the lead phosphate system support the suggestion made by Sridhar^(57) that the ion PO_5^{5-} exists at very rich PbO compositions. It is suggested that the reaction $\text{PO}_5^{5-} \rightarrow \text{PO}_4^{3-} + \text{O}^{2-}$ occurs as the P_2O_5 content is increased, followed by polymerisation of the PO_4^{3-} ions. The enthalpy data determined by Kleppa^(8) of the lead borate system tends to support the suggestion^(4) that the ion BO_4^{5-} exists at the lead rich compositions.

In the $n \text{ PbO} \cdot \text{PbCl}_2$ system, it has been shown that the presence of chloride ions lowers the oxygen ion activity to a much greater extent than the presence of fluoride ions. This has been explained in terms of the relative polarising powers of the relevant anions. Also the heats of mixing in the $n \text{ PbO} \cdot \text{PbCl}_2$ system are correspondingly larger than in the $n \text{ PbO} \cdot \text{PbF}_2$ system, which has again been shown to be attributed to polarisation.

A study of the thermodynamical data available for the sodium phosphates indicates that the entropy and heat requirements necessary to place an NaPO_3 group into a ring structure are similar to those required to place such a grouping into a long chain structure, which supports the evidence that long

chains contain a certain proportion of rings.

It is suggested that the structure of sodium Kurrol salt is based on the sodium trimetaphosphate structure, with the necessary rearrangement of bonds to produce two intertwined infinite double chains, which spiral in opposite directions along a screw axis. The heat of conversion from this structure, which is a high temperature metastable compound, to Maddrell salt, which is an infinite single chain, was found to be -2.16 ± 0.36 Kcal's/ NaPO_3 , which appears to be analogous to the transition of pseudo wollastonite to wollastonite in the $n \text{ CaO} \cdot \text{SiO}_2$ system.

Appendix.

An attempt to study silicate structures.

Up to the present time the structure of silicate melts has only been postulated from the experimental results of various structure sensitive properties, and from the present day knowledge of the structures of the phosphates. Earlier in the present study structural aspects of the silicates have been deduced from thermodynamical measurements.

A number of attempts have been made to separate the silicate species by Lentz (81) and by Sridhar (4), and it appears that the main stumbling block is the relative ease of hydrolysis of the silicates to form condensed polysilicates (silica gel). In the case of the phosphates however, hydrolysis is slower and at 3-4°C is slow enough to permit a chromatographic separation of the species using an aqueous solvent. Lentz (81) has attempted to make trimethylsilyl derivatives of various silicate minerals followed by a chromatographic separation, but it seems unlikely that the structures deduced from these results are representative of the structure of the original mineral, simply from hydrolysis considerations. Sridhar (4) has recognized this fault, and has attempted to methylate sodium silicates with dimethyl sulphate. Although he has demonstrated that the heat of such a methylating reaction is very exothermic,

unfortunately no methyl derivative was produced.

Various workers (82) have considered the esterification of sodium and potassium clays to produce an esterclay. Although direct esterification with the sodium clay proved unsuccessful, however in the esterification of potassium clays a reaction did occur to some extent since potassium iodide was formed. An explanation for the lack of reaction with the sodium clays was attempted in terms of the ionic sizes of sodium and potassium ions, and the sizes of the hexagonal voids in the lattice. As the clays are considered as being analogous to the binary silicates, an attempt was made by this author at an esterification process with lead silicate rather than sodium silicate.

The proposed reaction can be represented by:-

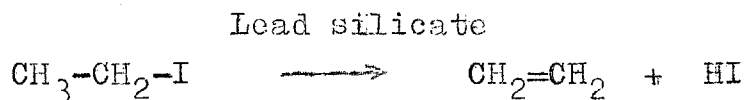


was considered. The heat of such a reaction determined from the heats of formation of each of the components is $\Delta H_R = -59.4$ Kcals and this is thus thermodynamically possible.

The reaction was carried out in a controlled atmosphere of dry nitrogen by boiling under reflux with firstly ethyl alcohol and then toluene. The experiment was also attempted at room temperature. In every instance lead iodide was formed, which suggested a successful esterification process. However no ethyl silicate was detected on the G.L.C.

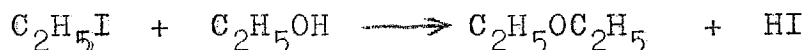
chromatogram and attempts at separating such a product, by fractional condensation also failed.

It seems likely that a reaction represented by the equation:-



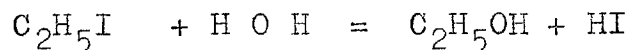
occurs at the surface of the lead silicate. The hydriodic acid could then react with the lead silicate to form lead iodide, and the C_2H_4 would be lost in the refluxing operation.

Another possibility is the reaction:-



This is unlikely however since no $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$ was detected in the G.L.C. chromatogram and also lead iodide was formed under reflux in toluene.

Another real possibility could result from the presence of absorbed water which could react with the ethyl iodide to form hydriodic acid and alcohol:-



It is of interest to note that at least eight silicate species have been separated from organic silicates, which were formed by an organic preparation, by liquid gas chromatography. This knowledge is of utmost importance, if one wishes to consider the structures of the silicates in an analogous manner to those of the phosphates.

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