SULPHUR CAPACITIES OF $CaO-Na_2O-SiO_2$ SLAGS

A THESIS

submitted in fulfilment of the requirements
for the award of the degree
of
DOCTOR OF PHILOSOPHY
in
METALLURGICAL ENGINEERING

By

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November, 1983

to
my
PARENTS

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled, "SULPHUR CAPACITIES OF $CaO-Na_2O-SiO_2$ SLAGS" in fulfilment of the requirement for the award of the Degree of Doctor of Philosophy, submitted in the Department of Metallurgical Engineering of the University is an authentic record of my own work carried out during a period from ~~November~~ Dec. 1980 to ~~May~~ Nov. 1983 under the supervision of Dr. M.L. Kapoor, Dr.G.C.Kaushal and Dr.S.S.Gupta.

The matter embodied in this thesis has not been submitted by me for the award of any other degree.

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This is to certify that the above statement made by the candidate is correct to the best of our knowledge.

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ABSTRACT

Quality raw materials having lower percentage of unwanted elements like sulphur are depleting with time and at the same time development of new special alloys warrants very low sulphur content. These constraints are sufficient to keep the metallurgists and material scientists engaged in study of behaviour of sulphur in metals, alloys and slags necessary to develop processes to produce quality alloys at economical price. Extensive work has been done in past on removal of sulphur during extraction and refining but at the cost of productivity and economy. However, external desulphurisation has off late proved to be quite useful process for removal of sulphur in between iron making and steel making stages. Still, substantial work may be done to optimize the external desulphurization process with regard to the technology and desulphurising agents used to improve the economy of the process. Soda base slags have been established to be very useful for bringing down the sulphur level in the melts. However, they can not be used successfuly during smelting and refining as they attack the refractory lining and give out irritating fumes.

In external or ladle desulphurisation use of soda base slags may be made more efficiently because of low temperatures prevalent bringing down the magnitude of slags attack on refractories. However, only a few studies carried

out on external desulphurization using soda-slags but the data obtained has evoked the need for detailed study on soda-based slags.

The present work has, therefore, been taken up to study systematically the soda-silica binary system and the effect of lime additions on the sulphur capacity of soda-silica slags. Thus, the binary Na_2O-SiO_2 and ternary $CaO-Na_2O-SiO_2$ slag systems of varying compositions have been selected for experimental study using gas condensed phase equilibria technique. The slag samples have been equilibrated with a gas phase of known sulphur and oxygen potentials. The sulphur capacities of binary soda-silica slags with varying Na_2O/SiO_2 molar ratios, namely, 0.26, 0.40, 0.52, 0.84, and 1.03 at temperatures 1373, 1423, 1473, 1523 and 1573 K have been determined. Effects of lime additions in soda-silica slags of the above mentioned Na_2O/SiO_2 ratios on their sulphur capacities at the same temperatures have also been studied. Oxygen and sulphur-di-oxide potentials ranged in between 10^{-11} to 10^{-8} and 0.07 to 0.10 atm. respectively. Oxygen potentials were measured in different gaseous mixtures using a suitably designed oxygen sensor.

The entire text of the dissertation has been spread over five chapters.

Chapter 1 has been devoted to the brief introduction of the problem and critical review of literature comprising of different techniques used and various systems studied for determination of sulphur capacity.

Design and fabrication of experimental set-up has been described in detail in Chapter 2. A detailed description has also been given on materials and methods used in the present work.

Chapter 3 deals with the experimental results and discussion for the binary Na_2O-SiO_2 system. Results of present investigations have been analysed and compared with the existing data on soda-silica slag and other binary silicate systems.

In Chapter 4 the experimental results and discussion for the ternary $CaO-Na_2O-SiO_2$ system have been reported. Results of present work are compared with the earlier work on this system and other ternary silicate systems.

In Chapter 5, the experimental results on sulphur capacity of soda base binary and ternary slag systems have been summarized and concluded.

ACKNOWLEDGEMENTS

The author deems it his profound privilege to record, with a deep sense of gratitude, his indebtedness to Dr.M.L. Kapoor, Professor in Extractive Metallurgy and Head of the Department of Metallurgical Engineering, Universsity of Roorkee, Roorkee, for not only suggesting the problem of the present investigation but also his timely, relentless and untiring assistance, able guidance as also the fruitful and constructive criticism during the entire period of experimentation and preparation of this dissertation. He would also like to record very sincerely and most humbly the valuable suggestions and fruitful discussions and criticism, he received from his co-superisors- Dr.G.C.Kaushal, Lecturer at this Department and Dr.S.S.Gupta, Senior Research Engineer (Iron-making Group), R and D Centre, Steel Authority of India Ltd., Ranchi, to enable him to complete his investigation and prepare the dissertation in the form, it is presented now.

Sri V.N.S.Mathur and Dr.R.D.Agrawal- both Readers at this Department, have been source of constant encouragement due to their ready availability for discussions and valuable advice at all stages of this work. Sri Surendra Singh, Lecturer at this Department has rendered invaluable help in correcting the typed manuscript of this dissertation. The author wishes to record his very sincere gratefulness to all three of them.

My friends Sarvasri K.C.Sharma, K.S.Pande, S.K.Gupta, N.C.Jain, A.Misra and Capt.L.P.Dasika have also been a source of strength to me and have given me excellent company and whatever other assistance demanded from them, during the long periods of experimentation. Mr.K.C.Sharma deserves special appreciation for the most readily available assistance rendered in computer calculations and preparation of this dissertation. The author expresses his gratefulness to all of them.

Dr.V.K.Gaur, Dean, Research and Industrial Liaison, University of Roorkee has provided research fellowship for limited period. Steel Authority of India Ltd. has financed the research project. Indian Navy, my present employers helped me during writing of dissertation by granting extension of joining date, M/S Modi Steels, Modinagar and the Director, University Service and Instrumentation Centre, University of Roorkee have provided facilities for chemical analysis of equilibrated slag-samples. Grateful thanks are due to all of them.

Members of technical staff of fabrication laboratory of the Department have assisted in the fabrication of experimental set-up and those of the Thermodynamics and Kinetics Laboratory during the long-hours of experimentation. They all deserve sincere appreciation. Sarvasri S.R.Kaushik, S.B.Sharma, Rakesh Misra, Abdul Razak and Rishipal deserve special mention of the assistance rendered by them.

But for the excellent draftsmanship of Sri M.C.Vaish and meticulous typewriting of Sri R.C.Sharma, this thesis could not be presented in its present form. The author expresses his very sincere appreciation of their efforts.

My wife, Smt.Veena Prasad, deserves special acknowledgement, who not only provided her most affectionate, cheerful refreshing company but also showed exemplary understanding and greatest perseverence by singularly shouldering the entire responsibilities of the family at the home-front, due to gross negligence on my part as a result of my involvement in the present work. My sons, Neerav and Nitin, had also to face similar gross neglect during most of this period. Most affectionate gratitude and sincere appreciation are due to all of them.

Last, but not the least, the author would also express his sincere gratitude to several other friends and authors of research publications, who made available reprints of the papers not available locally.

Roorkee
Dated .1983

Sahab Prasad

CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER -I

GENERAL

1.1 INTRODUCTION

Behaviour of sulphur has always attracted attention of Metallurgists and material scientists involved in alloy development. This element, if present in concentrations in excess of solubility limit tends to 'segregate' generally along the grain boundaries or form inclusions thereby adversely affecting the physical, mechanical and other engineering properties of metals and alloys. The major deleterious effects specially in ferrous alloys includes introduction of hot shortness, increase in hardness and electrical resistance and general reduction in ductility, toughness, forgeability, weldability and corrosion resistance. The degree to which these properties are affected varies in proportion to sulphur content and hardness of such alloys[1]. However, only in case of free machining alloys (specially steels and brasses). This segregation has been advantageously exploited.

Sims and other workers[2] concentrated their efforts on utilisation of sulphur to advantage particularly in steels and developed the concept of 'Sulphide Inclusion Shape Control'. They noticed a consistent and reproducible pattern of these inclusions and also found that a relationship could be worked out between the size, shape and distribution of such sulphide inclusions and ductility of steels. Strong deoxidisers, besides having greater affinity for oxygen, also form sulphides,nitrides and carbides, consequently affecting the composition of these inclusions and hence their effect on properties of steels. Aluminium, for example, changes the size and distribution morphology of oxides as well as sulphides and therefore results in high ductility and low gas-porosity of steels [3]. Hiam[4] also observed an improvement in transverse ductility of steel during cold working by lowering sulphur content but concluded that it was not as effective as that attained by inclusion shape control. Addition of rare-earth elements also change morphology of sulphide inclusions from elongated to spherical shape and hence results in marked reduction in senstivity of steels to hydrogen-induced cracking during welding[5].

Sulphur is invariably associated in pyritic- or sulphatic- form with ores of different metals due to its high reactivity and stability of compounds. It can only be partially removed during ore preparation and is removed invariably either in slags, fumes, vapours or gases emerging out of the furnaces in pyrometallurgical processing of such ores or concentrates. Fuel, especially coke, is another major source of sulphur in the charge of smelting furnaces. The residual sulphur in the refined metallic phase is therefore present as dilute solution because of its low concentrations resulting due to its partitions between the metallic, gaseous and/or slag phases. Lower sulphur steels can therefore be produced using high slag basicities but generally at the cost of 'productivity' and at high production costs resulting from burden adjustment for blast furnaces. Several attempts were therefore made for external desulphurisation of hot metal. Moore[6] has described the different techniques used successfully for such external desulphurisation of iron and steel. A good desulphuriser should obviously be low in cost, give reproducible results, evolve minimum toxic fumes and dust, form stable sulphides of desirable morphology and react in a non-violent manner.

For production of low sulphur, high purity steel metals, therefore, the significance of sulphur transfer capacity of refining slags or gaseous phases can not be over-emphasized. Several studies have therefore been made in the recent past for determination of sulphur between metal and slag and 'Sulphur Capacity' of slags. These will be reviewed in the next section. As will be evident, most of these studies have been restricted to the ferrous systems and involving silicate and aluminate slags and only a few on soda-lime slags.

1.2 LITERATURE REVIEW

Having realized the harmful effects on the final properties of metal(s) and alloys owing to the presence of metallic sulphide inclusions, chemists and metallurgists have concentrated their efforts to fight it out. Minimization of sulphur levels in the melts has been the subject of extensive research programme for a long time. Desulphurisation of different metallic systems yielded a volumenous thermodynamic data related to partition of sulphur in metals and slag, sulphur capacity of slags, solubility of sulphides in oxide melts, activity coefficients of sulphides, activity of oxides, effect of composition and temperature and viscosity of oxide melts in addition to the data on free energy of formation of sulphides, heats of formation of silicates from oxides, activation energy for ionic condition etc. However, the published data is not adequate for the development of a standardised desulphrisation process perhaps due to the changing pattern of acceptable sulphur levels and various stages of refining it and, thus, necessitates further investigations to achieve optimum slag composition and establish conditions for developing a well controlled desulphurisation process to bring down the sulphur to desired levels.

1.2.1 Sulphur Equilibria-Concept and Terminology

The sulphur equilibrium between slag and metal may be represented by following expression:

$$[S] + (O^{2-}) = (S^{2-}) + [O] \qquad \ldots (1.1)$$

which involves no assumptions concerning the cations associated with oxygen and sulphur in slag. The equilibrium constant, K_1, for the reaction 1.1 is expressed as:

$$K_1 = \frac{(a_{S^{2-}})[a_O]}{[S][a_{O^{2-}}]} \qquad \ldots (1.2)$$

which, on rearrangement of terms gives

$$\frac{(a_{S^{2-}})}{[S]} = K_1 \frac{(a_{O^{2-}})}{[a_O]} \qquad \ldots (1.3)$$

Assuming Henrian behaviour for all components, eq.(I.3) may be rewritten as

$$\frac{(Wt\%.S)}{[Wt\%.S]} = K_2 \frac{(n_{O^{2-}})}{[Wt\%.O]} \qquad \ldots (1.4)$$

where $n_{O^{2-}}$ is the number of gram ions of oxygen in 100 gms of slag after the oxygen requirements for the formation of SiO_4^{4-}, PO_4^{3-} and AlO_3^{3-} ions have been satisfied [8].

Carter [9] verified the linear behaviour of eq.(1.4) by plotting $(Wt\%.S)/[Wt\%.S]$ versus $n_{O^{2-}}/[Wt\%.O]$

calculated from the data of Fetters etal[10] and Grant etal[11] on equilibrium sulphur distribution between slag and metal at 1600°C and illustrated the near equivalence of all basic oxides during desulphurisation. It has been reported that sulphur does not dissolve as such in the silicate melts to any significant extent but, sulphides and sulphates are soluble [12].

Fincham and Richardson[13] have shown that in gas-slag equilibrium, the sulphur equilibria may be represented by the following chemical reactions,

$$\tfrac{1}{2}S_2 + (O^{2-}) = \tfrac{1}{2}O_2 + (S^{2-}) \qquad \ldots (1.5)$$

$$\tfrac{1}{2}S_2 + \tfrac{3}{2}O_2 + (O^{2-}) = (SO_4^{2-}) \qquad \ldots (1.6)$$

and,

$$S_2 + 3O_2 + (O^{2-}) = (S_2O_7^{2-}) \qquad \ldots (1.7)$$

or, $$2SO_2 + O_2 + (O^{2-}) = (S_2O_7^{2-}) \qquad \ldots (1.8)$$

for which equilibrium constants may be expressed as:

$$K_3 = \frac{(a_{S^{2-}})\, p_{O_2}^{1/2}}{(a_{O^{2-}})\, p_{S_2}^{1/2}} \qquad \ldots (1.9)$$

$$K_4 = \frac{(a_{SO_4^{2-}})}{(a_{O^{2-}})\, p_{S_2}^{1/2} . p_{O_2}^{3/2}} \qquad \ldots (1.10)$$

$$K_5 = \frac{(a_{S_2O_7^{2-}})}{(a_{O^{2-}})p_{S_2} \cdot p_{O_2}^{3/2}} \qquad \ldots (1.11)$$

and,
$$K_6 = \frac{(a_{S_2O_7^{2-}})}{(a_{O^{2-}}) \cdot p_{SO_2}^2 p_{O_2}} \qquad \ldots (1.12)$$

Richardson and Withers[14] advocated that sulphide equilibrium (eq.1.5) should be applicable under more reducing conditions, while sulphate equilibrium (eq.1.6) should be dominant under more oxidising conditions. When partial pressure of SO_2 and O_2 both are high in gas phase, pyrosulphates are formed as represented by equations 1.7 and 1.8, but, these reactions are important only at temperatures below 1500°C and lime rich slags[13].

On the basis of the results on studies conducted on blast furnace slags, Holbrook and Joseph[15] and Holbrook[16] defined the desulphurising power (D.P.) of the slag by the following relationship,

$$D.P. = \frac{\%\ S\ \text{in slag}}{\%\ \text{in metal}}$$

$$= \frac{(\%S)}{[\%S]} \qquad \ldots (1.13)$$

In other words it is equal to the sulphur distribution or partition coefficient between slag and metal.

Sulphur affinity of a slag has been described as sulphur capacity by Fincham and Richardson[13] and it is mathematically expressed as:

$$C_S = \frac{(Wt\%.S)p_{O_2}^{1/2}}{p_{S_2}^{1/2}} \qquad \ldots (I.14)$$

As can be noted from the expression above, a slag with higher value of C_S will hold or absorb sulphur more strongly at constant conditions of oxygen and sulphur pressures than one with lower C_S value and thus prove a better desulphuriser in a refining process [12].

With the knowledge of sulphide capacity, the sulphur which a slag will contain, can be predicted quantitatively under known oxygen and sulphur pressures, data on C_s, it can also be applied over a wide range of calculations to determine sulphur partitions in comparison to slag-metal partition data, since sulphide capacity is independent of metal or alloy involved, therefore, slag metal partition as defined by eq.1.13 can be predicted provided thermodynamics of sulphur in liquid alloy are known [17]. Eq.1.14 has been modified to determine activity of lime, a_{CaO}, for small slag sulphur percentages by Carter and MaCfarlane [18-19] in their $CaO-SiO_2$ and $CaO-Al_2O_3$ melts as:

$$a_{CaO} = \frac{a_{CaS}/A}{a^o_{CaS}/A^o} = \frac{(\%.S).\gamma_{CaS}/A}{(\%.S)^o.\gamma_{CaS}/A^o} \qquad \ldots (1.15)$$

where $A = p_{S_2}^{1/2}/p_{O_2}^{1/2}$ referenced as the sulphurising potential and (%S/A) gives the sulphide capacity, and γ_{CaS} is the activity coefficient of sulphide in slag. Superscript 'O' refers to the slag having lime activity equal to unity.

1.2.2 EXPERIMENTAL TECHNIQUES

Published work pertaining to the measurement of sulphide capacities reports the use of chemical equilibria technique. Most of the workers have equilibrated slag samples with sulphur bearing gaseous mixtures flowing in the reaction chamber. Bronson and St.Pierre[20] have used encapsulation technique where equilibrium is approached by static gas environments.

1.2.2.1 CHEMICAL EQUILIBRIA

It is the most extensively used technique in physico-chemical studies of metallurgical systems and extensive data is reported for different materials. Equilibrium measurements are helpful in the determination of the activity of components forming gaseous components. In this technique, high temperature studies of the reactions between gaseous and condensed phases either a solid or liquid are conducted. The chemical potential of reacting species used for equilibrating the condensed phase, is readily controlled with an appropriate choice of the composition and temperature of the gaseous mixture. The experimental data thus produced is utilized for computing the thermodynamic behaviour of of the species in the condensed phase. Gaseous mixtures used to establish and control the chemical potential of the reacting species are presented in table 1.1.

Choice of gaseous mixtures to be used in a particular investigation largely depends not only on the specific chemical potential required but also on the ease of developing the mixture, simplicity in apparatus design and the capability of transporting the reacting species at such a rate so as to attain equilibrium in a reasonable length of time.

Gas-condensed phase equilibria for dissolution of sulphur in slags can be expressed by equations 1.5, 1.6 and 1.7, in which (S^{2-}), (SO_4^{2-}) and ($S_2O_7^{2-}$) can be regarded as the representative amounts of dissolved sulphur in slags in form of sulphide, sulphate or pyrosulphate respectively.

From the value of equilibrium constant (expressed by equations 1.9 and 1.10) for the respective equilibrium), free energy and the thermodynamic enthalpy of the equilibrium reaction can be estimated using standard thermodynamic relationships.

Different techniques have been applied for the establishment of gaseous mixture of definite composition to yield chemical potential of the desired species. Different

Table 1.1 Gaseous mixture used for establishing different chemical potentials

Gas Mixture	Chemical potential established
$CO-CO_2$	$O_2(C)$
H_2-H_2O	O_2
CO_2-H_2	$O_2(C)$
CO_2	$O_2(C)$
H_2S-H_2	S_2
H_2O-S_2	S_2
N_2-S_2	S_2
SO_2-O_2	$S_2(O_2)$
S_2-SO_2	S_2, O_2
$SO_2-CO-CO_2$	S_2, O_2
$SO_2-H_2-CO_2$	S_2, O_2
$CO-CO_2$	$C(O_2)$
CH_4-H_2	C
$HCl-H_2$	Cl_2
NH_3-H_2	N_2
H_2-H_2O-SiO	Si

gases can be mixed together in the laboratory using constant pressure head capillary flowmeters to yield multicomponent gaseous mixtures with desired potential of the reacting species. One such apparatus for binary gaseous mixture preparation was developed by Johnston and Walker[21] and modified later by Darken and Gurry[22]. In cases where gas-mixing is not convenient technique, chemical potentials can best be controlled by passing a pure gas (or gaseous mixture) over the condensed phase(s) containing the desired reacting species. The gas reacts with the condensed phase to yield a gaseous phase of the desired composition, hence chemical potential of the solute under study. The gaseous phase, thus obtained, is swept over the material understudy, held in condensed state and the desired reacting vapour specie is transferred to the condensed phase. The different techniques for establishing chemical potential in this fashion may be classified into three categories.

(i) Open Circuit Technique

In this case both the source of the reacting specie and the system under study are held in a same reaction vessel. Example of this technique include establishment of phosphorus and oxygen potentials or the desired silicon potential.

(ii) Closed Circuit Technique

In such technique the source and the system under study are held into different vessels and the gas cycled between them. Example of this include generation of sulphur potential by passing pure hydrogen over a metal-metal sulphide mixture (source of sulphur specie) to yield a gaseous mixture of H_2-H_2S gases which is circulated over the system under study.

(iii) Static Atmosphere Technique

In such experiments twin quartz capsules have been successfully employed. A selected source of the reacting specie is kept in one limb of the capsule. Static atmosphere of the reacting specie, potential of which depends upon the temperature at which the capsule is held, is generated inside the capsule and system is equilibrated in the atmosphere so prepared.

As pointed out by Richardson and **Alcock** [23], the phenomenon of thermal diffusion or thermal segregation causes the main inaccuracy in the experimental data in chemical equilibration studies. Thermal diffusion occurs when a gaseous mixture is passed through an apparatus having low and high temperature zones. The lighter components concentrate in the hotter part and the heavier in the colder. The degree of segregation increases with increasing temperature and increasing temperature gradients and also due to larger difference in the molecular weights and sizes of the components in the gaseous mixture. However, the extent of this phenomenon can be reduced by maintaining high flow rates of the gaseous mixture.

For establishing sulphur potentials, gas mixing as well as the closed-circuit and the static atmosphere techniques have been adopted by different investigators. However, for the measurement of sulphide capacity, till 1978, only chemical equilibria technique was adopted. Based on this technique Fincham and Richardson[13], St.Pirre and Chipman[24] and Carter and MaCfarlane[18] have designed their apparatus, which are essentially similar in principle. Different gaseous mixtures containing sulphur bearing gas were made to flow in the reaction chamber to equilibrate the oxide mixtures. The apparatus after Fincham and Richardson[13] have been extensively used by subsequent workers.

1.2.2.2 Encapsulation Method

Bronson and St.Pierre[20] have developed a new technique for sulphur capacity determination. Broadly speaking the techniques take advantage of gas-condensed phase equilibria but in a static gas atmosphere. Sulphur capacity of slag is related by the expression

$$(C_s)_s = \frac{(Wt\%.S)_s}{(Wt\%.S)_r} (C_s)_r \qquad \ldots (1.16)$$

where subscript 'r' and 's' refers to reference slag and slag under study. Since gas-environ is static, p_{O_2}/p_{S_2}

remains constant throughout the experiment for all the slag samples.

A number of slag samples under study and reference slag whose sulphur capacity is known from previous measurements are placed in the tight container or capsule alongwith the source of sulphur bearing gas. The capsule is heated to the temperature of interest. Slags is condensed phase and the gas containing sulphur specie adjust to establish mutual equilibrium.

1.2.3 Experimental Studies on Sulphur Capacity of Slags

In the following sub-sections, results on sulphur capacity measurement of slags are critically reviewed. Binary, Ternary and complex slags are discussed separately.

1.2.3.1 Binary Slag Mixtures

It is well known that desulphurisation is more efficient at higher basicity ratio or the basic oxide/acid oxide ratio. Ores, invariably consist of silica, and alumina. Alumina due to its amphoteric nature has been added as flux for the adjustment of basicity ratio. Thus, silicate and aluminates of various basic cations have been extensively studied. Different binary silicate and aluminates and other slags containing lime are reviewed in the following sub-sections.

1.2.3.1.1 Binary Silicate Melts

Fincham and Richardson[13] have extensively studied the sulphide capacity of a number of slag systems. Amongst the binary silicate mixtures of $CaO-SiO_2$, $MgO-SiO_2$ and $FeO-SiO_2$ equilibrated with a gaseous mixture of H_2, SO_2, CO_2 at 1500° and 1650°C, $MgO-SiO_2$ has the least value, $FeO-SiO_2$ has the highest while $CaO-SiO_2$ has intermediate value of sulphide capacities. The workers, in another investigation[25] explain the high C_s values for $FeO-SiO_2$ than $CaO-SiO_2$ at given oxygen pressure by attributing this to the greater metal oxide activity in ferrous silicate melts. The statement is valid for acid slags having more than 33% of silica. With temperature, sulphide capacity increases. It increases with increase in molar fraction of base contents so in so that $CaO-SiO_2$ slag with molar fraction of lime equal to 0.35 at 1650°C and with molar fraction lime equal to 0.55 at 1500°C has similar C_s values. Richardson and Fincham[25] found that when p_{O_2} is less than $10^{-5}-10^{-6}$ atm, sulphide equilibria (eq.1.5) is prevalent while sulphate equilibria(eq.1.6) is dominant when p_{O_2} is greater than $10^{-3}-10^{-4}$ atm. and in between these limits of p_{O_2} both sulphides and sulphates may exist. The workers had discussed the results of binary silicate melts in relation to desulphurisation in iron- and steel-making. The results were applied to the transfer of sulphur between gas and slag in open-hearth to desulphurisation of blast furnace slag with reasonable agreement. Carter and MaCfarlane[19] measured lime activity in lime-silica melts using a gaseous mixture $CO+CO_2+SO_2$. Abraham and Richardson[26] calculated C_s from the data of Carter and MaCfarlane and reported a sharp disagreement between the values of Fincham and Richardson[13] and Carter and MaCfarlane[19]. Abraham and Richardson also corrected their thermodynamic data of the gaseous mixture and recalculated C_s values. Satisfactory agreement was found between the two modified values on the experimental data of the investigators[19,26]. Abraham etal[27] determined sulphide capacities of $MnO-SiO_2$ melts and pseudobinary systems of the type $CaO \cdot SiO_2$-, $MnO \cdot SiO_2$ and $MgO \cdot SiO_2-CaO \cdot SiO_2$ at temperatures of 1500, 1575 and 1650°C sulphide capacity for $MnO-SiO_2$ were found to be of the order of $FeO-SiO_2$. In the $CaO \cdot SiO_2-MnO \cdot SiO_2$ system, sulphide capacity increases with increase in the molar fraction of MnO, while there was a sharp fall in the C_s value with increasing MgO mole fractions in the $MgO \cdot SiO_2-CaO \cdot SiO_2$ system.

Results on sulphide capacity measurements of $CaO-SiO_2$, $MnO-SiO_2$ and $MgO \cdot SiO_2$ reported by Sharma and Richardson [28,29] are in close agreement to the work reported[13] after modification. Hino and Fuwa[30] have reported C_s measurement on liquid $MnO-SiO_2$ melts.

1.2.3.1.2 Binary Aluminate Melts

Lime and alumina melts were studied by Fincham and Richardson[13,25], Carter and Macfarlane[18], Sharma and Richardson[31], Cameron etal[32] and Kor and Richardson[33]. Fincham and Richardson[13,25] measured sulphide capacities of $CaO-Al_2O_3$ at 1650°C by gas-slag equilibria. The C_s values lied in between those of $CaO-SiO_2$ and $FeO-SiO_2$ and increased with increase in lime mole fraction. Carter and Macfarlane[18] measured sulphide capacity and also activity of lime at 1500°C and used a gaseous mixture of $CO-CO_2-SO_2$, while Sharma and Richardson[31] used the gaseous mixture of $CO_2-H_2-SO_2-N_2$ at 1500°C and the results of the workers are in satisfactory agreement. Cameron etal.[32] reported the C_s value by equilibrating the melts with $CO-CO_2-SO_2$ and $H_2-H_2S-H_2O$-Argon at 1550°C. Their [32] results were in sharp disagreement with those of previous works[18,31]. Therefore, Richardson with Kor[33] repeated the earlier experiment to test their validity in the light of Cameron's[32] work and the results were found in close confirmity with the earlier work[18,31].

Kor and Richardson[33] also determined C_s values for $CaF_2-Al_2O_3$ melts at 1500°C. Equilibrium was maintained with a gaseous mixture of $N_2+CO+CO_2+SO_2$. C_s values never exceeded 10^{-4} and were much lower than those obtained for $CaF_2+Al_2O_3+CaO$. Sharma and Richardson[29] conducted the experiments for sulphide capacity determination of $Al_2O_2-SiO_2$ at 1650°C using a gaseous mixture of CO_2, SO_2, H_2 and N_2. A peak was observed at about 0.074 mole fraction of alumina. This may be attributed to the formation of solid mullite. Drop in C_S value with an increase in mole fraction of Al_2O_3 may be due to presence of mullite which has no significant absorbance of sulphur. A plot of C_S versus $N_{Al_2O_3}$ extrapolates to zero at zero revealing that in these silica rich melts alumina acts as base.

1.2.3.1.3 Other Calcium Bearing Slags

Gurry and Darken[34] equilibrated lime-iron oxide slags with SO_2+O_2 gas mixtures and concluded that sulphur content increases with increasing lime content in this system which is equilibrated with a gaseous mixture of higher oxygen pressure (10^{-2} atm.).

St.Pirre and Chipman[24] reported that the distribution of sulphur between slag and gas depends upon the oxygen pressure of the gas. In FeO slags, a change in oxygen produced a change in ferric oxide content. These workers equilibrated lime-iron oxide melts with SO_2 containing CO and CO_2 at 1450°, 1500°, 1550° and 1600°C and their data indicate that additions of lime to iron oxide (pure iron-oxide has a sulphur capacity of less than 10^{-2} Wt percent) slags containing S^{2-} ions upto CaO saturation, produce a slight lowering of sulphur content. With increasing temperature of equilibration, sulphur content decreases. At constant atmospheric conditions, the substituion of lime for iron lowers the sulphide content and greatly enhances the sulphate content.

$CaO-P_2O_5$ slag system was studied by Abraham and Richardson[26] who equilibrated the samples at 1650°C with mixture of H_2, CO_2 and SO_2. Data reported on sulphide capacities indicate that a slight increase in lime content increases C_s value sharply, for instance for lime content from 52.4 to 50 Wt.% . Log C_s increases by a factor of 15.

Kor and Richardson[33] while determining sulphide capacities for $CaO-Caf_2$ melts, also equilibrated Caf_2 melts with a mixture of CO, CO_2, SO_2 and N_2 at 1500°C. They predicted a greater solubility than that of CaO from an argument based on the lack of dependence of γ_{CaS} on N_{CaO}, although thermodynamic data [35,36] on free energy changes makes it impossible to convert CaF_2 to CaS. However, CaF_2 in combination with lime gives exceptionally high C_s values. These workers concluded further that desulphurising power of fluoride slags can be used under highly reducing as well as oxidising conditions in advantage to other more effective silicates viz. $FeO-SiO_2$ and $MnO-SiO_2$ and basic open hearth slag which warrants for relatively oxidising conditions. Hawkins etal[37] conducted measurements at 1500 and 1550°C on sulphide capacities and plotted activities of CaF_2 CaO and CaS over the whole range of liquid compositions. Their results at 1500°C were in good agreement with those of Kor and Richardson[33], Edmunds [38] and Yuan Sun etal[39]. It has also been concluded that sulphide capacity increases with increasing CaO content and decreases slightly with temperature with the replacement of Ca ions by Mg or Si ions. Their results were applied to the practical operation of an electroslag rig and good agreement was observed.

Results of different workers on binary systems described are presented in Fig.1.1 which is self explanatory.

1.2.3.2 Ternary Slag Mixtures

Third component may be added to a binary slag mixtures to obtain the desirable physico-chemical properties. Various ternary systems have been the subject of investigation to study the effect of the additive on sulphur transfer capacity of the parent binary slag mixtures.

1.2.3.2.1 Ternary Silicate Melts

St.Pierre and Chipman[24] carried out investigations on system lime-silica-iron oxide with CaO/SiO_2 ratios namely 0.524, 1.275 and 2.235. It has reported that equilibrium values increase with increasing CaO/SiO_2 ratios and a function $(Ca+\frac{3}{2}Si)$. Effect of increasing oxygen potential

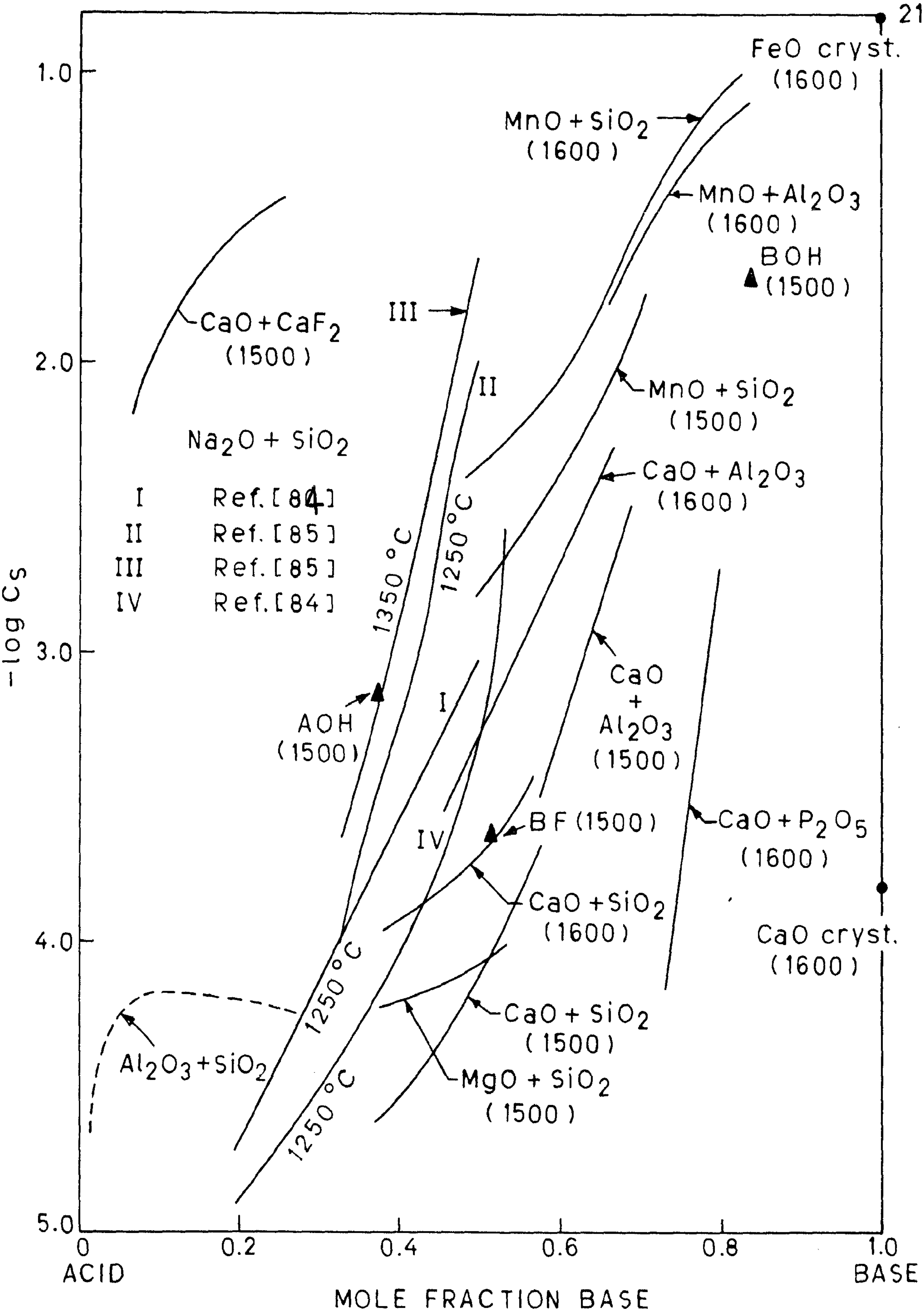

FIG.1.1 SULPHUR CAPACITIES OF BINARY SLAGS.

on the gaseous phase for slags of constant CaO/SiO_2 ratio of 1.275 shows the similar trend. Sulphide capacities were also plotted against mole percent of silica. The results are in good agreement with thoseoof Fincham and Richardson[13]. St.Pierre and Chipman concluded that addition of silica to lime-iron oxide system lowers the sulphur content under a given conditions of atmosphere on the reaction chamber, because of the lowering in oxide ion activity.

Kalyanram et al[40] investigated the $CaO-MgO-SiO_2$ slag equilibrating it with a mixture of $SO_2-CO-CO_2$ at 1500°C and utilised the results to assess the activity of lime in these slags. The results were expressed in the form of A_{CaO} as:

$$A_{CaO} = \frac{a_{CaO} \cdot \gamma^{o}_{CaS}}{\gamma_{CaS}} = \frac{(\% \, S)A^{o}}{(\% \, S^{o})A} \qquad \ldots (1.16)$$

where superscript 'o' refers to reference slag with until lime activity and A, the sulphurising potential, as equal to $(p_{S_2})^{1/2}/(p_{O_2})^{1/2}$. A_{CaO} values were found to be a simple function of $(N_{CaO}+N_{MgO})/N_{SiO_2}$. For slags of constant $(\% \, CaO)/(\% \, SiO_2)$ ratio, A_{CaO} was found to increase with increasing MgO additions and then increase was more marked as the $(\% \, CaO)/(\% SiO_2)$ ratio was raised. At constant silica content A_{CaO} value decreased with increasing MgO content. Since A_{CaO} is correlated with sulphide capacity

(% S/A = C_s), C_s value can also be calculated.

Abraham and Richardson [26] studied $CaO-P_2O_5-SiO_2$ slags containing J/mole P_2O_5 at 1650°C and calculated sulphide capacities. Gaseous mixture used was H_2, CO_2 and SO_2. P_2O_5 requires more of CaO content than required for $CaO-SiO_2$ for obtaining similar values. Desulphurising power for $CaO-P_2O_5-SiO_2$ and $CaO-SiO_2$ with CaO 0.57 and 0.5 mole fractions respectively.

Sharma and Richardson [29] equilibrated $MgO-MnO-SiO_2$ slags at 1650°C with a mixture of CO_2, SO_2, H_2 and N_2 to estimate sulphide capacity. Considering the system as a pseudo-binary of the type $MgO.SiO_2+MnO.SiO_2$ the logarithm values of molar sulphide capacity* varies linearly for $N_{SiO_2} = 0.5$ with $MgO.SiO_2$ equal to 5-7 approximately. But with $N_{SiO_2} = 0.4$, there is significant divergence from the straight line behaviour (as high as 35 percent).

1.2.3.2.2 Ternary Aluminate Melts

Abraham and Richardson [26] conducted experiments to measure

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* molar sulphide capacity, C_s', defined as $C_s' = N_{MS}(p_{O_2}/p_{S_2})^{1/2}$ for the equilibria of the type $(O'') + \frac{1}{2}S_2 = (S'') + \frac{1}{2}O_2$ and $2(Si-O') + \frac{1}{2}S_2 = 2(Si-O-Si) + S'' + \frac{1}{2}O_2$.

sulphide capacity of the lime alumina with P_2O_5 additions upto 0.07 mole fraction under similar conditions as were for $CaO-P_2O_5-SiO_2$ slags. Sulphide capacity were found to be of the order of $1.17x10^{-2}$ for CaO 60 Wt.% and $5.00x10^{-3}$ for CaO 54.2 Wt.% . Addition of P_2O_5 lowered C_s but to the lesser extent in comparison with $CaO-P_2O_5-SiO_2$ melts.

Kor and Richardson[33] studied the effect of CaF_2 additions in the lime-alumina melts by ~~equilibrating with $CO+CO_2+SO_2+N_2$ mixture by~~ equilibrating with $CO+CO_2+SO_2+N_2$ mixture at 1500°C. Sulphide capacity values lie in between the binaries of $CaO-CaF_2$ and $CaO-Al_2O_3$. They compared their results with those of Zmojdin et al[41] and observed a marked difference in iso-sulphur capacity contours. The sulphur capacities values determined by Zmojdin et al were 20 times as much as that calculated by Kor etal[33]. These workers[33] assigned the reason for this difference to be the use of radio-chemical technique and/or inadequate CO pressures, used by Zmojdin et al[41].

1.2.3.2.3 Silliminite Melts

Fincham and Richardson[13] studied the system $CaO-SiO_2-Al_2O_3$ at 1500 and 1650°C by attaining equilibrium with a gaseous mixture of H_2, CO_2 and SO_2 in order to calculate sulphide capacity values, which were plotted in ternary diagram as iso-sulphur-capacity contours. The lines follow the pattern as could be expected if activity coefficient of CaS were approximately constant and the sulphide capacities followed lime activities. The C_s values tend to a maximum along with the $CaO-Al_2O_3-SiO_2$ join. Based on the thermodynamic data [42], maximum lime activities are expected for melts in which molar fractions of SiO_2 and Al_2O_3 are approximately equal. The same workers further reported [25] that there is a reasonable agreement in the C_s values between their results and those obtained by Hatch and Chipman [43]. Hatch and Chipman measured sulphide partitions between carbon saturated iron and silicate melts containing sulphur (in varying proportions) and carbon monoxide gas at 1 atm. pressure at 1500°C (i.e. $p_{O_2} = 10^{-15.72}$ atm). The basis of comparison of results [13] with those of Hatch and Chipman was the latter's data with 1.5 percent sulphur contained in this ternary melt.

Kalyanram et al [40] studied the lime-sillimanite slag at 1500°C being under equilibrium with a gaseous mixture of $CO-CO_2-SO_2$ for determining activity of lime, in the form of A_{CaO}, which is proportional to C_s of Fincham and Richardson. Numerical values of sulphide capacity for comparable slag compositions used by Kalyanram were half than those reported earlier [13]. The reason, that could be attributed to this difference, is the different thermodynamic data used by the two group of workers for the calculation of oxygen and sulphur potentials in the different gaseous mixtures. In this work [40], the results were expressed as a ratio of sulphide capacity of the slag under study to that of the reference (standard) slag having unit lime capacity.

Shama and Richardson[29] investigated the MgO- and MnO-sillimanite at 1650°C in view of activity determination of MnO as well as the sulphide capacity. Equilibrium was attained with a mixture of CO_2, SO_2, H_2 and N_2 gases. Thessulphide capacities for this system reflects the amphoteric nature of alumina. For instance, at a mole fraction of 0.6 silica, the substitution of alumina for MgO at first lowers the C_s value, but beyond 0.23 alumina mole fraction it began to raise it such that at 4.18 contour could eliminate at alumina saturation in the $Al_2O_3 \cdot SiO_2$ binary. This rise presumably occurs at higher silica levels also when $N_{Al_2O_3}$ is less than N_{MgO}, the C_s value falls as alumina is substituted for MgO at constant mole fraction of silica. Here the alumina appears to act as an acid. But, when the ratio $N_{Al_2O_3}/N_{MgO}$ is greater than that of 1.5, similar substitution at constant mole fraction of SiO_2 cause C_s to rise and alumina presumably takes over as a base. Sulphide capacity values for the slag system, $MnO-SiO_2-Al_2O_3$, show an increase with increase in base content, however, no amphoteric nature of Al_2O_3 could be observed in this system.

1.2.3.2.4 Other Complex Mixtures

Fincham and Richardson [13] measured sulphide capacity of compositional iron and steel making slags viz. basic open hearth, acid open hearth and blast furnace slags[25]. Their sulphide capacity values are 3.16×10^{-2}, 1.26×10^{-3} and 3.16×10^{-4} (approximately) respectively as measured by these workers. The results indicate that iron blast furnace slag has least desulphurising power in comparison to acid open hearth and basic open hearth slags, latter of which is observed to be the best desulphuriser amongst them. Chipman et al[43] had earlier reported a value of sulphide capacity for basic open hearth slag greater by a factor of two based on the sulphur partition ratio determined by slag-metal equilibrium. These workers[13] accounted for this difference to the different choice of oxygen partial pressure (10^{-6} in case of Fincham and Richardson while 10^{-8} in case of Chipman et al) which resulted into the higher proportions of iron and lime being associated as ferrites under former conditions [13] so that lime and ferrous activities and hence sulphide capacity was lowered [25].

To maintain the fluidity of blast furnace slags at 1500°C inspite of the high concentration of metal oxide which give the high sulphide capacities, additions of MgO are made. to $CaO-SiO_2-Al_2O_3$ slags. Hatch and Chipman[43] carried out investigations in the direction of sulphur partition ratio between iron blast furnace slag and metal at 1500°C and established that the desulphurisation ratio (S) $(S)/[S]$ is controlled by excess base (equal to $(CaO + \frac{2}{3} MgO)-(SiO_2+Al_2O_3)$ in moles per 100 gm of slag) for slags with 1.5 per cent sulphur. Later Osborn et al[44] advocated the use of such slags in iron making and concluded that sulphur distribution are determined solely by the Wt.% ratio $(CaO+MgO)/(SiO_2+Al_2O_3)$ and that provided this ratio is constant, the capacities are unaffected by the alumina content. However, Abraham and Richardson [26] carried out sulphide capacity of lime-magnesia-sillimanite slags and their results invalidated the conclusions of Osborn because they observed C_s values being improved by almost 70 percent when 10 percent alumina replaces silica on weight percent basis. Prior to the work of Abraham and Richardson, Burges and Baldwin[45] had shown that high magnesia slags are better desulphurisers than those normally used. Partition ratios as obtained, in practice, by a high magnesia slag (approximate composition CaO43, MgO 12, $SiO_2$30 and Al_2O_3 15) are four times more than those with usual slag (CaO_{44}, MgO 3, SiO_2 33 and Al_2O_3 20), although the sulphide capacities are improved by a factor of 2. Abraham and Richardson[26] accounted for this difference as the contribution of the factors like higher temperature of metal and slag and sulphur partition close to equilibrium becauseeof decreased viscosity[46].

Kalyanram etal[40] carried out activity measurements on such slags. Revised values of sulphide capacity for from the available data [40,43] show reasonable agreement within experimental limits with sulphide capacity data of Abraham and Richardson.

In view of growing importance of titania-slags, in practice, Brown et al.[17] carried out measurements of sulphide capacity at 1500°C for liquid slags containing CaO, Al_2O_3, TiO_2 and MgO by equilibrating with a mixture of CO_2, H_2 and SO_2 gases. Their results indicated that when TiO_2 replaced SiO_2 or Al_2O_3 at a given CaO level, the sulphide capacity increased which is explained as partially due to an increase in the oxide ion activity and partly to an iincrease in sulphur solubility of slags. Although, T_i^{3+} levels are higher at lower oxygen pressures over the sulphur capacity was not marked. Furthermore, it is also shown that the effect of adding TiO_2 to a blast furnace slag ($CaO-Al_2O_3-SiO_2$) will increase rather than decrease the sulphur partition ratio under the conditions: temperature = 1500°C, p_{CO} = 2 atm, a_C = 1 and f_s = 5.5. As far as sulphur control is concerned, the effect of introducing some titania into the slag is relatively small and hence it is unlikely to have titania additions to control sulphur.

Bronson and St.Pierre[20,47] have determined C_S values for $CaO-SiO_2-CaF_2$ and $CaO-SiO_2-Al_2O_3$ slags having (CaO/SiO_2 ranging from 1.00 to 1.28) at 1503°C with CaF_2 and B_2O_3 [20] additions and $CaO-SiO_2$ melts containing MgO, FeO*, TiO_2* and Al_2O_3 [47], It is reported [20] that at fixed CaO/SiO_2 ratio, the sulphide capacity increased with increasing CaF_2 content, while B_2O_3 additions results into the reduction of C_s value. Substitution of CaF_2 for CaO does not show any marked alteration in C_s value. On the other hand B_2O_3 replacements for SiO_2 has shown slight increase in sulphide capacity. Results of Abraham and Richardson [26] for $CaO-SiO_2$ melts were taken as reliable and used for calculation of sulphide capacities of other melts with CaF_2 and B_2O_3. In $CaO-SiO_2$ slags containing FeO, TiO_2, MgO and Al_2O_3 it is found that substitution of MgO for CaO decreases sulphide capacity significantly while substitution FeO increases C_s. The substitution of Al_2O_3 and B_2O_3 increases C_s to the same extent. TiO_2 additions show a slightly more increase in C_s values. For a basicity ratio of 1.21, the $a_{O^{2-}}/f_{S^{2-}}$ ratio is increased by substitution of Al_2O_3 and TiO_2 for SiO_2, while the ratio shows a significant decrease on replacing CaO with MgO.

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* Total iron content expressed as equivalent FeO and total titanium content expressed as equivalent TiO_2.

1.2.3.3 Soda Base Slags

Low sulphur steels can be tapped by carrying a higher slag basicity in the steel making vessel, which would result into lower production rates and higher operating cost, thus it is preferable to charge low sulphur charge in the steel making vessel. For obtaining low sulphur charge for steel making, low sulphur burdens in the blast furnace again results into decreased productivity with increased production costs and hence it is wise to desulphurise iron at post iron making and pre-steel making conditions. This would lead to carry out desulphurisation of iron in ladles before taking melts to the steel making vessel[7].

Jacquemot[48] reviewed theddifferent possible desulphurisation mechanisms for steel and showed the desulphurisation can be accelerated in ladle and certain techniques allow very low sulphur levels to obe obtained. Kamardin et al[49] studied the effect of metallurgical factors viz. temperature, chemical composition of the metal and slag composition on equilibrium and actual distribution of sulphur between metal and slag in ladle refining of steel, with alumino-silicate slags of basic type. On using alumino-silicate slags containing 20 percent SiO_2 with traces (5%) of MgO and CaF_2, the same degree of desulphurisation was achieved as on using $CaO-Al_2O_3$ slags of conventional type.

Ohman and Lehner[50] studied metallurgical factors affecting ladle refining of steel, viz. homogenisation of temperature and composition, deoxidation, desulphurisation, modification of non-metallic inclusions etc. The advantage of ladle refining include reduced gas pick-up, less temperature variations, shorter time between end of refining and teeming and thus less risk of reversion from slag, lower percentage of non-metallic inclusions since there is no extra-tapping and removal of unwanted elements from metal is promoted by stirring during treatment in the ladle. Gruner and Bardenheuer [51], too, advocate desulphurisation subsequent to the melting process. They claimed reproducible desulphurisation of steel by a slagging reaction of greater than 90 percent.

Various methods that could be used for adding desulphuriser during external desulphurisation[6]. (a) blowing inert gas (to cause stirring (b) injection of desulphurising agent with carrier gas, (c) vibration treatment of ladle, (d) electric induction stirring, and (e) double ladling. In past various desulphurisers that have been tried in practice for ladle desulphurisation of pig iron, foundry iron and steel by different workers have been summed up by Kurzinky[7] to name a few of importance calcium carbide [52-57], magnesium[58-60], lime [61-65], soda ash[66-70], caustic soda [68,69] and calcium carbonate [64]. Out of these, soda ash has been acclaimed to be a potent desulphuriser which is frequently utilized for desulphurisation of pig iron both for steel making and foundry purpose[71], but, this could rarely be given importance due to rapid attack of alkali bearing slags on refractories [8], although high soda content in slags leads to better desulphurisation. Ward[8] has tabulated the relative desulphurising power of different cations, taking that of calcium as unity. The table shows the desulphurising powers as equal to 0.325, 0.25, 0.0075 and 1070 for Fe^{2+}, Mn^{2+}, Mg^{2+} and Na^{+} respectively.

With the use of soda, a large volume of objectionable fume is released and has a tendency to pick-up moisture from atmosphere resulting into excessive iron splashing. However, these shortcomings can be overcome by stirring soda bearing fluxes in air-tight containers and subsequent removal of reaction slag shortly after addition to avoid reversion of sulphur from slag to iron[7]. Use of soda ash in the desulphurisation of iron, for foundry purpose dates back to 1934. Besides all this, soda ash is the cheapest material, that can be used for desulphurisation using simple techniques such as pouring iron on top of the desulphuriser in an open ladle, sulphur levels of the order of 0.015% could be obtained and, therefore, it is now in considerable use, specially in Europe[73]. Furthermore, soda ash, as has been reported by many workers [72-75], has in addition to better desulphurising power, deposphorising powers too. Yamamoto[76-77] has developed new steel making process with sodium carbonate flux, which states that best conditions for refining include the slag composition of Na_2O/SiO_2 greater than 2 at temperature below 1400°C. Hafmann etal[78] discussed the use of soda in ladle in context with effect of slag separation, sulphur contents of rion and carbon activity in metal as well as the relationship of sulphur-carbon activity in various types of iron.

Elermann et al[79] have carried out kinetic investigatio ns to study the mechanism and kinetics of sulphur transfer from carbon saturated iron to slag at 1250°C during desulphurisation with $CaO-SiO_2-Na_2O$ slags and interpretted their experimental results in terms of electrochemical process taking place between metal and slag. They reported that the iron content in slag abruptly increases at its initial stage and thereafter decreases to equilibrium value. It was in 1972 that a serious though was given to Na_2O-SiO_2 system and Nagashima and Katsura[80] carried out investigations on solubility of sulphur in sodium silicate of Na_2O/SiO_2 ratios 1/3, 1/2 and 1/1 melts at 1100, 1250 and 1300°C under varying oxygen pressure with the following objectives (1) to obtain fundamental thermodynamic information about the solubility of sulphur and (2) actually prove the dissolving state of sulphur in silicate melting by chemical analysis. Holmquist [81] studied solubility of sulphur at very high oxygen partial pressure and no study has ever been made over the wider range of oxygen partial pressure. Sulphide, sulphate and total sulphur was chemical analysed by a method out lined by Nagashima[82] and partial pressure of oxygen were calculated as well as measured directly with a solid electrolyte method. Their results showed that at 1100°C, the equilibrium within the gaseous phase is not established while at 125C and 1300°C, the gas phase is considered to be close to equilibrium. At 1250°C, their results showed a minimum solubility of sulphur at specific oxygen pressure. At 1250° and 1300° it has been inferred that (a) at constant temperature and constant Na_2O/SiO_2 ratio, solubility of sulphur increases with an increase in the total sulphur content of gaseous phase, (b) at definite temperature, Na_2O/SiO_2 ratio and input sulphur, sulphate formation takes place at p_{O_2} 10^{-6-8} atm while sulphide is formed at p_{O_2} 10^{-9} atm, which is similar to the inference made by Richardson and Withers[14] Aand (c) when the temperature and input sulphur content are constant, the solubility rises with an increase in Na_2O/SiO_2 ratio in the melt. In case total input sulphur remains constant, the minimum solubility limit shifts in the direction of higher p_{O_2} with an increase in temperature corresponding to the change in equilibrium gas composition as temperature rises. As reported by Bahout etal[83] and Inoue and Suito[84] Denier [85] have also conducted experiments to determine the sulphide capacity of Na_2O-SiO_2 melts.

Their results compare well with those of [80,85] at 1250° for $Na_2O/SiO_2 = 0.5$ but for $Na_2O/SiO_2 = 1$, Nagashima obtained a logarithm of sulphide capacity value as equal to -3 while Denier's is -2 and the reason attributed to the loss of sodium by vapourisation resulting into relatively high activity of Na_2O.

Sulphur partition between carbon-saturated iron melt and Na_2O-SiO_2 slags was investigated by Inoue and Suito [84] under the inert gas, argon, atmosphere of SO_2-CO_2-H_2 gases. It has been shown from the measurement [84] that sulphide capacity value of Na_2O-SiO_2 slags lies between those of CaO-CaF_2 and CaO-SiO_2. Compositions studied were $Na_2O/SiO_2 = \frac{1}{3}$, 1/2, 1/1 and 3/2 at 1250° and 1350°C. The sulphide capacity values $[C_s^* = (Wt.\%S)\,\frac{a_O}{a_S}]$ calculated from sulphur partitions were found to be in the range of 10^{-3} to 10^{-4}, however, their temperature dependence was not observed. These values were lower than the previous measurements for $Na_2O/SiO_2 =$ 0.5, 0.7, but, higher in case of slags having Na_2O/SiO_2 ratios below the former. The sulphur partitions between carbon-saturated iron and Na_2O-CaO-SiO_2 melts were measured at 1250°C at constant SiO_2 content. Logarithmic value of (S)/[S] in the $3Na_2O.2SiO_2$-$3CaO.2SiO_2$ and the $Na_2O.SiO_2$-(pseudo-binary system) decrease linearly with increasing $3CaO.2SiO_2$ and $CaO.SiO_2$ contents. The Na_2O equivalent of CaO for the sulphur partition was found to be 0.3. Presence of FeS was confirmed and its total sulphur was maximum at the composition of Na_2O/SiO_2 = 0.9 (molar ratio).

Oelsen[86] found out that CaO additions to the $Na_2O \cdot SiO_2$ or $2Na_2O$-$3SiO_2$ melts upto 40% favoured desulphurisation because of increase in basicity. The Na_2O equivalent of CaO was estimated to be 1.2 to 1.6 from comparison of his results with those of Na_2O-SiO_2 melts by Korber and Oelsen[87,88]. Domalski et al[89] discussed the possibility of desulphurisation in Na_2O-CaO-SiO_2 slags from the view point of better fluidity and suggested that the regions in the Na_2O-CaO-SiO_2 ternary system whose liquidus are below 1150°C are favourable for desulphurisation.

Jwamoto etal.[90] investigated the state of sulphur and sulphur iron interaction in Na_2O-SiO_2 slags by optical absorption, electron spin resistance (ESR) and S-K_α, X-ray emission spectroscopy and concluded that in Na_2O-SiO_2 slags polysulphide ions such as S_2^- are formed as an intermediate constituent with decreasing oxygen partial pressure. Their results indicated further that Fe^{3+}-S^{2-} interaction begins to occur in the vicinity of $p_{O_2} = 10^{-6}$-10^{-7} atm.

Bahout et al[83] published their data on desulphurization of iron by pneumatic injection of soda ash in 200 t torpedeo ladles. The work was carried out at Usinor Dunkirk works, France by JRSID with collaboration of Solvay and Usinor. Soda ash was deep injected pneumatically and their results were quite encouraging. Sulphur levels as low as 0.005% were obtained as against 0.015% by simple treatment. with soda ash with relatively low flux consumption. The treatment took 20 minutes and thermal and silicon losses were not increased significantly.

Use of soda slags to desulphurise the ferrous melts has inherent drawbacks namely-refractory attack and evolution of fumes. Nevertheless soda slags could lead very low sulphur levels at relatively lower operating costs. Deficiency associated with the use of such slags could be taken care of by deployment of improved techniques whereby better desulphurisation is achieved economically as compared to expensive desulphurisers like CaF_2, CaC_2, magnesium etc.

1.3 FORMULATION OF THE PROBLEM

In Section 1.2 it has been amply demonstrated that most of the measurements of sulphur capacity (or the sulphide capacity, where limited to calcium-, maganese-, and magnesium-silicates, aluminate, fluoride, and sillimanite systems and at temperature beyond 1500°C possibly from the view point of development of slags for desulphurisation in iron- and steel. Also the reliability of the reported data could be doubted as pointed out by Nagashima and Katsura[80] who found wide variations in the observed and theoretically calculated values of oxygen pressures, especially at 1100°C.

Soda ash has been successfully used for external desulphurisation of hot metal in iorn and steel ind us industry due to its relatively high desulphurising power and lesser requirements of activation energy for ionic conduction of sodium oxide. However, this requires relatively lower temperature for treatment of hot-metal because of which the damage to lining of the vesecl due to alkali attack is minimum.

The present investigation was therefore undertaken to study the sulphur capacity of Na_2O-SiO_2 melts with varying Na_2O/SiO_2 ratio at teemperatures ranging from 1373 to 1573 K. Effect of lime additions on sulphide capacities of sodium-silicate melts will also be studied in the same temperature range for compositions having liquidus temperature below 1473 K. The results, so obtained, will also be compared with the data obtained by other workers for these slags and slags of other components. Oxygen pressure in the reaction zone will also be measured through a suitable oxygen sensor to improve the reliability of the data so obtained.

CHAPTER -2

EXPERIMENTAL

The present chapter deals with the methods and materials used in the present investigation. The gas-condensed phase chemical equilibria technique using open system has been adopted for the purpose to study the effects of temperature of equilibration and composition of different binary and ternary slags on their sulphur capacities. The different materials used and methods adopted for preparation of slags and gaseous mixtures, actual equilibration runs and also the analysis of equilibrated slag samples are described in the following sections.

2.1 MATERIALS USED

Pure quartz lump were picked from a quarry near Delhi and Analar grade chemicals such as sodium carbonate anhydrous-make M/S Glaxo Laboratories (India) Ltd., Bombay, calcium oxide- make M/S Fisons, Philadalphia, U.S.A., sodium sulphite-make M/S Polypharm Pvt. Ltd., Bombay, India, conc. sulphuric acid-make M/S Polypharm Pvt Ltd., Bombay India, conc hydrochloric acid-make Glaxo Laboratories (India) Ltd., Bombay etc. were used for the present work.

2.2 PREPARATION OF SLAG SAMPLES

Soda-silica and lime-soda-silica slags of different composition were chosen in the Na_2O/SiO_2 molar ratio range varying from 0.25-1.0 and falling within 1200°C isotherm of the $CaO-Na_2O-SiO_2$ diagram[91]. The different slag compositions prepared and their melting points are presented in table 2.1.

2.2.1 Purification of Quartz

Quartz lumps picked up from quarry were crushed and ground to -48 # (tyler) size. This powdered silica was treated several times with conc.HCl and finally washed with distilled water and dried to render it free of any clay or other soluble impurities. The product analysed silica greater than 99%.

2.2.2 Blending and Melting of Slags

Accurately weighed quantities of purified silica, sodium carbonate and/or calcium oxide were used for preparation of slags of desired composition. The ingradients were mixed thoroughly in a hand mortar and these mix. transferred to graphite crucibles were melted in a vertical tubular furnace at temperatures approximately greater by 100° than their their respective melting points (table 2.1) in a nitrogen atmosphere for nearly four hours. The molten slags were withdrawn from furnace and air-cooled. The solidified slags were again crushed and ground in hand-mortar and remelted in nitrogen atmosphere. The doubly melted slags were finally ground for homogenisation.

2.2.3 Homogenisation

The powdered doubly melted slags obtained as above and contained in alumina boats were heated in horizontal tubular furnace at temperatures nearly 200° below their normal melting point for about 24 hours for their homogenisation and for elimination of carbon picked up during melting.

2.3 EXPERIMENTAL SET UP

Essential features of the experimental set up are-

a) gases, either from cylinder(s) or produced insitu, and their purification - to be referred as 'Gas Production and Purification Unit' henceforth.

b) a gas-mixer for obtaining a gaseous mixture of interest - to be termed as 'Gas Mixing Unit' onwards, and

c) a chamber for slag incondensed phase, and gas interaction under desirable and measurable conditions- named as 'Reaction Unit'.

Combination of the three units forms the experimental set up as a whole. The three units are briefly discussed in the following sub-sections.

2.3.1 Gas Production and Purification Unit

The unit has further been divided into three sub-units, namely i) nitrogen purification, ii) sulphur-di-oxide production and storage-, and iii) SO_2 purification sub-units.

High purity nitrogen, made available from M/S Modi Gas and Chemicals Ltd., Modi Nagar, was further purified with the aim of lowering down the oxygen potential of the gas. Purification train used to remove moisture and lower down the oxygen partial pressure of the gas is shown in fig.2.1a.

Sulphur di-oxide gas was, however, generated in the laboratory according to the chemical reaction

$$Na_2SO_3 + H_2SO_4 = Na_2SO_4 + SO_2 + H_2O \qquad \ldots (2.1)$$

in the all glass Kipp's apparatus (of 1 litre capacity). SO_2 produced was stored in a tank called buffer tank. SO_2 production and storage sub-unit is shown in fig.2.1b. SO_2 was purified before it reached gas mixing unit. Details of purification are shown in fig.2.1c.

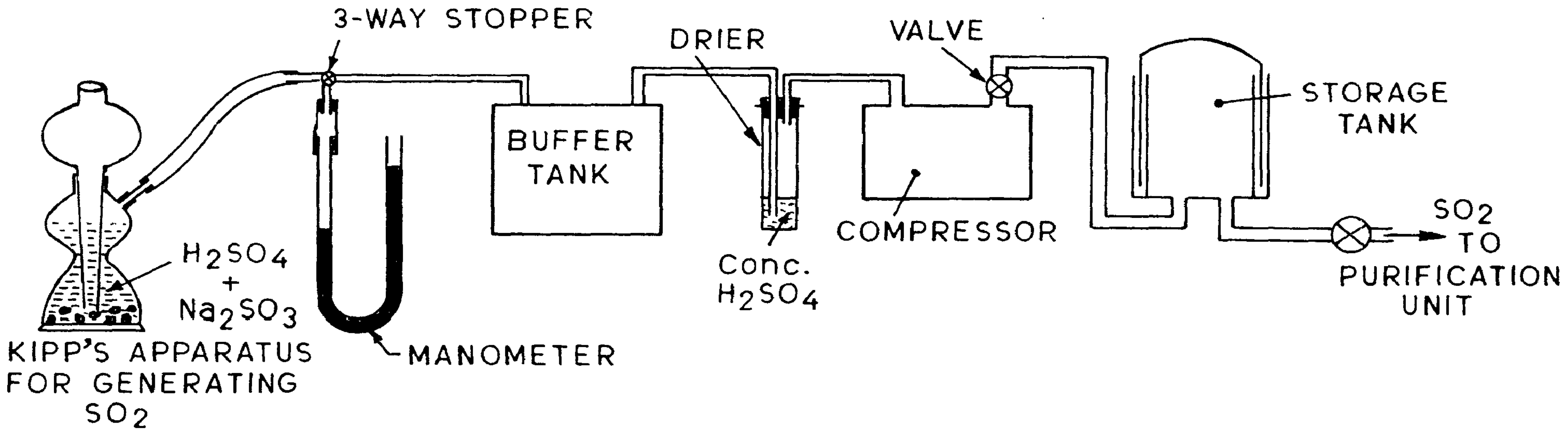


FIG.2.1(a) SO_2 PRODUCTION & STORAGE UNIT

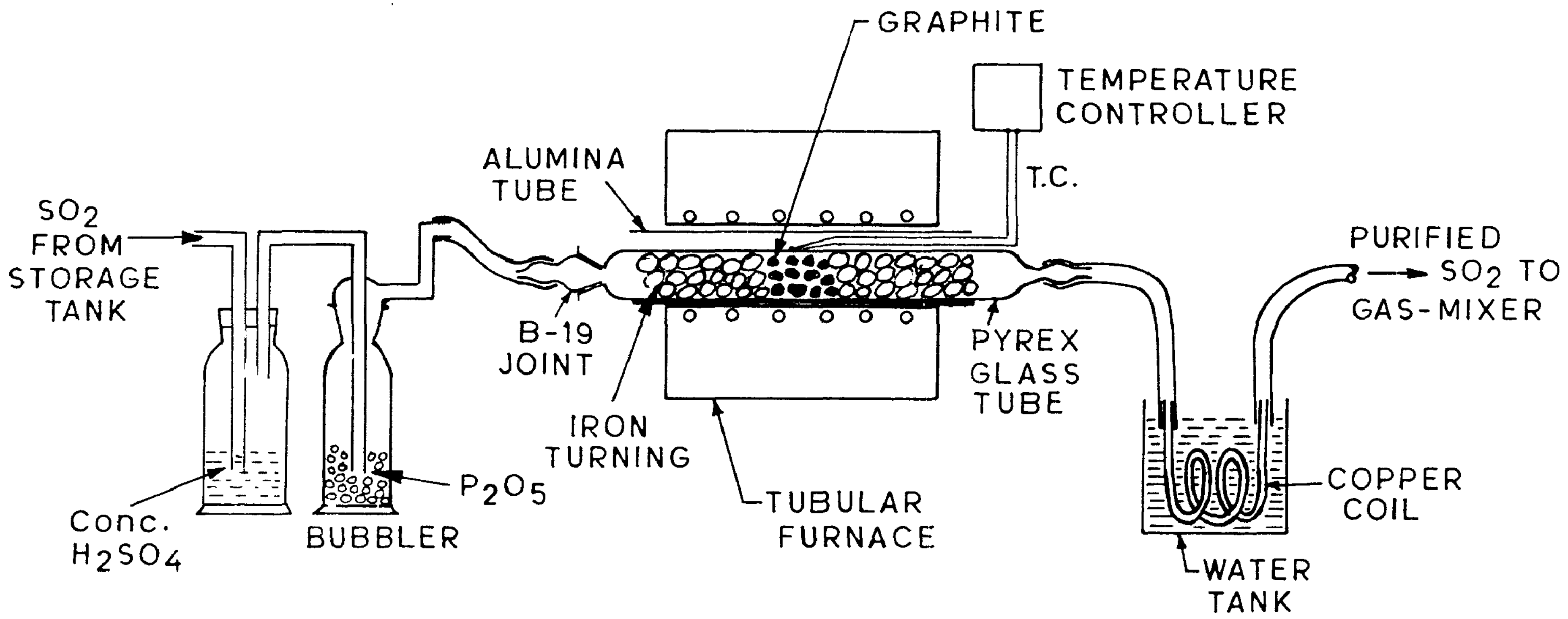


FIG. 2.1(b) SO_2 PURIFICATION UNIT

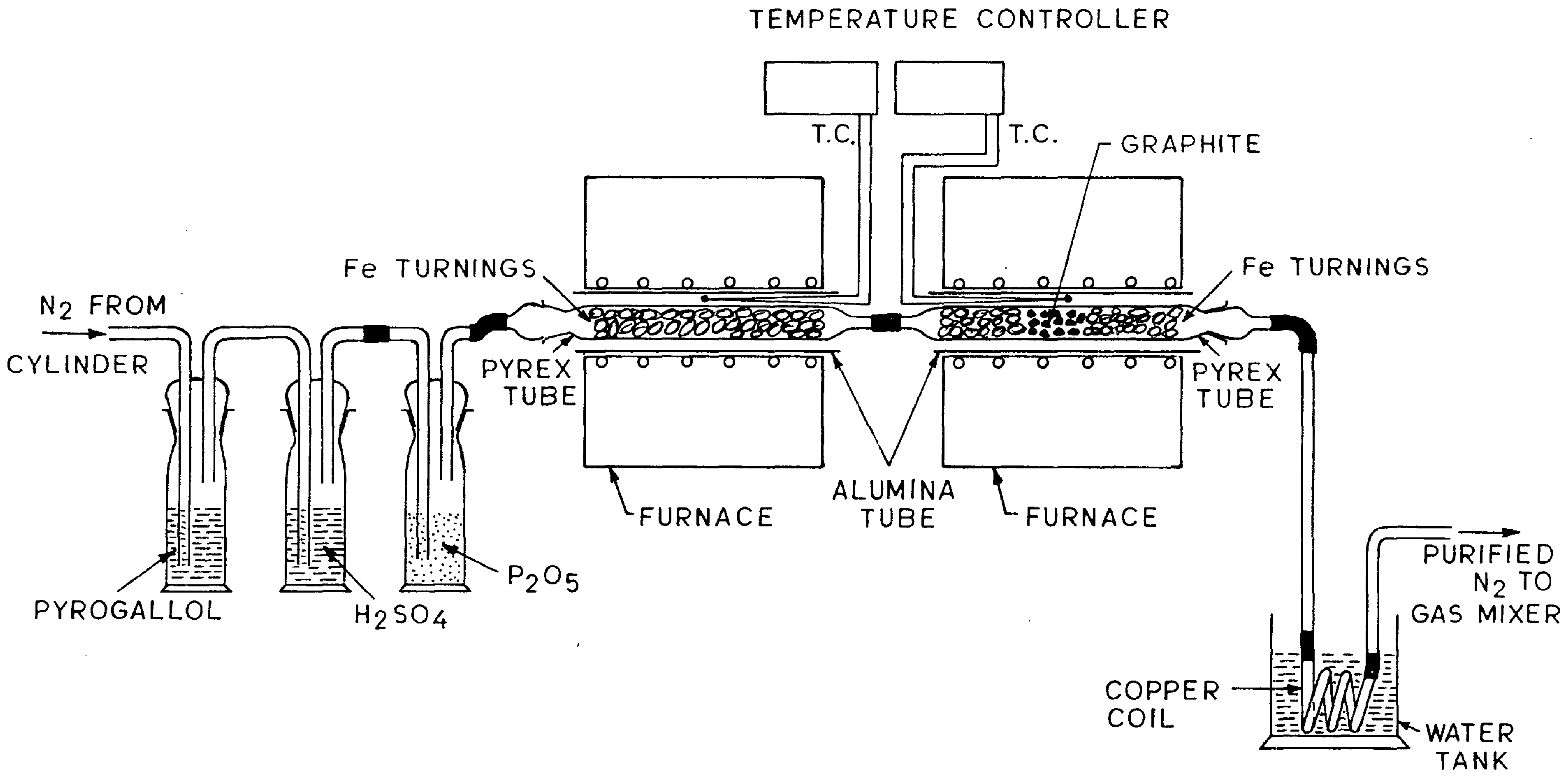


FIG. 2.1 (c) N_2 PURIFICATION UNIT

2.3.2 Gas Mixing Unit

For preparing the SO_2-N_2 gaseous mixture of desired composition, a constant pressure head flowmeter type gas mixer (modified design of what was originally suggested by Johnston and Walker)[2] was used. By adjusting the flow rates of N_2 and SO_2, a gaseous mixture of desired composition could be obtained in this unit.

An Orsat-apparatus was introduced in the line, between the gas mixing unit and reaction unit, to facilitate rapid and frequent analysis of gaseous mixture. Alkaline pyrogallol was used to find out the partial pressure of SO_2 in the gaseous mixture. The gaseous mixture was analysed for SO_2 at regular intervals. Fig.2.2 depicts the gas mixing unit.

2.3.3 Reaction Unit

Details of the reaction unit are schematically shown in fig.2.3. It consists of a horizontal globar furnace, capable of maintaining the temperature upto 1400°C. (silicon carbide furnace, Bysakh and Co., Calcutta). In this furnace, control thermocouple (Pt/13%Rh-Pt) is placed at the outer periphery of the furnace tube and temperature is controlled by means of an electronic temperature controller-(M/S Applied Electronic Ltd., Thana, India).

Recrystallised alumina tube (40 mm dia and 800 mm long),

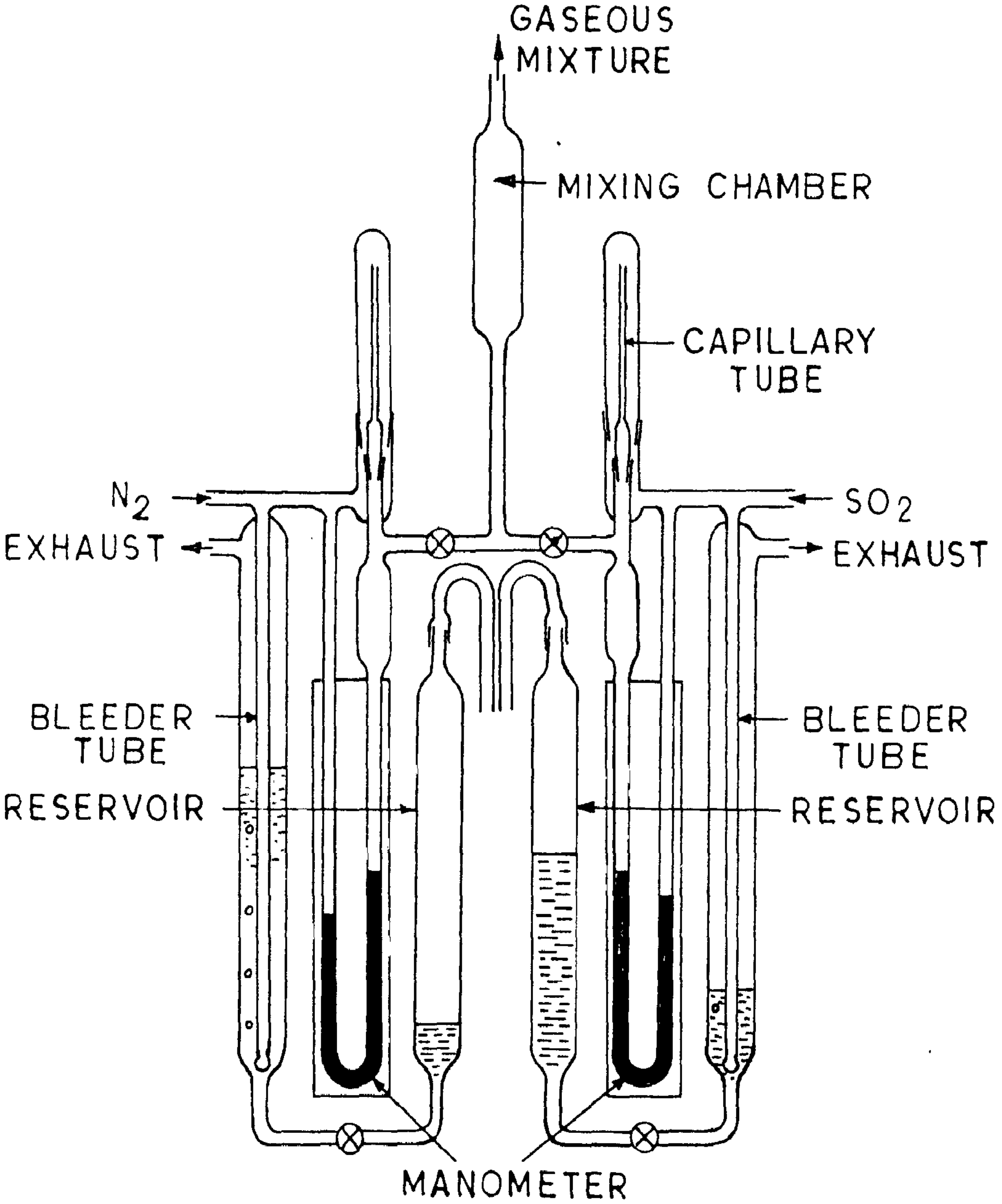


FIG. 2.2 GAS MIXER USING CONSTANT PRESSURE HEAD CAPILLARY FLOWMETER.

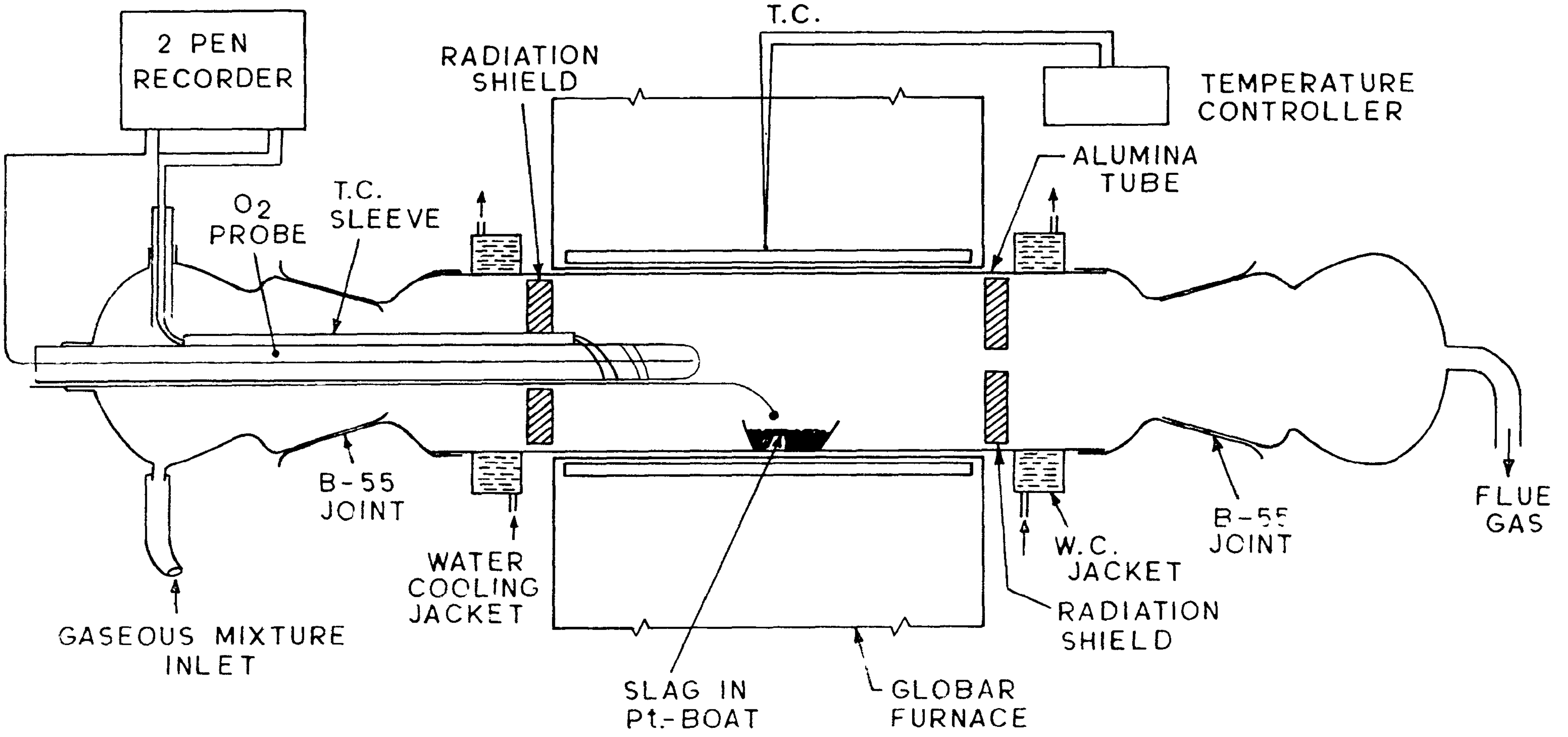


FIG. 2.3-REACTION UNIT

cemented with B-55 pyrex glass joints by means of araldite on both ends, has been used as reaction chamber. The ends of the reaction tube were water cooled by means of copper cooling jackets.

Actual oxygen partial pressure was measured for each gas mixture, by an oxygen probe (using one end closed calcia stabilized zironia tube as solid electrolyte and Fe-FeO as reference electrode). The oxygen pressure, alongwith the temperature, was continuously recorded on a 2 pen recorder (Omniscribe, Digital Electronics Ltd., Bombay).

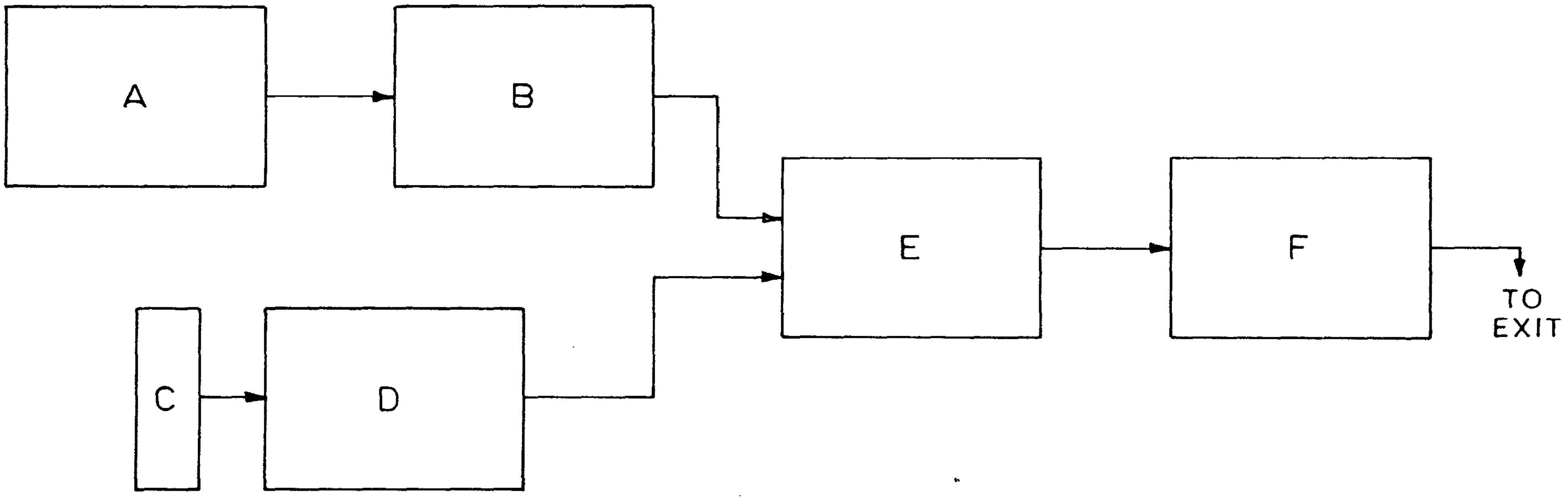
Temperature of the samples was measured through a Pt/10% Rh-Pt thermocouple, placed inside the reaction tube by a potentiometer. Temperature of the reaction zone could be controlled within ± 2°C.

Fig. 2.4 represents the block diagram of the experimental set-up, described above.

2.4 EQUILIBRATION RUNS

2.4.1 Selection of Oxygen Potential

Slag samples of composition $N_{Na_2O} = 0.199$, $N_{SiO_2} = 0.769$, $N_{CaO} = 0.033$ were equilibrated with a $(SO_2 + N_2 + O_2)$ gas mixture at 1373, 1473 and 1573K. P_{O_2} was varied from 10^{-4} to 10^{-11} and P_{SO_2} was maintained at 0.09 atm. Figure 2.5 shows the relation between equilibrium sulphur content and P_{O_2} at which samples were equilibrated. Log C_S and



A. SO_2 PRODUCTION AND STORAGE UNIT
B. SO_2 PURIFICATION UNIT
C. N_2 CYLINDER
D. N_2 PURIFICATION UNIT
E. GAS MIXING UNIT
F. REACTION UNIT

FIG. 2.4 BLOCK ASSEMBLY OF EXPERIMENTAL SET-UP FOR SULPHUR CAPACITY DETERMINATION.

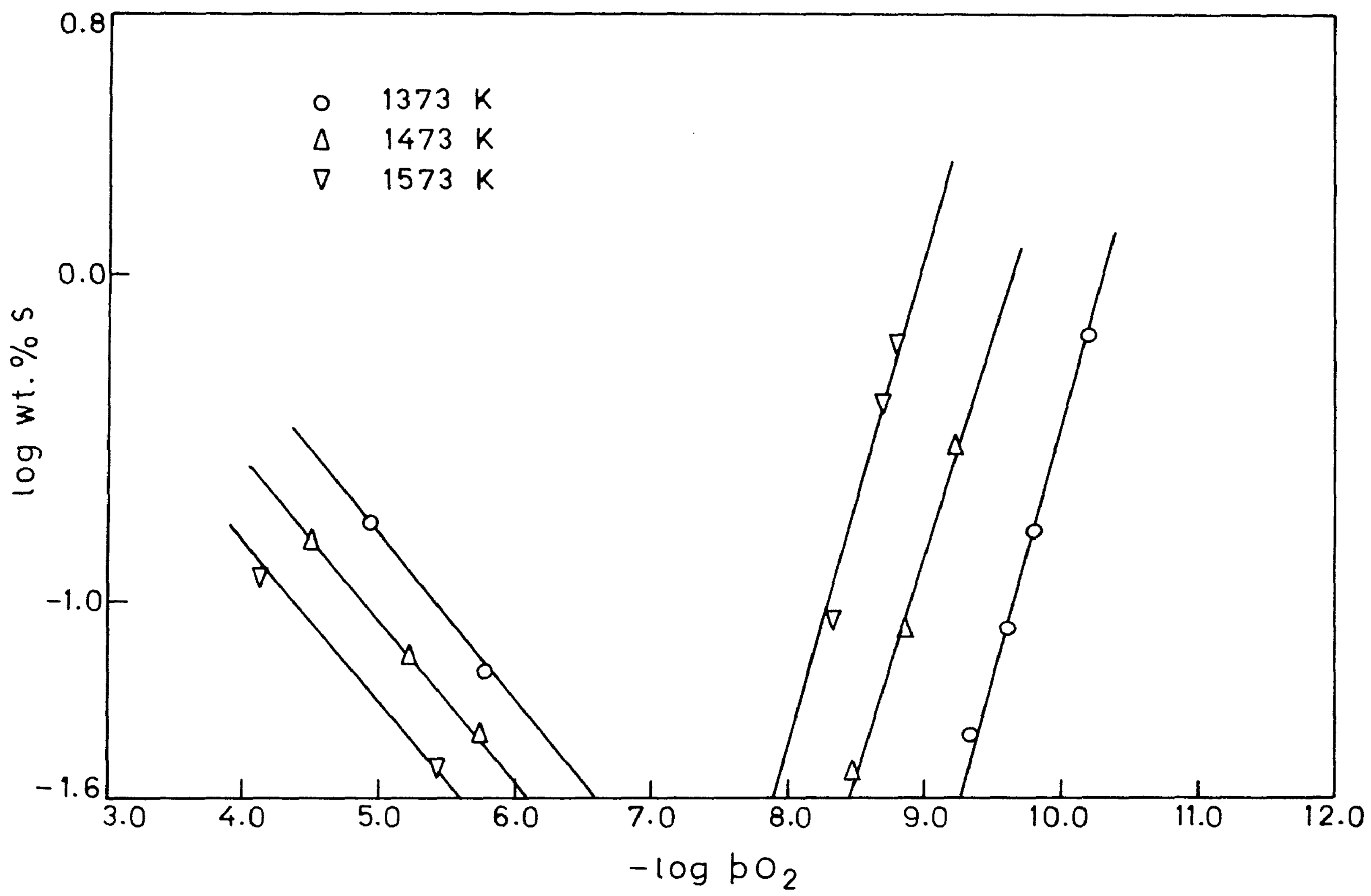


FIG.2.5 EFFECT OF OXYGEN PARTIAL PRESSURE ON THE EQILIBRIUM SULPHUR CONTENT AT DIFFERENT TEMPERATURES OF A TERNARY SLAG ($N_{CaO} = 0.33$, $N_{Na_2O} = 0.199$ AND $N_{SiO_2} = 0.769$) AT $p_{SO_2} = 0.09$ atm.

log C_{SO_4} were calculated for different samples at 1373, 1473 and 1573 K. Figure 2.6 shows the variation of log C_S and log C_{SO_4} with log p_{O_2} at 1373 and 1573 K. This plot was used as a basis for selecting oxygen potential and p_{O_2} in the gaseous mixture was maintained below 10^{-9}-10^{-8} atm.

2.4.2 Selection of SO_2 Potential

Partial pressure of sulphur dioxide in the gaseous mixture was maintained in the range of 0.07-0.10 as further increase in SO_2 concentration may cause precipitation of elemental sulphur resulting in an erroneous sulphur capacity estimation, whereas lower SO_2 levels lead to lower content of the equilibrium sulphur dissolved in the melt which may lead to inaccurate sulphur estimation and hence the sulphur capacity.

2.4.3 Flushing of the Reaction Unit

After intermittent suspension of the experiments, the reaction unit was flushed with purified nitrogen before starting actual equilibration runs. As soon as the reaction furnace attained the desired temperature of study, purified nitrogen was swept in the reaction chamber via mixing unit. When the reaction chamber attained a p_{O_2} less than 10^{-8} atm, which was shown by oxygen probe, purified sulphur dioxide flow was also started and the two gases were mixed in the mixing unit. Gaseous mixture of the desired composition thus

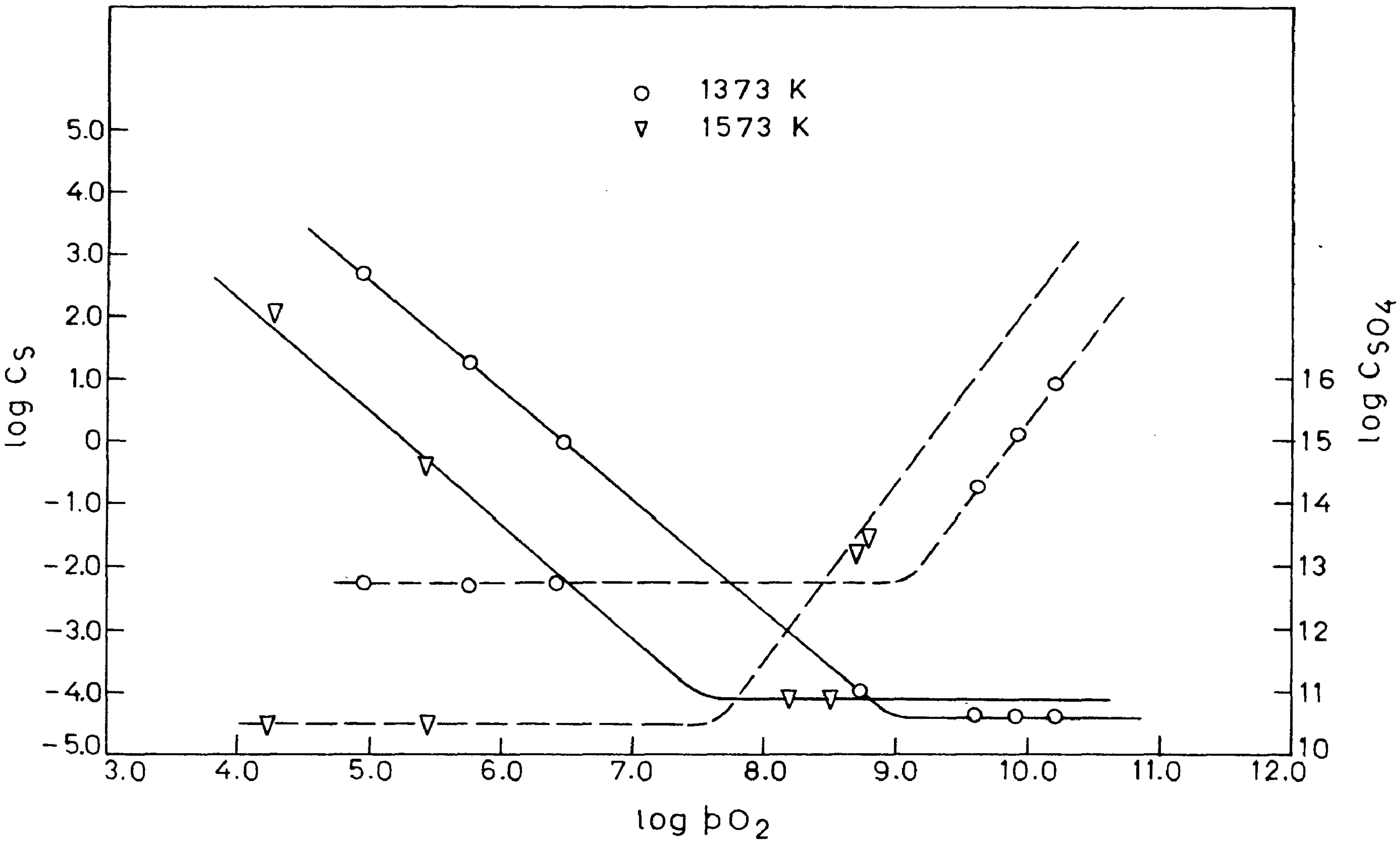


FIG.2.6 PLOT SHOWING FORMATION OF SULPHIDE (FULL LINES) AND SULPHATE (BROKEN LINES) DISSOLVED IN TERNARY SLAG AT TEMPERATURE 1373 K AND 1573 K AND p_{SO_2} = 0.09 atm.

obtained was passed in the reaction chamber and actual experimental runs could be started as soon as the oxygen potential in the reaction chamber was constant, as shown by a straight line on the recorder chart. This process of flushing normally lasted 20-24 hours.

2.4.4 Actual Equilibration of Slag Samples

Around 1 gm of slag sample, contained in a platinum bowl which was made from platinum circular blanks (35 mm ∅, 0.15 mm thickness) by cold forming in a hemispherical die, was mounted on a ceramic boat with a capacity of admitting two or three platinum bowls.

The outlet socket and the radiation shield were removed and the ceramic boat, containing slag samples was pushed in the reaction zone slowly in a span of 10 minutes. Radiation shield and the outlet socket were replaced at their respective positions. After the stipulated time for equilibration given, the outlet socket and the radiation shield were removed and the boat was immediately pulled in the water cooled region of the reaction tube. After 4-5 minutes, the platinum bowl with slag sample was transferred to dessicator. Equilibrated slag sample was then removed from the Pt. bowl and ground. Powdered slag sample was stored in dessicator till it was analysed.

Flow-rate (80 ml/min) of the gaseous-mixture was sufficiently high to avoid the phenomenon of thermal diffusion and upsetting the equilibrium results.

2.4.5 Attainment of Equilibrium

It was noticed that practically no change occurs in the equilibrium sulphur content of the slag sample equilibrated for 6 hours or more as shown in fig.2.7, for the entire range of composition under consideration. Although equilibrium could be attained as deduced from trial runs, yet all the slag samples were exposed to gas-phase for 12 hours or more.

2.5 CHEMICAL ANALYSIS

Rapid instrumentation techniques were applied for the chemical analysis of slag samples before and after the equilibria run for the calcium, sodium and sulphur contents.

Calcium and sodium were analysed at USIC (University Service and Instrumentation Centre) by Atomic Absorption Spectrometer and Sulphur analysis was carried out at Modi Steels, Modinagar by LECO analyser (CS 044).

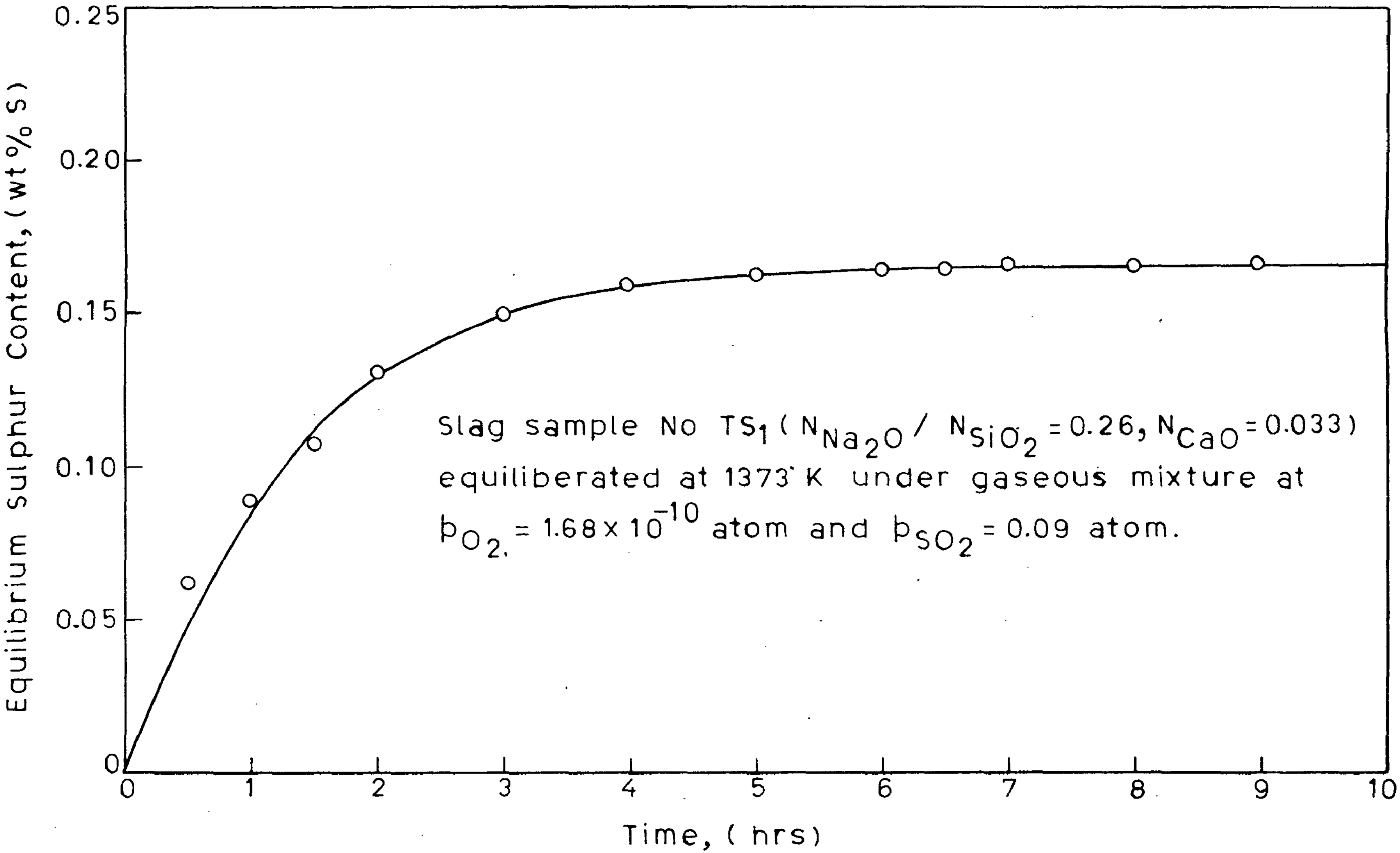


FIG.2.7 PLOT SHOWING VARIATION OF EQUILIBRIUM SULPHUR CONTENT OF SLAG WITH TIME.

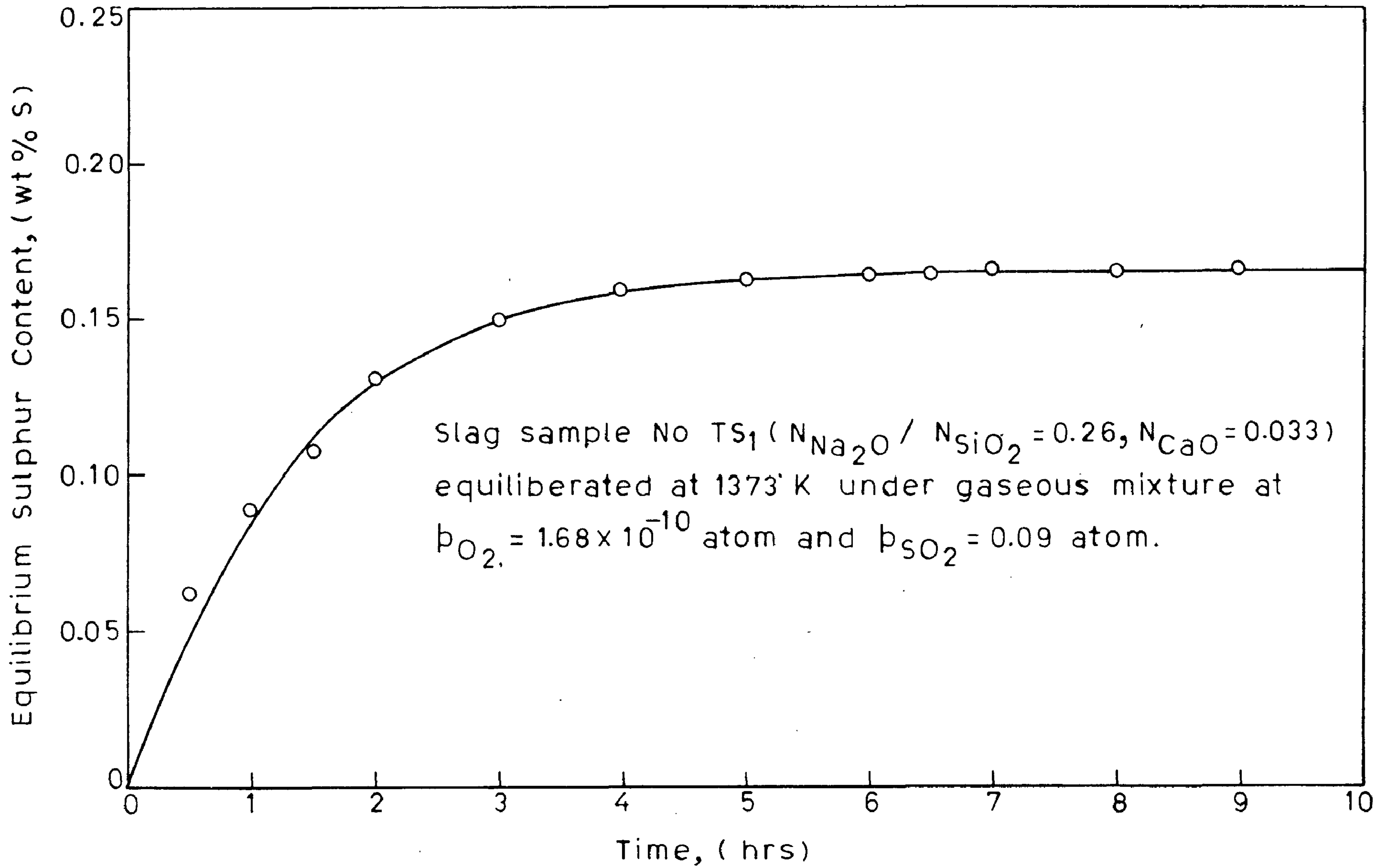


FIG.2.7 PLOT SHOWING VARIATION OF EQUILIBRIUM SULPHUR CONTENT OF SLAG WITH TIME.

Table 2·1- Chemical composition of slags under consideration and their melting points

N_{Na_2O}/N_{SiO_2}	N_{Na_2O}	N_{SiO_2}	N_{CaO}	Melting Point (°C)
0·26	0·205	0·795	-	1140
	0·199	0·769	0·033	990
	0·192	0·743	0·066	1000
	0·183	0·708	0·109	950
	0·170	0·657	0·173	1100
0·40	0·288	0·712	-	825
	0·274	0·682	0·044	850
	0·262	0·651	0·087	950
	0·243	0·605	0·152	1100
	0·226	0·559	0·215	1180
0·52	0·340	0·660	-	875
	0·322	0·623	0·055	990
	0·304	0·588	0·108	1070
	0·282	0·545	0·173	1180
0·84	0·456	0·544	-	1020
	0·419	0·577	0·064	1050
	0·397	0·474	0·129	1130
	0·348	0·416	0·235	1180
1·03	0·508	0·492	-	1085
	0·470	0·455	0·076	1025
	0·432	0·418	0·150	1050

Table 2.2- Equilibrium sulphur content with varying oxygen partial pressure in gas-phase

Composition of slag : $N_{Na_2O} = 0.199$,
$N_{SiO_2} = 0.769$, $N_{CaO} = 0.033$

Partial pressure of SO_2, $p_{SO_2} = 0.09$ atm

Temp. =1373K

p_{O_2}	Wt.%S	log p_{O_2}	log W	log C_S	log C_{SO_4}
6.54×10^{-11}	0.665	-10.184	-0.117	-4.403	15.965
1.68×10^{-10}	0.165	-9.775	-0.783	-4.394	15.153
2.70×10^{-10}	0.0821	-9.569	-1.086	-4.388	14.749
3.467×10^{-7}	0.0295	-6.460	-1.530	-0.170	12.750
1.778×10^{-6}	0.0624	-5.750	-1.205	1.220	12.720
1.202×10^{-5}	0.1740	-4.920	-0.759	2.910	12.740
Temp. = 1473K					
5.75×10^{-10}	0.302	-9.240	-0.520	-4.270	14.210
1.41×10^{-9}	0.0832	-8.850	-1.080	-4.240	13.460
3.24×10^{-9}	0.0309	-8.490	-1.511	-4.130	12.850
1.82×10^{-6}	0.0398	-5.740	-1.400	0.104	11.580
6.17×10^{-6}	0.0684	-5.210	-1.165	1.130	11.550
3.16×10^{-5}	0.1570	-4.500	-0.804	2.560	11.560
Temp. =1573K					
1.58×10^{-9}	0.6240	-8.800	-0.205	-4.110	13.490
2.04×10^{-9}	0.4070	-8.690	-0.390	-4.130	13.250
6.17×10^{-9}	0.0933	-8.240	-1.030	-4.050	12.370
3.63×10^{-6}	0.0309	-5.440	-1.510	-0.370	10.510
5.75×10^{-5}	0.1190	-4.240	-0.924	2.010	10.493

CHAPTER - 3

SULPHUR CAPACITY OF THE SYSTEM Na_2O-SiO_2

This chapter is devoted to the experimental results and discussion for the binary Na_2O-SiO_2 system. The results of the present investigation have been analysed and compared with the existing data on the binary silicate systems as well as soda silica slags.

3.1 RESULTS

Soda-silica slags of varying Na_2O/SiO_2 molar ratios, namely 0.26, 0.40, 0.52, 0.84 and 1.03, were equilibrated with a gas phase of desired partial pressures of oxygen and sulphur dioxide at 1373, 1423, 1473, 1523 and 1573K. As has already been pointed in Section 2.4.1 of the previous chapter that the peak (or the break-even point) between sulphide and sulphate equilibria shifts to the higher oxygen potentials with the increase in temperature of chemical equilibrium and therefore the oxygen partial pressure during the experimental runs, was accordingly adjusted in the range $10^{-11}-10^{-8}$ atm. Sulphur dioxide content of the gas phase ranged between 7-10% for all equilibria runs, as sulphur di-oxide content beyond 10%

in gaseous mixture of N_2,SO_2 and O_2 might result into precipitation of elemental sulphur.

The experimental observations during the equilibria runs as also the equilibrium sulphur content of the equilibrated slag samples are reported in the columns of tables 3.1-3.5.

3.2 CALCULATIONS

The oxygen potential, p_{O_2}, in the gas phase was calculated from the emf data obtained with the help of oxygen probe at different temperatures. The emf E(millivolts), is related to p_{O_2} as given by the following expression

$$E = \frac{RT}{nF} \ln (p^{II}_{O_2}/p^{I}_{O_2}) \qquad \ldots (3.1)$$

where R-the universal gas constant (Cal K^{-1} $mole^{-1}$), F- the Faraday's constant (Cal/mV), n- the number of electrons participating in the reaction, p_{O_2}- the oxygen partial pressure (superscripts I and II refer to reference and the reaction media respectively) (atm), and T - the absolute temperature (K).

Substituting the values of constants appearing in eq.3.1, one gets the expression,

$$E = 2.154\times10^{-2}.T.\ln(p^{II}_{O_2}/p^{I}_{O_2}) \qquad \ldots (3.1a)$$

which on rearrangement of various terms is modified to

$$p^{II}_{O_2} = p^{I}_{O_2}.\exp(\frac{46.422E}{T}) \qquad \ldots. (3.2)$$

where $p^{I}_{O_2}$ - the equilibrium partial pressure of the Fe-FeO system (used as reference media in the present work) at the temperature of oxygen probe, is expressed [93], as

$$p^{I}_{O_2} = \exp(-\frac{62449.68}{T} + 14.996) \qquad \ldots (3.3)$$

Partial pressure oxygen in different reacting gaseous mixtures, $p^{II}_{O_2}$, calculated using eq.3.2 are tabulated in the columns of tables 3.1-3.5.

Further, to calculate the partial pressure of sulphur, p_{S_2}, following equilibrium reaction was considered,

$$\tfrac{1}{2}S_2+O_2 = SO_2 \qquad \ldots (3.4)$$

for which the equilibrium constant, K_7, is given by the expression

$$K_7 = \frac{p_{SO_2}}{p_{O_2} \cdot p_{S_2}^{1/2}} \qquad \ldots (3.5)$$

Rearranging the terms in eq.3.5 gives,

$$p_{S_2} = (p_{SO_2}/p_{O_2} \cdot K_7))^2 \qquad \ldots (3.5a)$$

Equilibrium constant, K_7, appearing in eq.3.5a is calculated for the temperature of interest by using available thermodynamic data [93],

$$K_7 = \exp(\frac{43588.969}{T} - 8.7107) \qquad \ldots (3.6)$$

Partial pressure of sulphur dioxide is calculated by analysing the gaseous mixture for SO_2 content and is given in tables 3.1-3.5. Subsequently sulphur potential in gaseous mixture is calculated with the help of eq.3.5a. These calculated values are presented in the column of tables 3.6-3.10 for corresponding gaseous-mixtures.

Sulphur capacity (or the sulphide capacity, since the conditions were maintained so as to promote formation of sulphide), C_S, defined earlier by Fincham and Richardson as,

$$C_S = (\text{Wt.\%.S})(p_{O_2}/p_{S_2})^{1/2} \qquad \ldots (3.7)$$

C_S is then computed from the already calculated values of oxygen and sulphur potentials. These values are averaged for respective slag compositions and temperatures. C_S and the average sulphur capacity (AvC_S) are given in tables 3.6-3.10 alongwith the logarithm of AvC_S(log C_S).

Results are plotted in terms of log C_S as functions of Na_2O/SiO_2 molar ratios at different temperatures (of study) and reciprocal of absolute temperature for Na_2O/SiO_2 molar ratios equal to 1/3, 1/2, 2/3 and 1 in figs.3.1 and 3.2 respectively.

3.3 INFERENCES AND DISCUSSION

Figure 3.1 depicts a marked effect of temperature as well as the composition on sulphur capaicty of soda-silica slags.

Logarithm of sulphur capacity increases linearly with increasing molar ratio of Na_2O/SiO_2. For 1373, 1473 and 1573K,

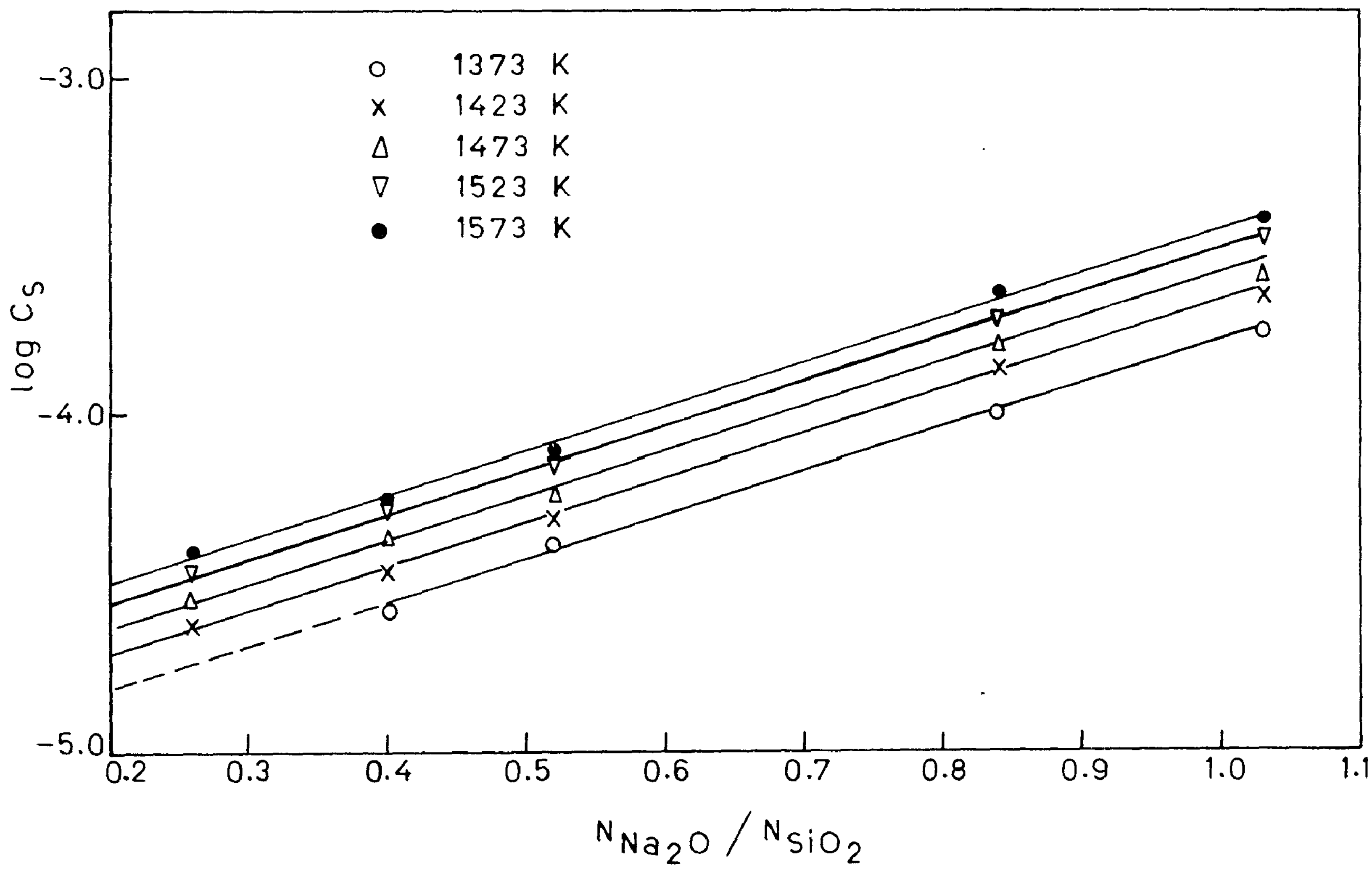


FIG. 3.1 VARIATION IN log C_S OF SODA-SILICA SLAGS AT DIFFERENT N_{Na_2O} / N_{SiO_2} RATIOS AND TEMPERATURES.

relationships between log C_S and molar ratio of Na_2O/SiO_2 may be quantitatively expressed as follows,

$$\log C_S = -1.286(N_{Na_2O}/N_{SiO_2})+5.066 \qquad \ldots (3.8a)$$

$$\log C_S = -1.314(N_{Na_2O}/N_{SiO_2})+4.894 \qquad \ldots (3.8b)$$

and

$$\log C_S = -1.329(N_{Na_2O}/N_{SiO_2})+4.779 \qquad \ldots (3.8c)$$

Increasing temperature of equilibration also amounts to the increase in sulphur capacity. From fig.3.2 one can arrive at following relationships between log C_S and absolute temperature for various Na_2O/SiO_2 molar ratios namely 1/3, 1/2, 2/3 and 1 respectively,

$$\log C_S = \frac{3529.412}{T} + 2.061 \qquad \ldots (3.9a)$$

$$\log C_S = \frac{3647.060}{T} + 1.776 \qquad \ldots (3.9b)$$

$$\log C_S = \frac{3411.770}{T} + 1.716 \qquad \ldots (3.9b)$$

and

$$\log C_S = \frac{3529.412}{T} + 1.201 \qquad \ldots (3.9d)$$

Present data could be analysed qualitatively by considering the gas-slag equilibrium given by eq.1.5 as

$$\tfrac{1}{2}S_2+(O^{2-}) = \tfrac{1}{2}O_2+ (S^{2-}) \qquad \ldots (1.5)$$

for which equilibrium constant, K_8, under the assumption that

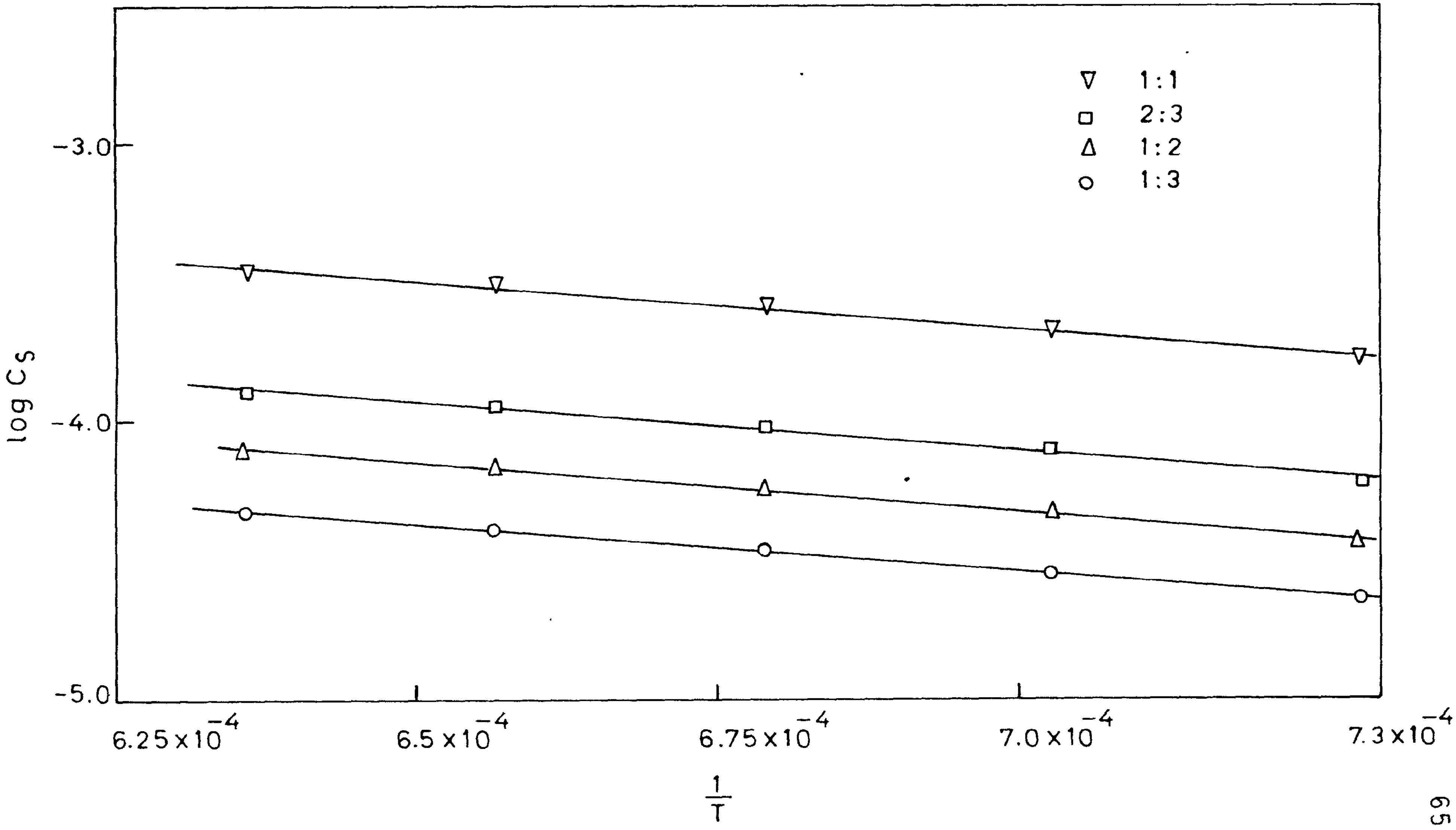


FIG. 3.2 VARIATION OF log C_S WITH 1/T FOR VARIOUS N_{Na_2O}/N_{SiO_2} RATIOS.

sulphide ions in slags for very low sulphur levels follow Henrian behaviour and Henrian activity coefficient can be taken as unity, may be written as

$$K_8 = \frac{(\text{Wt.\%S})}{a_{O^{2-}}}\left(\frac{p_{O_2}}{p_{S_2}}\right)^{1/2} \qquad \ldots\ (3.10)$$

Hence sulphur capacity, C_S, is represented as

$$C_S = K_8 . a_{O^{2-}} (\text{or } K.a_{O^{2-}}) \qquad \ldots\ (3.11)$$

where $a_{O^{2-}}$ is the oxygen ion activity in the melt and is equal to the activity of basic oxide in the binary silicate systems. Therefore, it becomes apparant that higher basic oxide content should result into increased number of free oxygen ions, increasing thereby the oxygen ion activity and hence, the sulphur capacity of slag. However, the linearity of log C_S versus Na_2O/SiO_2 molar ratio is only empirical and may be restricted only to the composition range under study.

Qualitatively, increased sulphur capacity with increasing temperature may also be argued with the help of eq.3.11, which can be written as

$$\begin{aligned}\log C_S &= \log K_8 + \log a_{O^{2-}} \\ &= -\frac{2.303}{R}\left[(\Delta H_1 - T\Delta S_1) - (\Delta S_1) - (\Delta\bar{\bar{H}}_{Na_2O} - T\Delta\bar{\bar{S}}_{NO_2O})\right] \\ &= -\frac{2.303}{RT}(\Delta H_1 - \Delta\bar{\bar{H}}_{Na_2O}) + \frac{2.303}{R}(\Delta S_1 - \Delta\bar{\bar{S}}_1 - \Delta\bar{\bar{S}}_{Na_2O})\end{aligned} \qquad \ldots\ (3.11a)$$

Since ΔH_1 and $\Delta \bar{H}_{Na_2O}$ can be taken as constant, over the temperature range under consideration, so log C_S versus 1/T plot should be linear as shown in fig.3.2.

Further, since $\Delta \bar{H}_{Na_2O}$ is expected to be strongly negative because of strong soda-silica reaction in the system under study and ΔH_1 may be slightly positive, hence the slope of log C_S versus 1/T lines at various Na_2O/SiO_2 molar ratios is expected to be positive, which is found to be true from fig.3.2.

3.4 COMPARISON WITH OTHER BINARY SILICATE SYSTEMS

Figure 3.3 represents a plot of logarithmic sulphur capacity as a function of base/acid molar ratio for different binary silicate systems (temperature is indicated inside brackets against each system) including the present work.

Position of Na_2O-SiO_2, system under present study, above $MgO-SiO_2$ and $CaO-SiO_2$ even at lower temperatures could be justified by considering a basic oxide-silica melt of orthosilicate composition. Basic oxide activity (a_{BO}) may be roughly indicated by the heat of formation, which has been compiled by Ward [8] . Approximate values of heat of formation of orthosilicates with iron-, manganese-, magnesium-, calcium- and sodium-oxides are -9.0, -11.8, -15.1, -29.8 and -74.9 KCal respectively. The lower the enthalpy of formation of orthosilicate more stronger the

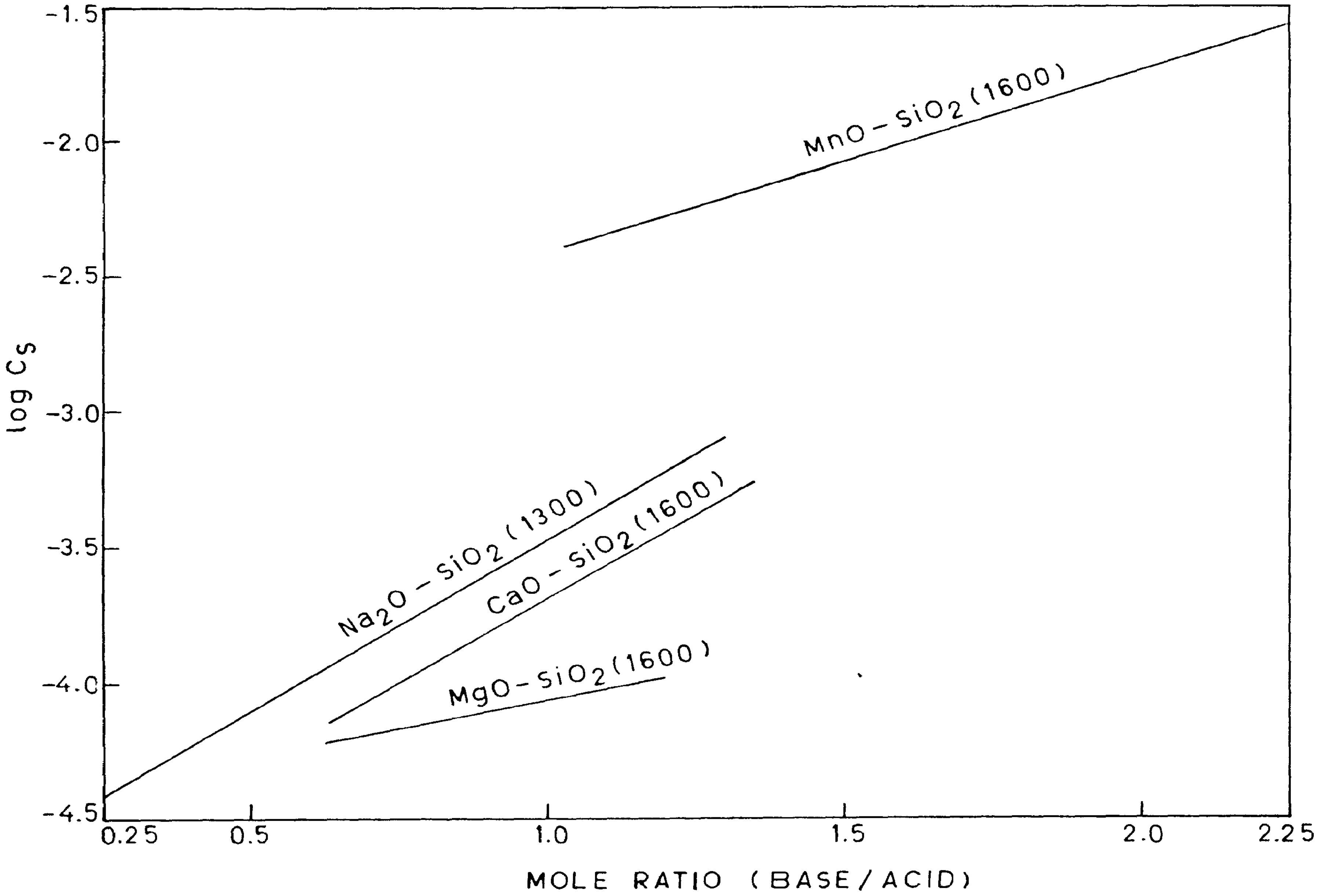


FIG. 3.3 SULPHUR CAPACITY OF VARIOUS BINARY SILICATE SYSTEMS.

basic oxide is bonded to silica and hence lower the value of activity of basic oxide. Thus it could be emphasized that at orthosilicate composition $a_{FeO} > a_{MgO} > a_{MnO} > a_{CaO} > a_{Na_2O}$. Furthermore, because of higher reactivity $a_{Na_2O} \ll a_{CaO}$ in their respective binary melts. Inoue and Suito have plotted a_{BO} versus mole fraction of SiO_2. After due temperature correction is applied, it is expected that the activity of Na_2O will be lower than that of lime by one or two exponents. It has also been shown [8] that sodium ion has a desulphurising power greater than calcium ion by a factor of 1070 and hence value of K_8 for the gas-slag reaction (eq. 1.5) will be approximately 10^3 times more for Na_2O in comparison to lime-silicate melts. Thus the product $K_8 \cdot a_{O^{2-}}$ from eq. 3.2 will be more and hence higher sulphur capacity values of soda-silica system. Similarly it may be argued for $MgO-SiO_2$ and Na_2O-SiO_2 systems too.

In $MnO-SiO_2$ System, although the value of K_8 is lower by a factor 2.34×10^{-4} in comparison to Na_2O-SiO_2 system. Yet, since a_{MnO} is far far greater than a_{Na_2O}, the overall effect on the product $K_8 \cdot a_{O^{2-}}$ is not very much significant, therefore, the difference in the sulphur capacity values of the two systems, under present discussion, too is not very much marked when they are brought to the same level of temperature and composition.

3.5 COMPARISON WITH PREVIOUS WORK ON SODA-SILICA SLAG SYSTEM

The reported work on sulphur capacity [80,84,85] of Na_2O-SiO_2 system along with the results of the present investigation are plotted as log C_S versus Na_2O/SiO_2 molar ratio in fig.3.4.

In the above mentioned figure it is observed that the nature of the plots is somewhat identical in all the cases, i.e. the sulphur capacity increases with increase in molar ratio, Na_2O/SiO_2 and temperature of equilibration, yet quantitatively the results of the present investigation are not in good agreement with those of Denier [85], and Nagashima and Katsura [80].

In the work of Bahout et al [83] the experimental condition employed in gas-slag reactive system. Because of air-borne soda injection, it is doubtful to achieve lower oxygen potential so that only sulphide would form. It is likely that in their experiements, sulphates, sulphites and pyrosulphates might have been formed as side-reactions alongwith sulphides. This would lead to higher content of sulphur dissolved in the slag and may lead to higher values of estimated sulphur capacity.

The discrepancy in the present data and that of Nagashima and Katsura [80] could be accounted for to the

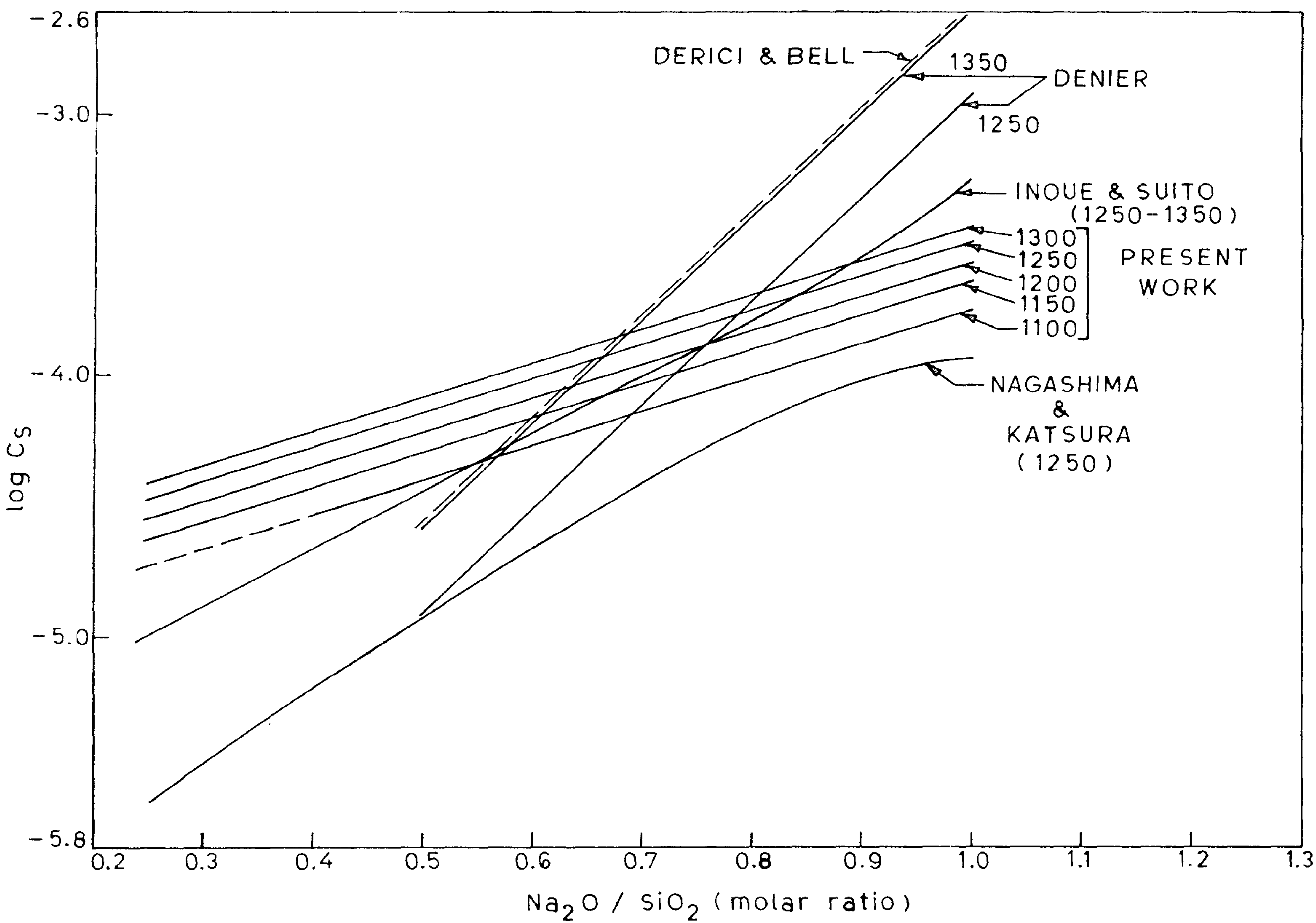


FIG. 3.4 COMPARISON OF PRESENT WORK WITH PREVIOUS WORK [40]

upsetting of their equilibrium sulphur estimate owing to the formation of NaOH by the reaction of soda with water vapour and also because of the loss of sodium due to vaporisation specially at higher mole fractions of sodium oxide.

Present data is in reasonable agreement with those of Inoue and Suito [84], but however small quantitative variation in their data may be due to the contamination of slag samples by MgO, graphite and Al_2O_3 first two of which were used as the materials for crucible and the last for stirrer respectively during experimentation.

Presence of other cationic species is expected to change the behaviour of slag as regards the sulphur transfer from metal to slag is concerned. This has been discussed at length in Section 3.4.

Table 3.1 Sulphur Equilibration Studies in Binary Soda Silica Slags at 1373 K

N_{Na_2O}/N_{SiO_2}	Sample Number	Oxygen potential in gas phase			p_{SO_2}	Wt%.S
		emf(mV)	Temp.(K)	p_{O_2} (atm.)		
0.40	BS_2	526	993	$7.99\text{x}10^{-11}$	0.0840	0.306
	BS_4	526	993	$7.99\text{x}10^{-11}$	0.090	0.333
	BS_5	529	993	$9.22\text{x}10^{-11}$	0.100	0.286
0.52	BS_7	531	993	$1.01\text{x}10^{-10}$	0.100	0.428
	BS_8	531	993	$1.01\text{x}10^{-10}$	0.100	0.421
	BS_{11}	536	993	$1.28\text{x}10^{-10}$	0.092	0.257
0.84	BS_{13}	536	993	$1.28\text{x}10^{-10}$	0.090	0.631
	BS_{15}	539	993	$1.48\text{x}10^{-10}$	0.080	0.448
1.03	BS_{16}	546	993	$2.04\text{x}10^{-10}$	0.098	0.592
	BS_{17}	546	993	$2.04\text{x}10^{-10}$	0.090	0.540
	BS_{18}	546	993	$2.04\text{x}10^{-10}$	0.090	0.545

Table 3.2- Sulphur Equilibration Studies in Binary Soda Silica Slags at 1423°K

$^{M}Na_2O/^{N}SiO_2$	Sample Number	Oxygen potential in gas phase			p_{SO_2}	Wt. % S
		emf(mV)	Temp. (K)	pO_2(atm)		
0.26	BS_{19}	514	1013	9.82×10^{-11}	0.07	0.519
	BS_{20}	514	1013	9.82×10^{-11}	0.07	0.523
0.40	BS_{23}	518	1013	1.18×10^{-10}	0.07	0.556
	BS_{25}	518	1013	1.18×10^{-10}	0.078	0.618
	BS_{26}	518	1013	1.18×10^{-10}	0.078	0.624
0.52	BS_{27}	522	1013	1.42×10^{-10}	0.080	0.707
	BS_{28}	522	1013	1.42×10^{-10}	0.084	0.717
	BS_{29}	514	1023	1.43×10^{-10}	0.084	0.746
0.84	BS_{31}	508	1023	1.09×10^{-10}	0.070	2.540
	BS_{32}	508	1023	1.09×10^{-10}	0.070	2.570
1.03	BS_{35}	516	1023	1.56×10^{-10}	0.080	2.820
	BS_{36}	516	1023	1.56×10^{-10}	0.080	2.860
	BS_{37}	516	1023	1.56×10^{-10}	0.086	3.060

Table 3.3- Sulphur Equilibration Studies in Binary Soda Silica Slags at 1473 K

N_{Na_2O}/N_{SiO_2}	Sample Number	Oxygen potential in gas phase			p_{SO_2}	Wt.% S
		emf(mV)	Temp(K)	pO_2(atm)		
0.26	BS_{39}	520	1043	3.84×10^{-10}	0.070	0.222
	BS_{41}	520	1043	3.84×10^{-10}	0.074	0.237
0.40	BS_{43}	525	1043	4.80×10^{-10}	0.076	0.278
	BS_{44}	525	1043	4.80×10^{-10}	0.076	0.273
0.52	BS_{45}	528	1043	5.48×10^{-10}	0.080	0.309
	BS_{47}	528	1043	5.48×10^{-10}	0.076	0.296
	BS_{48}	528	1043	5.48×10^{-10}	0.076	0.288
0.84	BS_{49}	534	1043	7.16×10^{-10}	0.080	0.575
	BS_{50}	534	1043	7.16×10^{-10}	0.080	0.582
1.03	BS_{52}	540	1023	4.64×10^{-10}	0.072	1.590
	BS_{53}	540	1023	4.64×10^{-10}	0.078	1.720
	BS_{54}	540	1023	4.64×10^{-10}	0.078	1.690

Table 3.4 Sulphur Equilibrium Studies in Binary Soda Silica Slags at 1523 K

N_{Na_2O}/N_{SiO_2}	Sample Number	Oxygen potential in gas phase			pSO_2	Wt.%S
		emf(mV)	Temp(K)	pO_2(atm)		
0.26	BS_{55}	512	1073	7.58×10^{-10}	0.080	0.297
	BS_{56}	512	1073	7.58×10^{-10}	0.080	0.305
	BS_{57}	512	1073	7.58×10^{-10}	0.074	0.276
0.40	BS_{59}	517	1073	9.42×10^{-10}	0.070	0.291
	BS_{61}	521	1073	1.12×10^{-9}	0.076	0.203
0.52	BS_{63}	532	1073	1.80×10^{-9}	0.080	0.164
	BS_{64}	532	1073	1.80×10^{-9}	0.080	0.169
	BS_{66}	538	1073	2.34×10^{-9}	0.086	0.119
0.84	BS_{68}	568	1053	4.52×10^{-9}	0.100	0.134
	BS_{69}	568	1053	4.52×10^{-9}	0.090	0.119
	BS_{70}	568	1053	4.52×10^{-9}	0.090	0.124
1.03	BS_{71}	574	1053	5.88×10^{-9}	0.086	0.141
	BS_{72}	574	1053	5.88×10^{-9}	0.086	0.144

Table 3.5 Sulphur Equilibrium Studies in Binary Soda Silica Slags at 1573 K

N_{Na_2O}/N_{SiO_2}	Sample Number	Oxygen potential in gas phase			pSO_2	Wt.% S
		emf(mV)	Temp(K)	pO_2(atm)		
0.26	BS_{73}	538	1093	4.42×10^{-9}	0.100	0.0739
	BS_{74}	538	1093	4.42×10^{-9}	0.100	0.0746
0.40	BS_{76}	540	1093	4.82×10^{-9}	0.100	0.0926
	BS_{77}	545	1093	5.96×10^{-9}	0.094	0.0626
	BS_{78}	545	1093	5.96×10^{-9}	0.094	0.0632
0.50	BS_{79}	558	1063	4.03×10^{-9}	0.100	0.1720
	BS_{81}	558	1063	4.03×10^{-9}	0.094	0.1610
	BS_{82}	558	1063	4.03×10^{-9}	0.094	0.1570
0.84	BS_{85}	562	1063	4.80×10^{-9}	0.090	0.3510
	BS_{86}	562	1063	4.80×10^{-9}	0.090	0.3430
	BS_{88}	567	1063	5.97×10^{-9}	0.084	0.2340
1.03	BS_{89}	552	1063	3.10×10^{-9}	0.084	1.0300
	BS_{90}	552	1063	3.10×10^{-9}	0.084	0.9970
	BS_{92}	556	1063	3.69×10^{-9}	0.090	0.8370

Table 3.6- Calculated Values of Sulphur Capacity of binary Soda-Silica Slags at 1373K

N_{Na_2O}/N_{SiO_2}	Sample Number	P_{O_2} $\times 10^{10}$	P_{S_2}	C_S	AvC_S	log C_S
0.40	BS_2	0.799	1.08×10^{-2}	2.630×10^{-5}	2.620×10^{-5}	-4.580
	BS_4	0.799	1.24×10^{-2}	2.671×10^{-5}		
	BS_5	0.922	1.15×10^{-2}	2.560×10^{-5}		
0.52	BS_7	1.010	9.56×10^{-3}	4.404×10^{-5}	4.275×10^{-5}	-4.370
	BS_8	1.010	9.56×10^{-3}	4.332×10^{-5}		
	BS_{11}	1.280	5.06×10^{-3}	4.089×10^{-5}		
0.84	BS_{13}	1.280	4.84×10^{-3}	1.026×10^{-4}	1.022×10^{-4}	-3.990
	BS_{15}	1.480	2.86×10^{-3}	1.019×10^{-4}		
1.03	BS_{16}	2.040	2.26×10^{-3}	1.779×10^{-4}	1.776×10^{-4}	-3.750
	BS_{17}	2.040	1.91×10^{-3}	1.767×10^{-4}		
	BS_{18}	2.040	1.91×10^{-3}	1.783×10^{-4}		

Table 3.7- Calculated Values of Sulphur Capacity of Binary Soda-Silica Slags at 1423 K

N_{Na_2O}/N_{SiO_2}	Sample Number	p_{O_2} x10^{10}	pS_2	C_S	AvC_S	log C
0.26	BS_{19}	0.982	4.63×10^{-2}	2.390×10^{-5}	2.399×10^{-5}	-4.62
	BS_{20}	0.982	4.63×10^{-2}	2.408×10^{-5}		
0.40	BS_{23}	1.180	3.21×10^{-2}	3.373×10^{-5}	3.378×10^{-5}	-4.47
	BS_{25}	1.180	3.98×10^{-2}	3.364×10^{-5}		
	BS_{26}	1.180	3.98×10^{-2}	3.397×10^{-5}		
0.52	BS_{27}	1.420	2.89×10^{-2}	4.954×10^{-5}	5.003×10^{-5}	-4.30
	BS_{28}	1.420	2.89×10^{-2}	5.024×10^{-5}		
	BS_{29}	1.430	3.14×10^{-2}	5.031×10^{-5}		
0.84	BS_{31}	1.090	3.76×10^{-2}	1.368×10^{-4}	1.376×10^{-4}	-3.86
	BS_{32}	1.090	3.76×10^{-2}	1.384×10^{-4}		
1.03	BS_{35}	1.560	2.40×10^{-2}	2.275×10^{-4}	2.293×10^{-4}	-3.64
	BS_{36}	1.560	2.40×10^{-2}	2.307×10^{-4}		
	BS_{37}	1.560	2.77×10^{-2}	2.297×10^{-4}		

Table 3.8- Calculated Values of Sulphur Capacity of Binary Soda-Silica Slags at 1473K

N_{Na_2O}/N_{SiO_2}	Sample Number	P_{O_2} $\times 10^{10}$	pS_2	C_S	AvC_S	$\log C_S$
0.26	BS_{39}	3.84	2.42×10^{-2}	2.795×10^{-5}	2.809×10^{-5}	-4.55
	BS_{41}	3.84	2.70×10^{-2}	2.822×10^{-5}		
0.40	BS_{43}	4.80	1.83×10^{-2}	4.505×10^{-5}	4.464×10^{-5}	-4.35
	BS_{44}	4.80	1.83×10^{-2}	4.424×10^{-5}		
0.52	BS_{45}	5.48	1.55×10^{-2}	5.803×10^{-5}	5.782×10^{-5}	-4.24
	BS_{47}	5.48	1.40×10^{-2}	5.851×10^{-5}		
	BS_{48}	5.48	7.40×10^{-2}	5.693×10^{-5}		
0.84	BS_{49}	7.16	9.10×10^{-3}	1.613×10^{-4}	1.622×10^{-5}	-3.79
	BS_{50}	7.16	9.10×10^{-3}	1.632×10^{-4}		
1.03	BS_{52}	4.64	1.76×10^{-2}	2.585×10^{-4}	2.567×10^{-5}	-3.59
	BS_{53}	4.64	2.06×10^{-2}	2.581×10^{-4}		
	BS_{54}	4.64	2.06×10^{-2}	2.536×10^{-4}		

Table 3.9- Calculated Values of Sulphur Capacity of Binary Soda-Silica Slags at 1523°K

N_{Na_2O}/N_{SiO_2}	Sample Number	p_{O_2} $\times 10^{10}$	pS_2	C_S	AvC_S	$LogC_S$
0.26	BS_{55}	7.58	5.67×10^{-2}	3.434×10^{-5}	3.471×10^{-5}	-4.46
	BS_{56}	7.58	5.67×10^{-2}	3.527×10^{-5}		
	BS_{57}	7.58	4.85×10^{-2}	3.450×10^{-5}		
0.40	BS_{59}	9.42	2.81×10^{-2}	5.328×10^{-5}	5.266×10^{-5}	-4.28
	BS_{61}	11.20	2.34×10^{-2}	5.203×10^{-5}		
0.52	BS_{63}	18.00	1.01×10^{-2}	6.940×10^{-5}	7.011×10^{-5}	-4.15
	BS_{64}	18.00	1.01×10^{-2}	7.151×10^{-5}		
	BS_{66}	23.40	6.87×10^{-3}	6.943×10^{-5}		
0.84	BS_{68}	45.20	2.49×10^{-3}	1.805×10^{-4}	1.814×10^{-4}	-3.74
	BS_{69}	45.20	2.01×10^{-3}	1.781×10^{-4}		
	BS_{70}	45.20	2.01×10^{-3}	1.856×10^{-4}		
1.03	BS_{71}	58.80	1.09×10^{-3}	3.277×10^{-4}	3.312×10^{-4}	-3.48
	BS_{72}	58.80	1.09×10^{-3}	3.347×10^{-4}		

Table 3.10- Calculated Values of Sulphur Capacity of Binary Soda-Silica Slags at 1573°K

N_{Na_2O}/N_{SiO_2}	Sample Number	p_{O_2} x10^{10}	pS_2	C_S	AvC$_S$	logC$_S$
0.26	BS_{73}	44.2	1.61×10^{-2}	3.876×10^{-5}	3.894×10^{-5}	-4.41
	BS_{74}	44.2	1.61×10^{-2}	3.913×10^{-5}		
0.40	BS_{76}	48.2	1.35×10^{-2}	5.533×10^{-5}	5.507×10^{-5}	-4.26
	BS_{77}	59.6	7.81×10^{-3}	5.469×10^{-5}		
	BS_{78}	59.6	7.81×10^{-3}	5.521×10^{-5}		
0.52	BS_{79}	40.3	1.93×10^{-2}	7.854×10^{-5}	7.767×10^{-5}	-4.11
	BS_{81}	40.3	1.71×10^{-2}	7.821×10^{-5}		
	BS_{82}	40.3	1.71×10^{-2}	7.626×10^{-5}		
0.84	BS_{85}	48.0	1.10×10^{-2}	2.315×10^{-4}	2.29×10^{-4}	-3.64
	BS_{86}	48.0	1.10×10^{-2}	2.262×10^{-4}		
	BS_{88}	59.7	6.21×10^{-3}	2.293×10^{-4}		
1.03	BS_{89}	31.0	2.30×10^{-2}	3.777×10^{-4}	3.718×10^{-4}	-3.43
	BS_{90}	31.0	2.30×10^{-2}	3.656×10^{-4}		
	BS_{92}	36.9	1.87×10^{-2}	3.720×10^{-4}		

CHAPTER -4

SULPHUR CAPACITY OF THE SYSTEM $CaO-Na_2O-SiO_2$

This chapter deals with the experimental results and their discussion for the ternary $CaO-Na_2O-SiO_2$ system. Results of present investigation are compared with the earlier work on this system and other ternary silicate systems.

4.1 Results

Lime-soda-silica slags of varying Na_2O/SiO_2 molar ratio namely 0.26, 0.40, 0.52, 0.84 and 1.03 were equilibrated with gaseous mixture of sulphur dioxide, oxygen and nitrogen having desired oxygen and sulphur dioxide partial pressures at 1373, 1423, 1473, 1523 and 1573K. Oxygen partial pressures during the equilibria runs was adjusted in the range $10^{-11}-10^{-8}$ atm and sulphur dioxide concentration varied in the range of 7-10%.

The experimental results of the equilibria runs along with the sulphur content of the equilibrated slags are reproduced in tables 4.1-4.25.

4.2 CALCULATIONS

Method adopted for the calculation of sulphur capacity is similar to the one already described in Section 3.2. Calculated values of the sulphur capacity, average C_S and log C_S are reported in tables 4.26 - 4.50 corresponding to the results given in tables 4.1-4.25.

4.3 INFERENCES AND DISCUSSION

Logarithm of sulphur capacity has been plotted as a function of mole fraction of lime for different molar ratio of Na_2O/SiO_2 under consideration. These plots, at different temperature of study are shown in Figs.4.1-4.5. From these figures it could be observed that

a) lime additions increase sulphur capacity at constant Na_2O/SiO_2 molar ratio,

b) variation of log C_S with N_{CaO} is very sharp initially upto approx. $0.1N_{CaO}$ and the curve gradually flattens with further lime additions, and,

c) variation of log C_S with N_{CaO} becomes more pronounced with increasing Na_2O/SiO_2 at constant lime levels.

These observations could be explained on the basis of eq.3.11, which states that the sulphur capacity of a slag is equal to the product of two functions, namely, the equilibrium constant and activity of oxygen ions in the system. Thus to explain the effect of lime additions in a melt of fixed Na_2O/SiO_2 ratio, variation in both the functions, described above, should be considered. For the ternary lime-soda-silica melt, the equilibrium constant can be obtained by the following

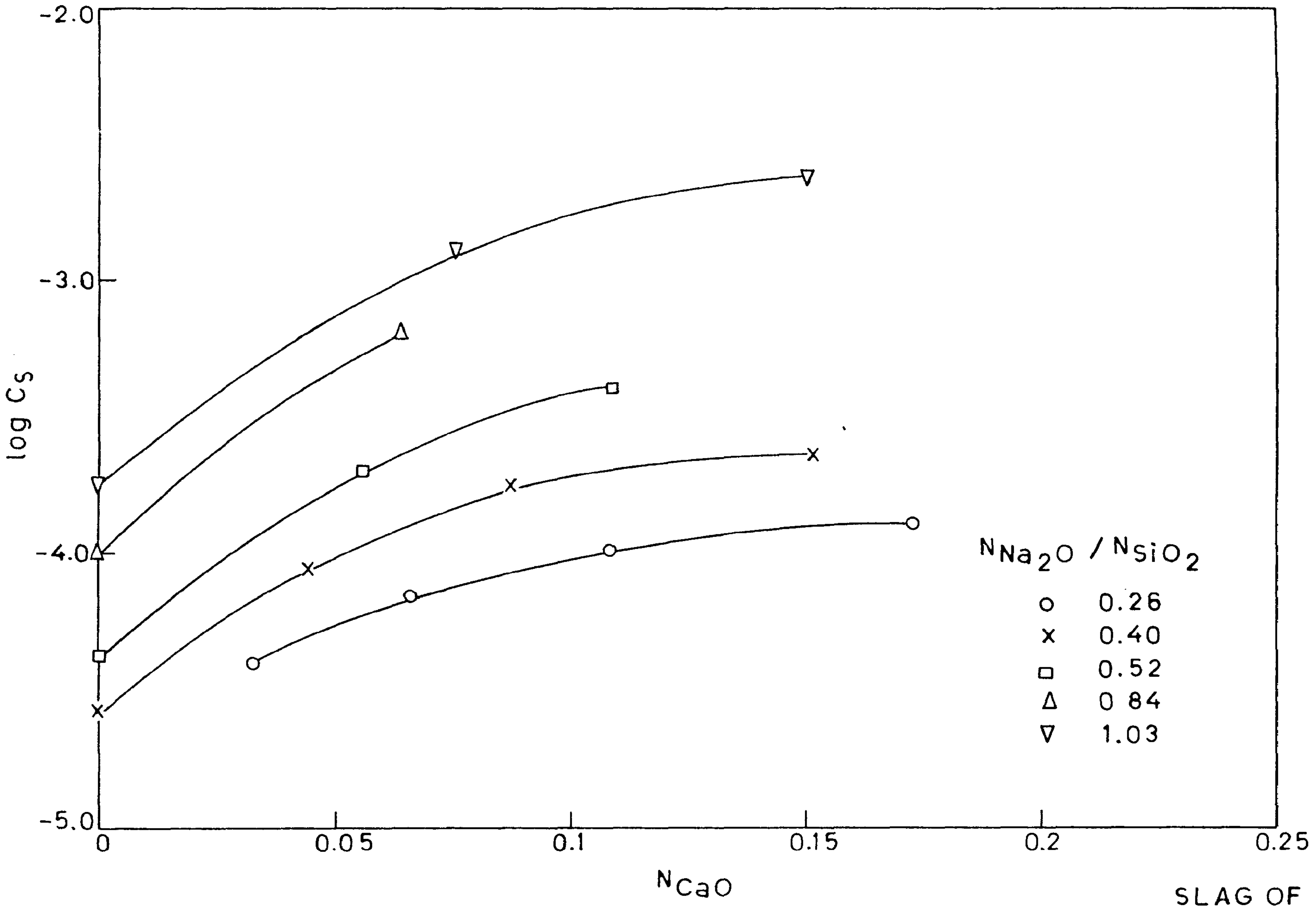


FIG. 4.1 EFFECT OF LIME ADDITION ON SULPHUR CAPACITY IN SLAG OF DIFFERENT N_{Na_2O} / N_{SiO_2} RATIOS AT 1373 K.

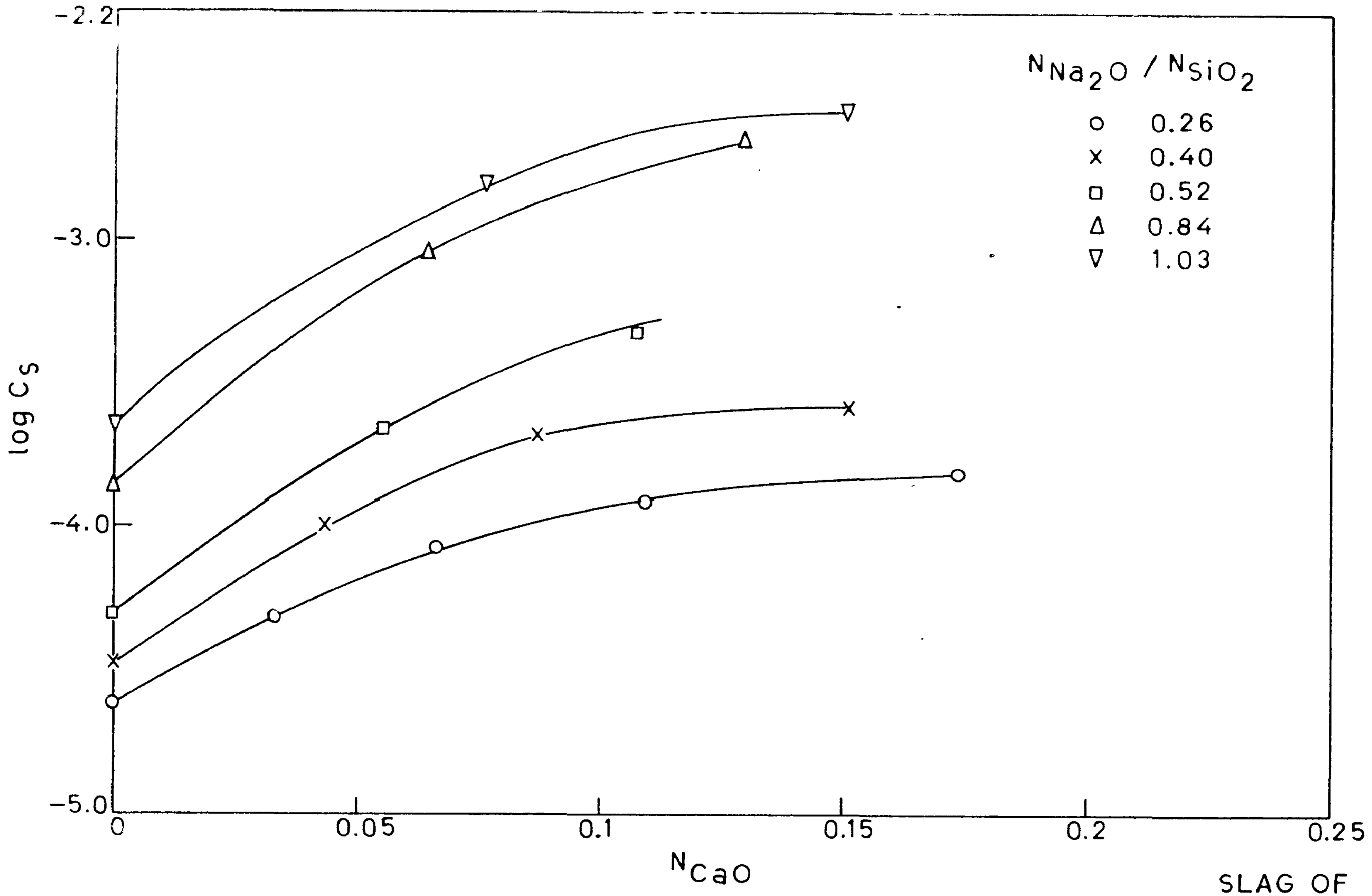


FIG.4.2 EFFECT OF LIME ADDITION ON SULPHUR CAPACITY IN SLAG OF DIFFERENT N_{Na_2O} / N_{SiO_2} RATIOS AT 1423 K.

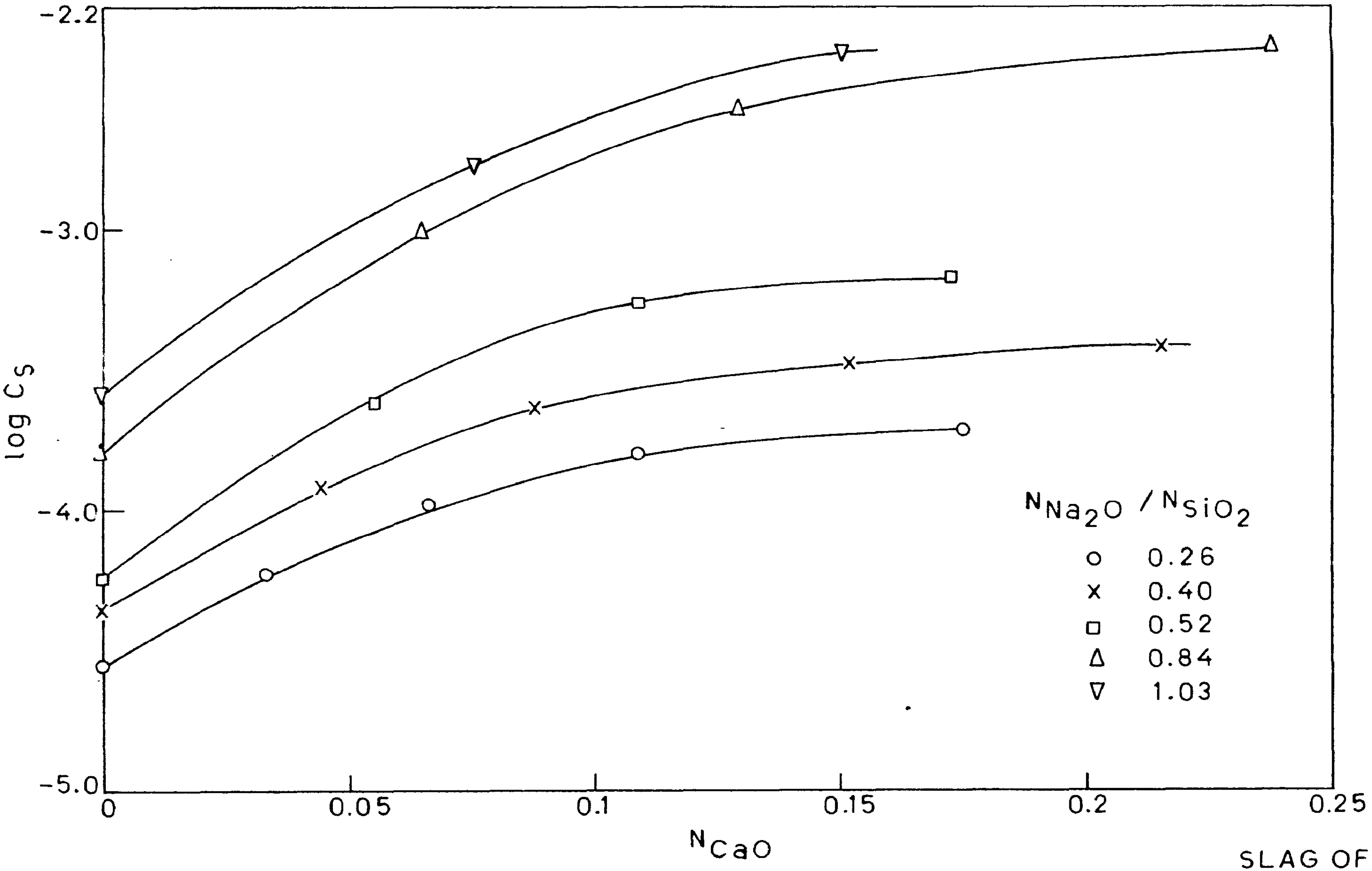


FIG. 4.3 EFFECT OF LIME ADDITION ON SULPHUR CAPACITY IN SLAG OF DIFFERENT N_{Na_2O} / N_{SiO_2} RATIOS AT 1473 K.

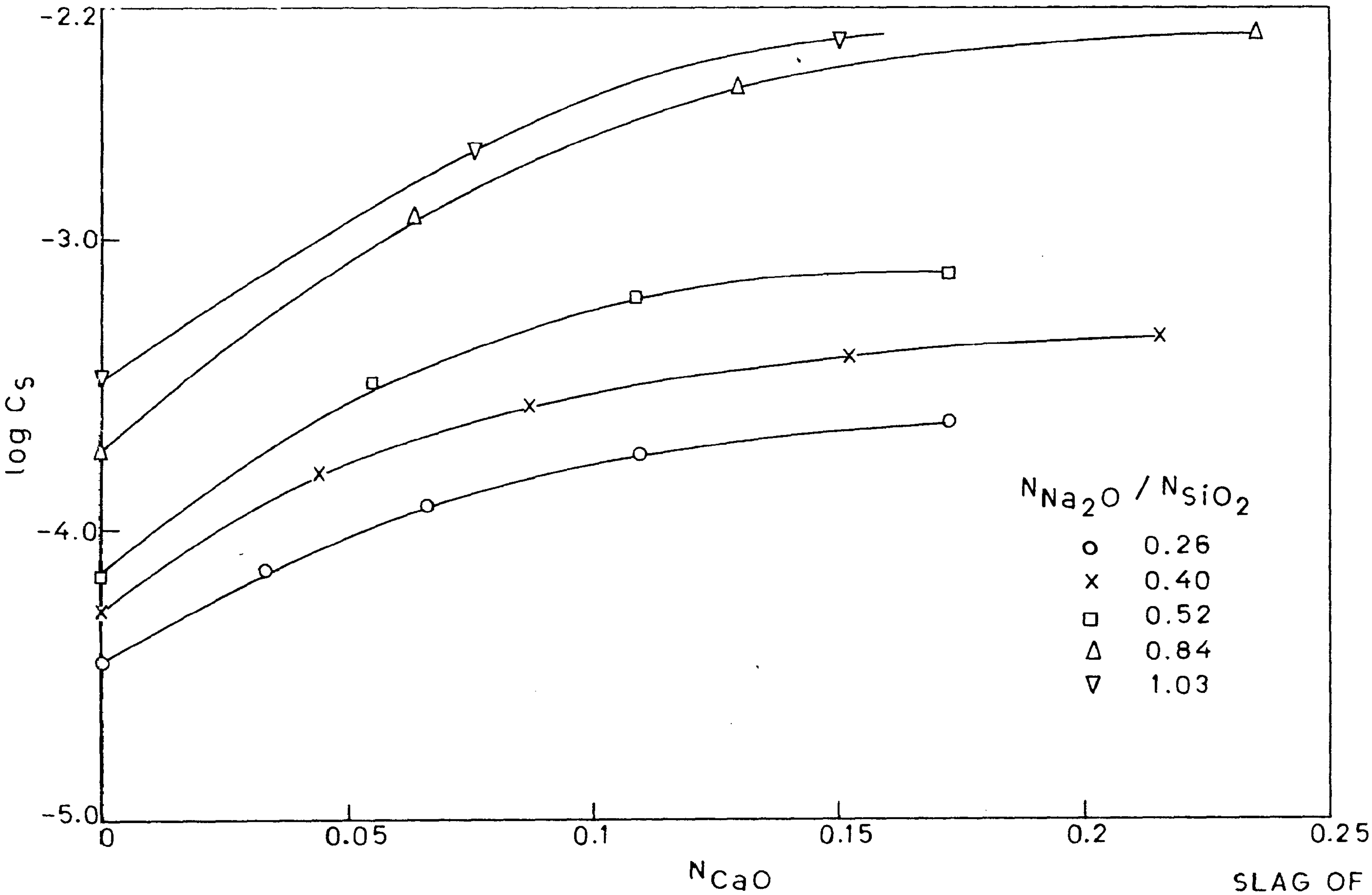


FIG. 4.4 EFFECT OF LIME ADDITION ON SULPHUR CAPACITY IN SLAG OF DIFFERENT N_{Na_2O} / N_{SiO_2} RATIOS AT 1523 K.

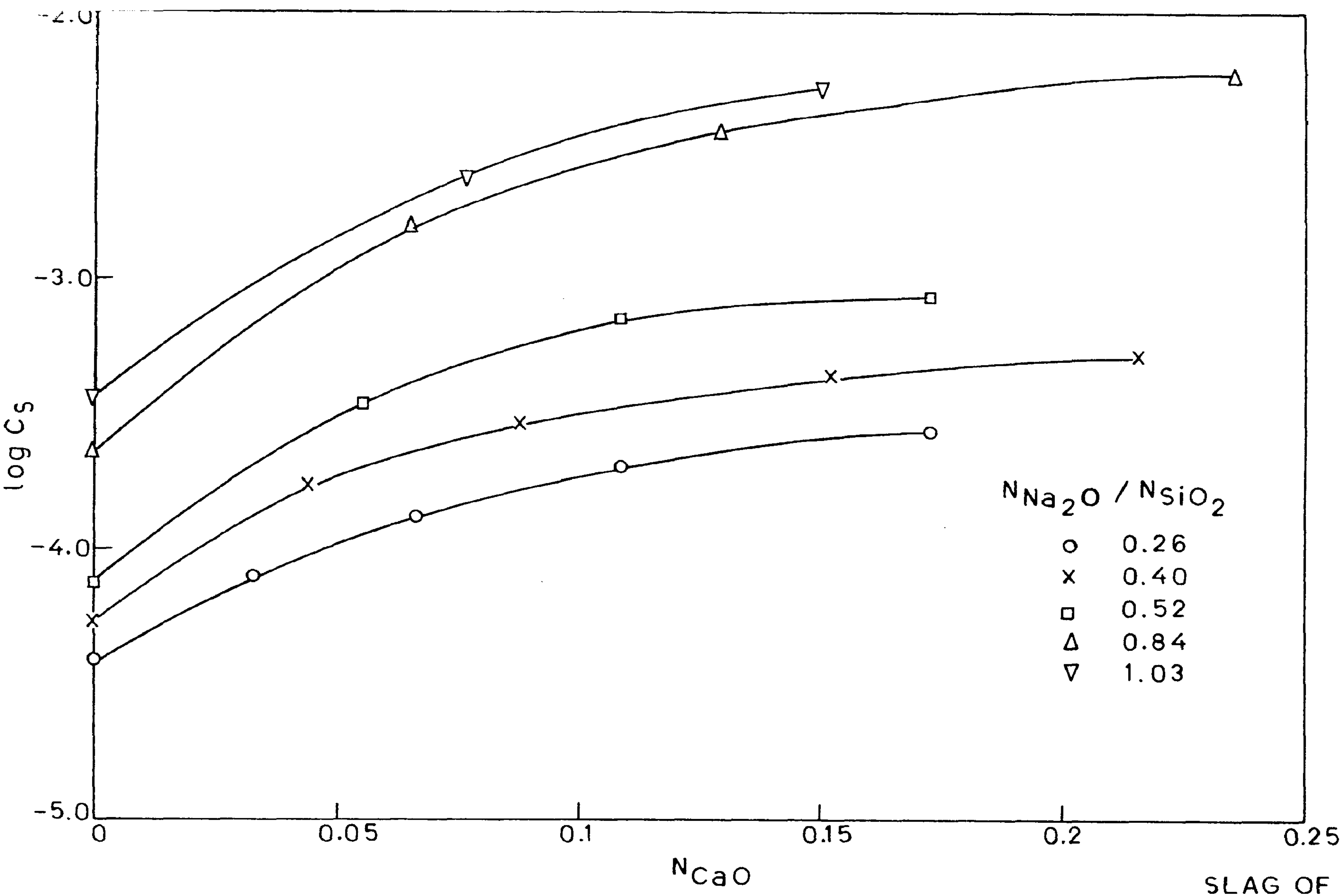


FIG. 4.5 EFFECT OF LIME ADDITION ON SULPHUR CAPACITY IN SLAG OF DIFFERENT N_{Na_2O} / N_{SiO_2} RATIOS AT 1573 K.

lationship proposed by Flood et al [94],

$$\log K' = N^{*}_{Ca^{2+}} . \log K_{CaO} + N^{*}_{Na^{+}} . \log K_{Na_2O} \qquad \ldots (4.1)$$

here $N_{Ca^{2+}}$ and $N_{Na^{+}}$ are the electrically equivalent ractions of Ca^{2+} and Na^{+} respectively in the melt. It may e pointed out that eq.4.1 is applicable strictly to regular olutions, however, it could be applied for other cases also to draw qualitative inferences.

As sulphur capacity of Na_2O is known to be approximately 10^3 times that of lime, it can be concluded from the eq.4.1 that addition of lime to the soda-silica melts will lower the value of logK. This decrease will be more for melts containing higher CaO. The variation in N^{*}_{CaO} as a function of N_{CaO} and Na_2O/SiO_2 ratio, designated by X, may be expressed as

$$N^{*}_{CaO} = \frac{N_{CaO}}{1 + X\, N_{CaO}} \qquad \ldots (4.2)$$

The above expression shows that for a constant value of N_{CaO}, N^{*}_{CaO} will increase with decreasing X. Hence, for higher values of X, the value of log K shall be lower for the same lime concentration but it may be pointed out that such changes in log K for small CaO content shall be small.

Let us now analyse as to how the activity, $a_{O^{2-}}$ will vary. First the addition of CaO in the melt of any Na_2O/SiO_2

molar ratio will increase the total base content of the melt and thus increase its basicity and hence the activity of oxygen ions. Such an increase is not expected to follow Raoult's law as slags form strongly interacting systems. The question thus arises as to how the activity of lime and hence that of oxygen ions shall vary. As limited thermodynamic data [100] is available on the system Na_2O-CaO-SiO_2 except for the phase relations, one has to take the help of similar systems for qualitatively arriving at the trend of variation in activity of lime. As sodium oxide is a stronger base than lime, so the present system consists of a stronger base- CaO-SiO_2. Other similar systems on which reliable thermodynamic data is available are CaO-FeO-SiO_2, CaO-MgO-SiO_2 and Na_2O-PbO-SiO_2. In these systems FeO, MgO and PbO are the weaker basic oxides than the other basic oxide in corresponding systems. In figs. 4.6 and 4.7, the activity of FeO and MgO are plotted against their mole fractions for different CaO/SiO_2 ratios. These curves show that in both the cases FeO and MgO, the weaker bases, show strong positive deviation from Raoults law. Further, this deviation is more pronounced as CaO/SiO_2 molar ratio approaches 2/3. Similar behaviour is also shown by PbO (Fig.4.8). Though in this case the complete thermodynamic data is not available. Thus it can be concluded that lime in the present system will also show a similar behaviour, and hence the term $a_{O^{2-}}$ will increase sharply with the initial addition of CaO resulting into increase in sulphur

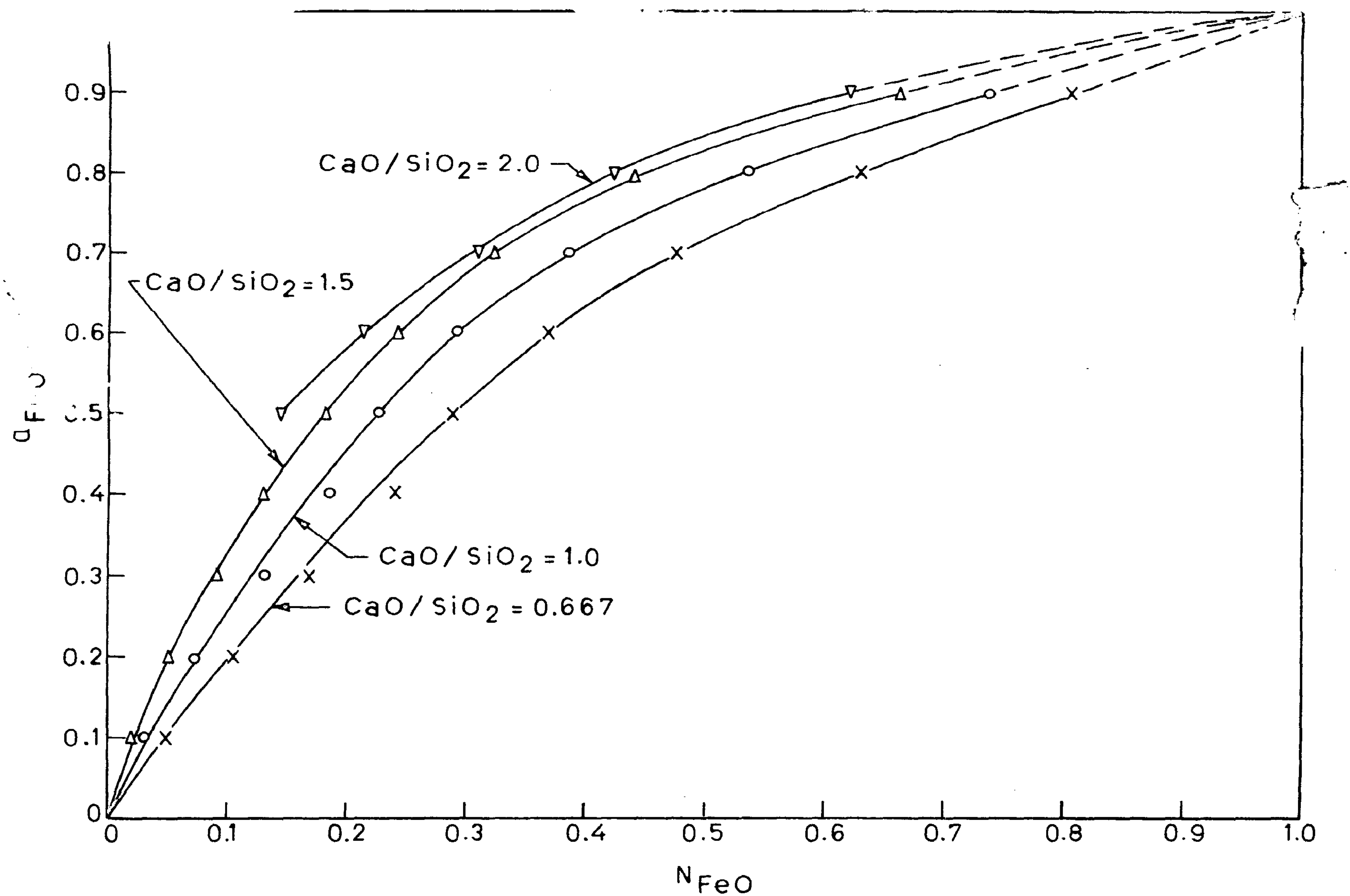


FIG. 4.6 PLOT OF ACTIVITY OF FeO WITH RESPECT TO MOLE FRACTION OF FeO IN $FeO-CaO-SiO_2$ SYSTEM AT 1600 °C, AFTER TAYLOR AND CHIPMAN [Ref. 95]

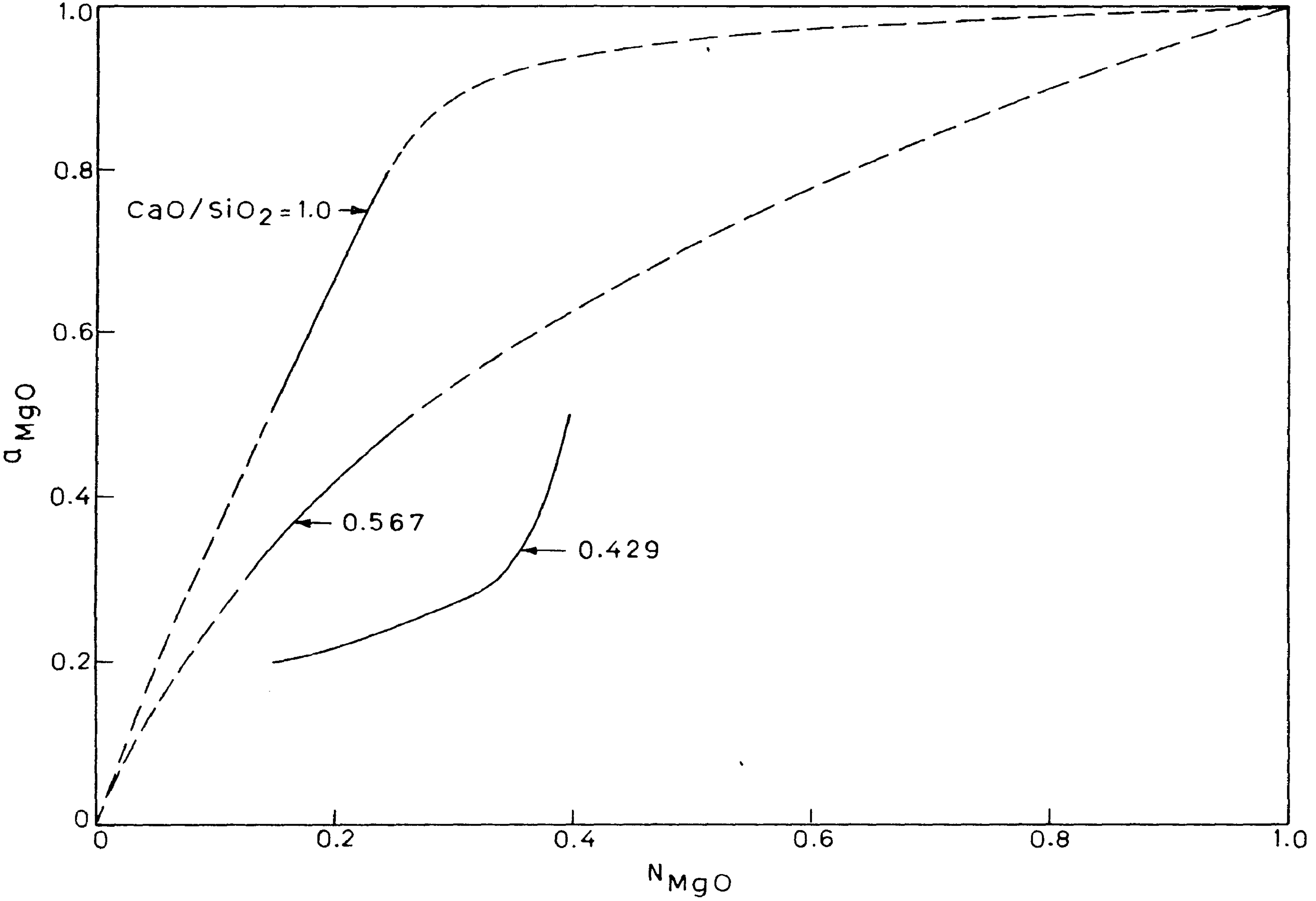


FIG. 4.7 PLOT OF ACTIVITY OF MgO vs N_{MgO} IN $MgO-CaO-SiO_2$ SYSTEM, AFTER HENDERSON AND TAYLOR [Ref. 96]

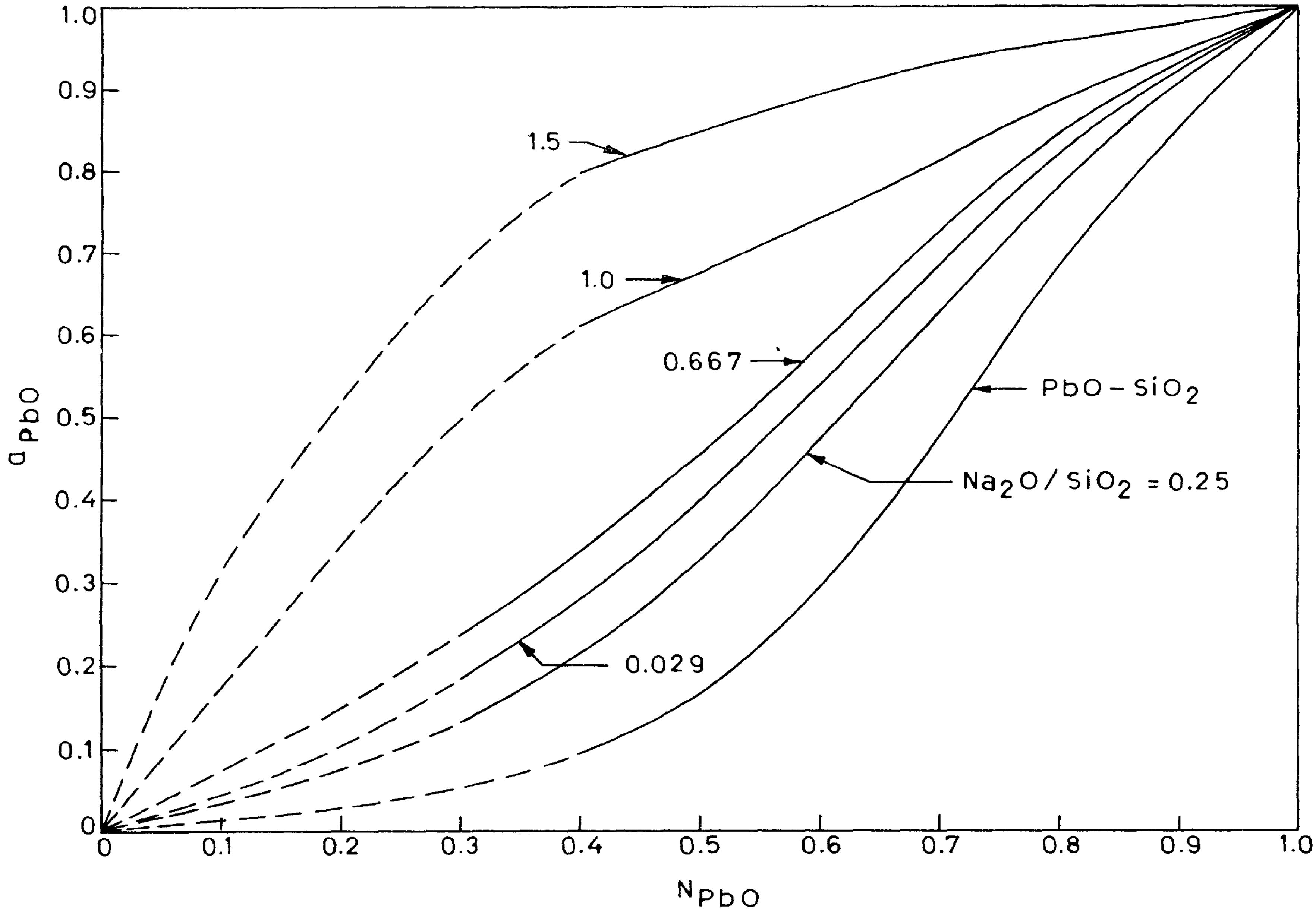


FIG.4.8 PLOT OF ACTIVITY OF PbO vs N_{PbO} IN Na_2O-PbO-SiO_2 SYSTEM AT 1000°C, AFTER KAPOOR AND FROHBERG [Ref.97]

capacity. As the amount of CaO is further increases in the melt, the positive deviation will become less pronounced and extent of decrease in K will be higher and therefore the rise in C_S value will be less pronounced. The sulphur capacity of such melts reaches a maximum value after which further increase in lime concentration may even cause a decrease in sulphur capacity for definite Na_2O/SiO_2 ratio (s)

To study the effects of the soda replacement by lime, log C_S is plotted against a function $N_{Na_2O}/(N_{Na_2O}-N_{SiO_2})$ for various lime concentrations at 1373, 1473 and 1573K and reproduced in figs.4.9-4.11. An examination of these figs.4.9-4.11 reveals that for constant Na_2O/SiO_2 molar ratio and hence constant value of the function $N_{Na_2O}/(N_{Na_2O}+N_{SiO_2})$ log C_S values increase with increasing lime concentrations in the melt, in the composition range under study. Various lime concentrations chosen for plots in figs.4.9-4.11 are in the range of 0.05-0.25. This could be explained from eq.4.2, in which at constant Na_2O/SiO_2 ratio or constant X, N^*_{CaO} will increase with increasing N_{CaO} resulting into an increase in the overall value of logK and hence an increase in the sulphur capacity. Further with increasing lime content, activity of lime will increase causing an increase in the value of $a_{O^{2-}}$ and hence, at increasing lime content, slope of the plot, of log C_S vs $N_{Na_2O}/(N_{Na_2O}+N_{SiO_2})$ would increase. This has been found true in figs.4.9-4.11.

Silica effect is also studied in terms of plots of

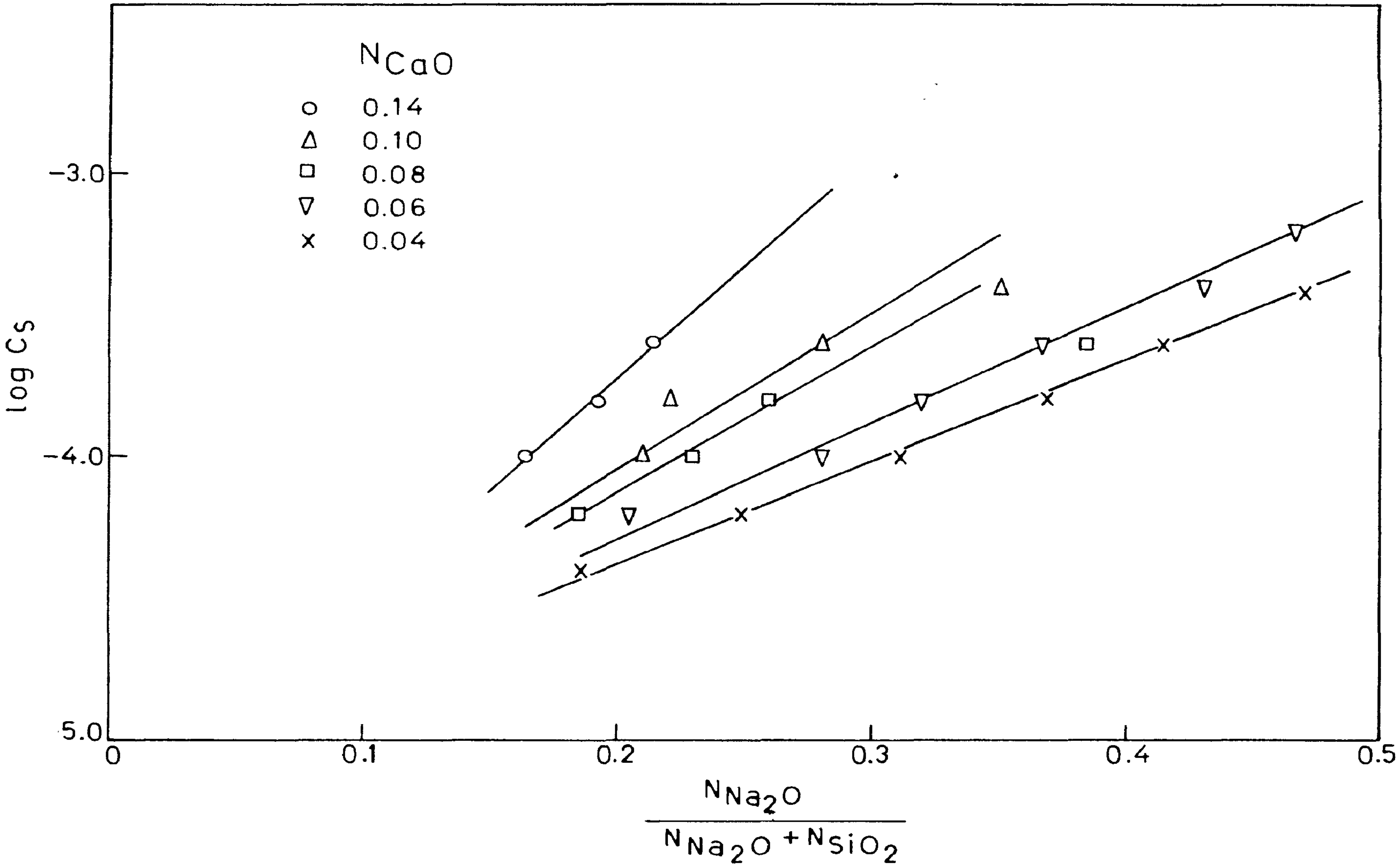


FIG. 4.9 VARIATION IN log C_S WITH N_{Na_2O} / (N_{Na_2O} $- N_{SiO_2}$) FOR SLAGS WITH CONSTANT N_{CaO} AT 1373 K.

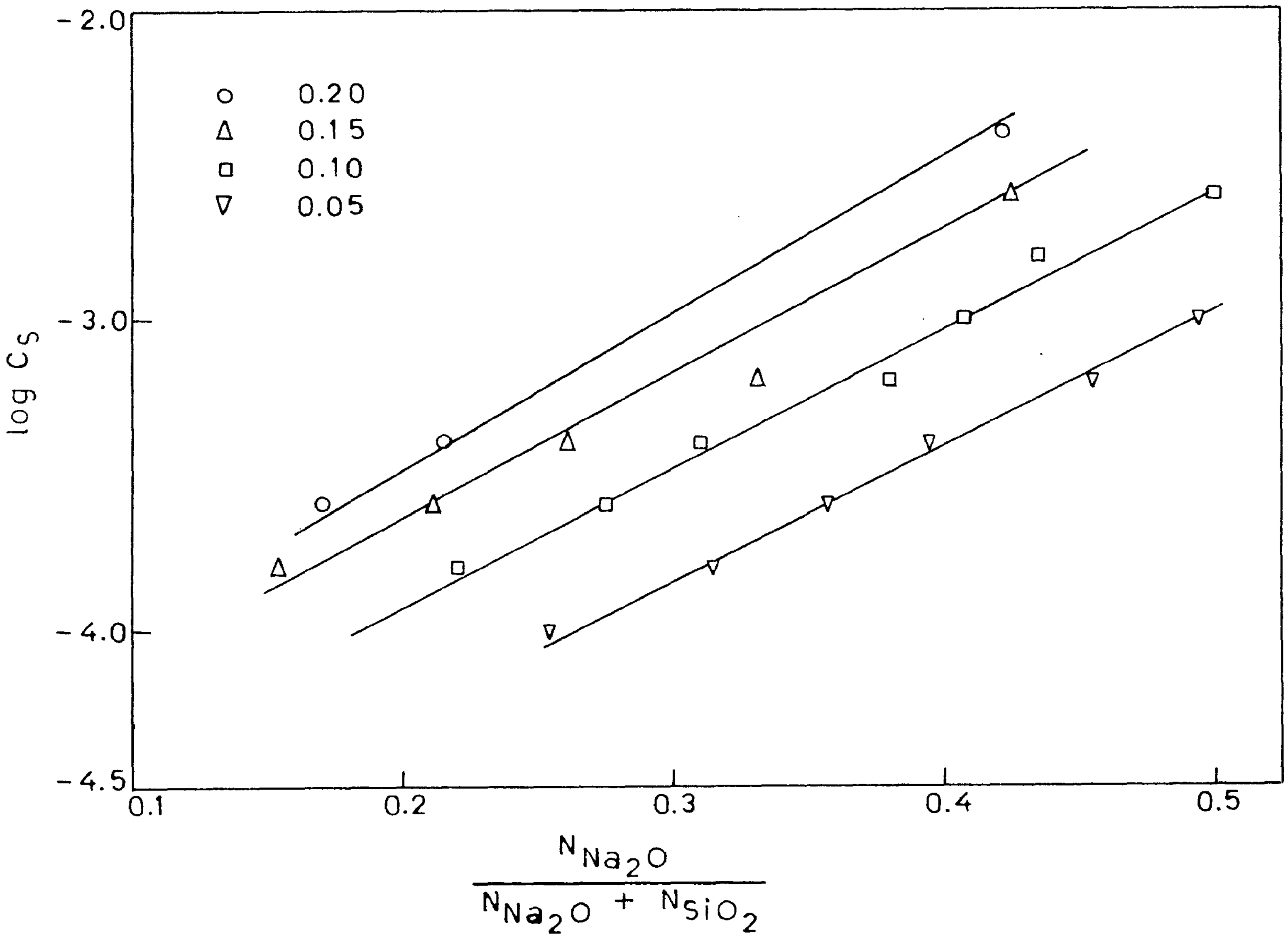


FIG. 4.10 VARIATION IN log C_S WITH $N_{Na_2O}/(N_{Na_2O}+N_{SiO_2})$ FOR SLAGS WITH CONSTANT N_{CaO} AT 1473 K.

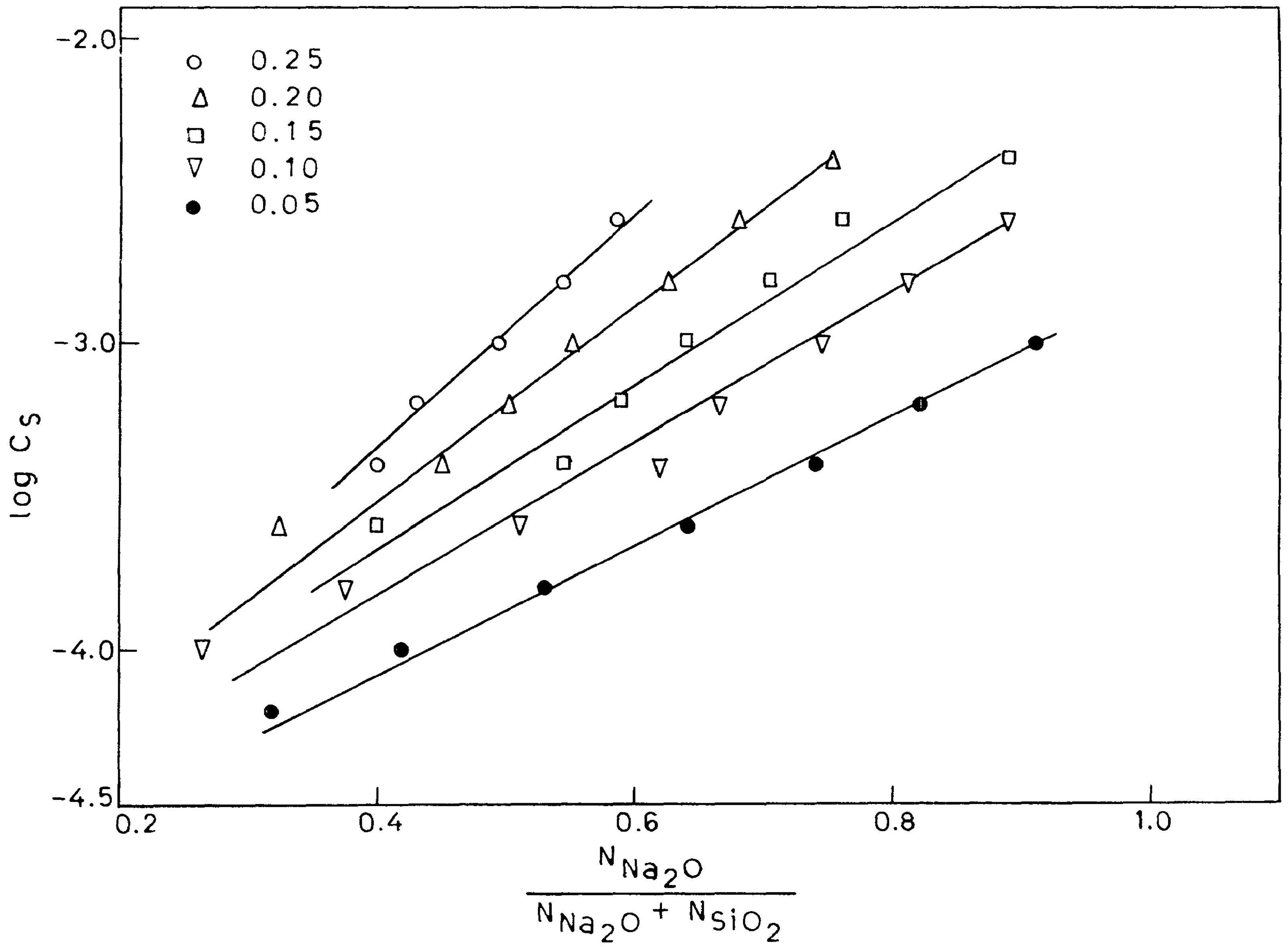


FIG. 4.11 VARIATION IN log C_S WITH $N_{Na_2O}/(N_{Na_2O} + N_{SiO_2})$ FOR SLAGS WITH CONSTANT N_{CaO} AT 1573 K.

log C_S as a function of $N_{Na_2O}/(N_{Na_2O}+N_{CaO})$ for various silica concentrations in the range of 0.50-0.65, at 1373, 1473, and 1573K and are shown in figs.4.12-4.14. These plots reveal that with increasing silica content, the sulphur capacity decreases. This could be explained as that decrease in silica concentration would cause an increase in the basic oxide content or the basicity and hence increase in oxygen ion activity. Equilibrium constant, however, remains unaltered with varying silica levels. Therefore the product K $a_{O^{2-}}$, as shown by the eq.3.11, will also increase resulting into an increase in sulphur capacity. One can also observe that with increasing $N_{Na_2O}/(N_{Na_2O}+N_{CaO})$ ratio or decreasing CaO addition, the sulphur capacity gradually decreases beyond a value of $N_{Na_2O}/(N_{Na_2O}+N_{CaO})$ equals to 0.8 and finally approaching to the C_S value of binary soda-silica melts with same SiO_2 mole fraction as that of the ternary. This trend of variation of log C_S with $N_{Na_2O}/(N_{Na_2O}+N_{CaO})$ ratio has already been discussed in the foregoing paragraph where effect of lime replacement for soda was explained. With the help of figs.4.1-4.5, logarithmic sulphur capacity at different temperatures of study in $CaO-Na_2O-SiO_2$ system is plotted on ternary composition diagram and is reproduced in figs.4.15-4.19. In these figures broken lines show the isO-sulphur capacity contours whereas heavy dash lines indicate the liquidus range at the temperature under consideration. Contour of lower log C_S value is observed near the

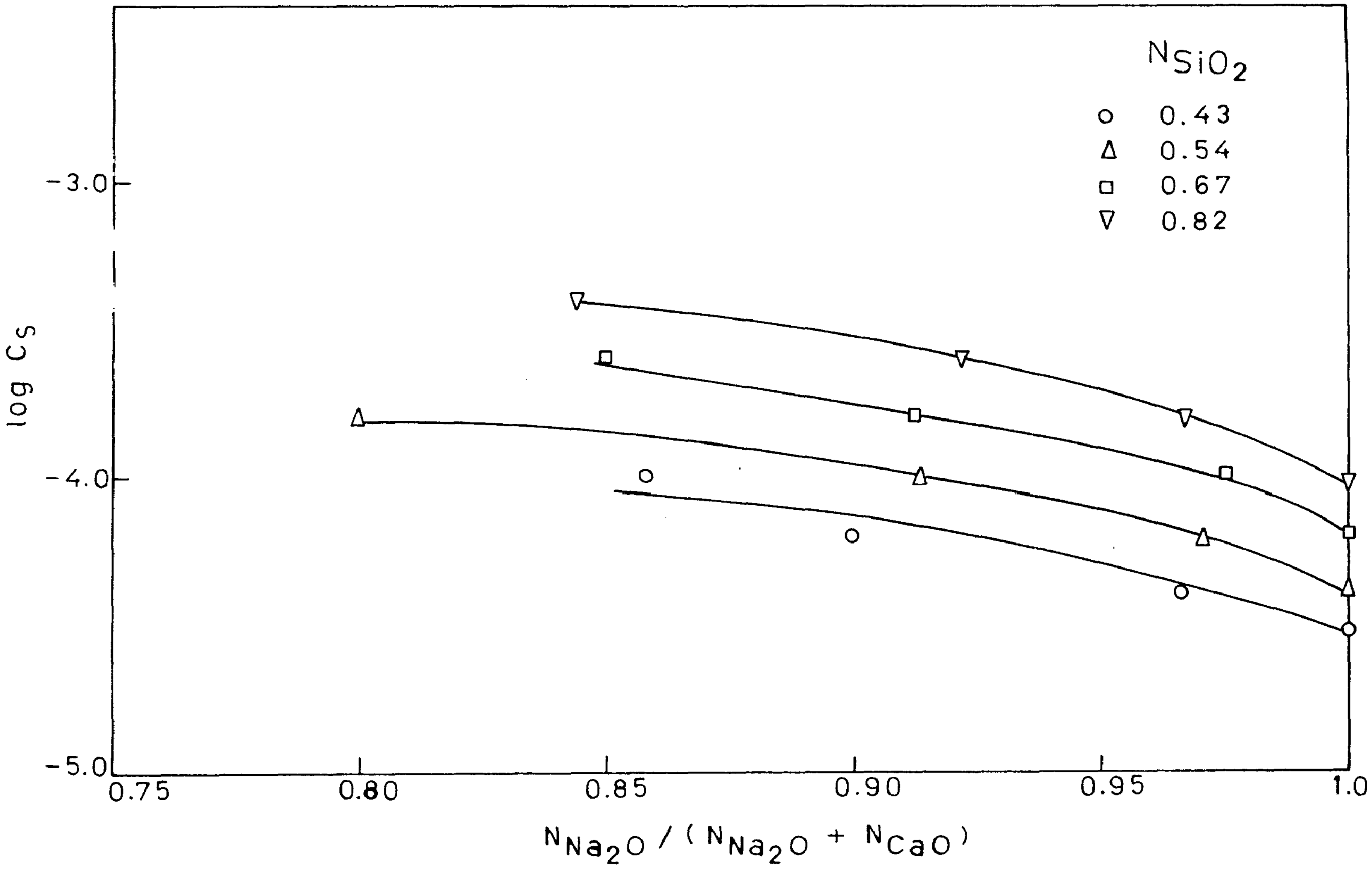


FIG. 4.12 VARIATION IN log C_S WITH $N_{Na_2O}/(N_{Na_2O}+N_{CaO})$ FOR SLAGS WITH CONSTANT N_{SiO_2} AT 1373 K.

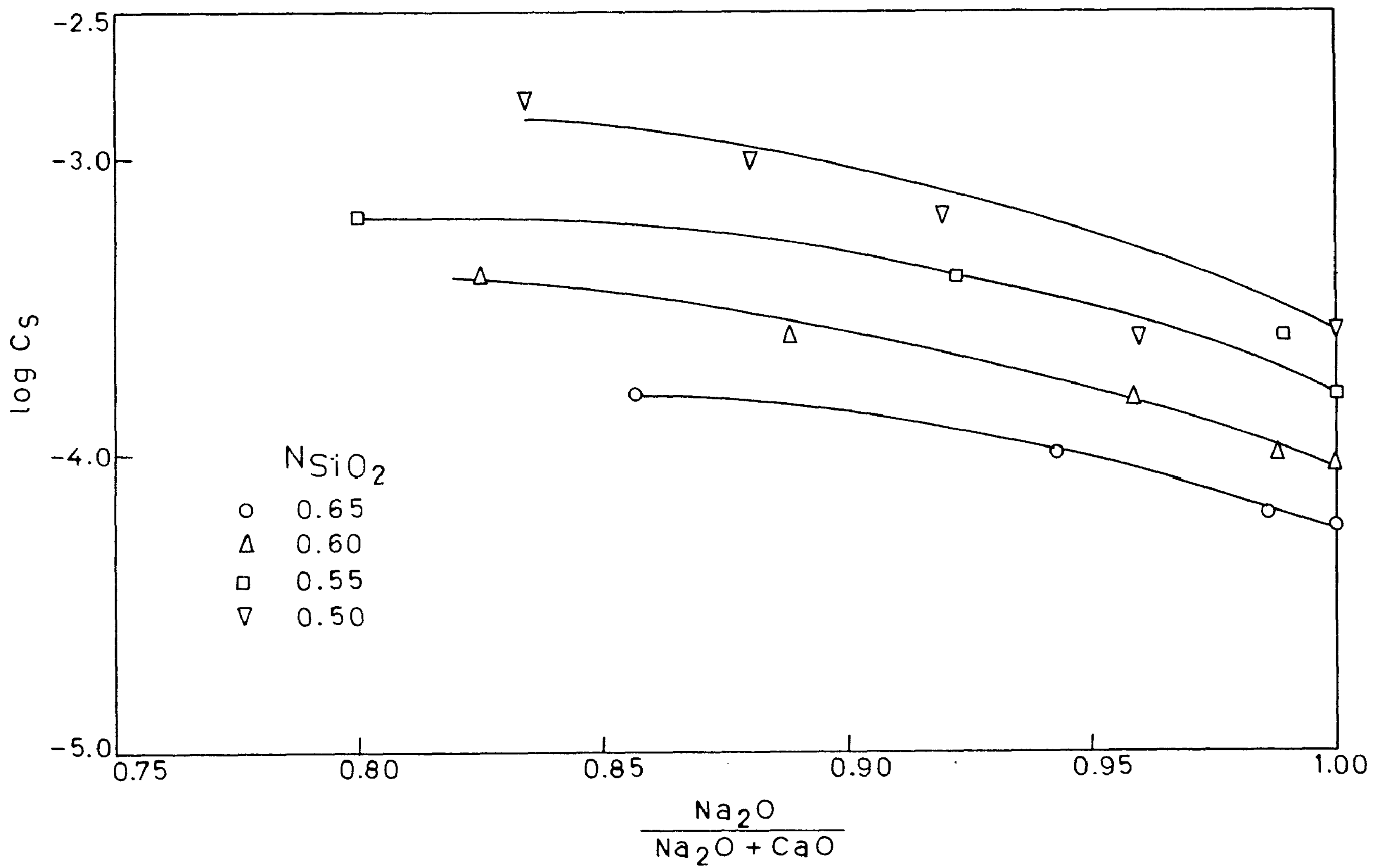


FIG. 4.13 VARIATION IN log C_S WITH $N_{Na_2O} / (N_{Na_2O} + N_{CaO})$ FOR SLAGS WITH CONSTANT N_{SiO_2} AT 1473 K.

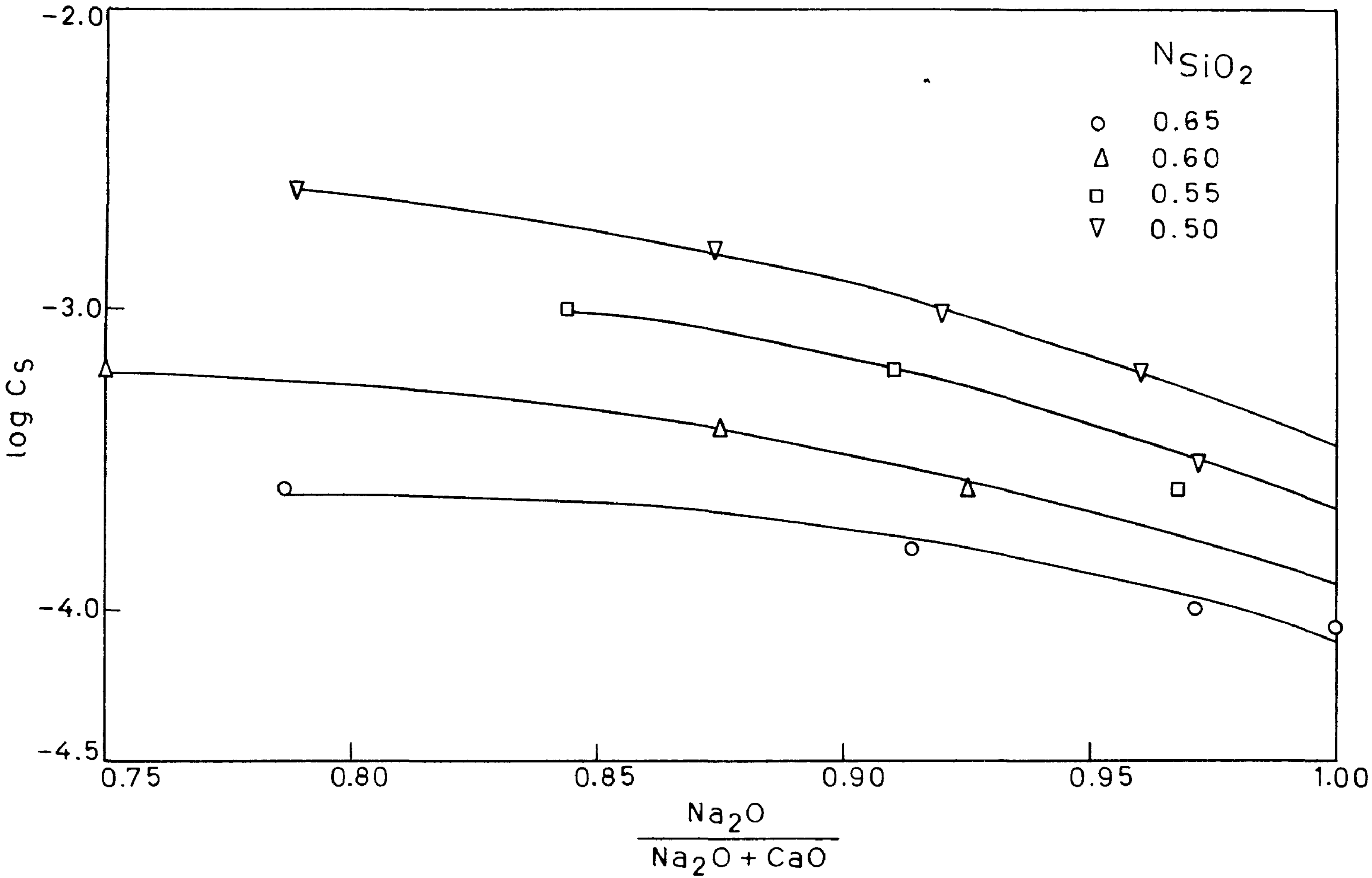


FIG. 4.14 VARIATION IN log C_S WITH $N_{Na_2O} / (N_{Na_2O} + N_{CaO})$ FOR SLAGS WITH CONSTANT N_{SiO_2} AT 1573 K.

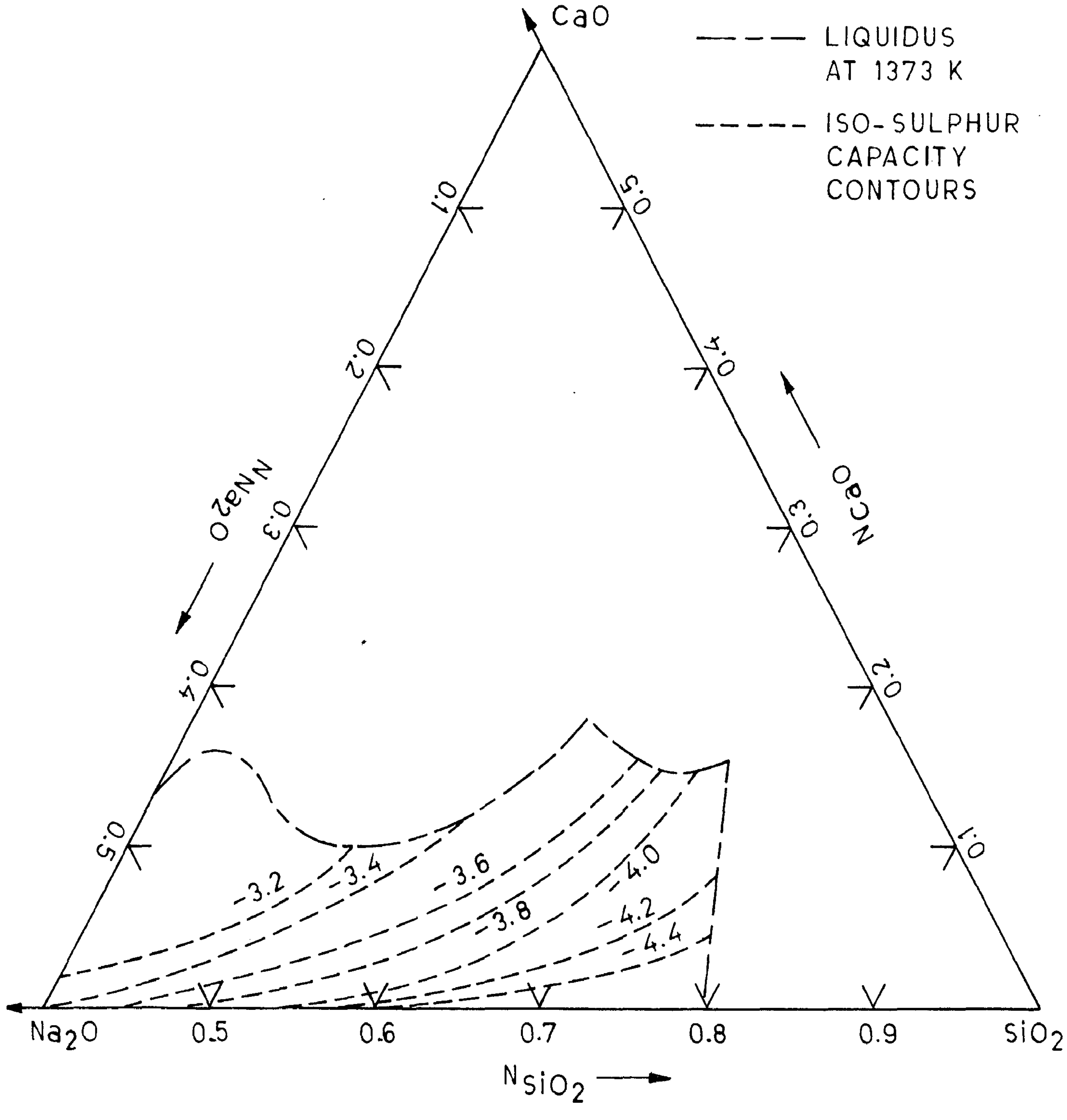


FIG. 4.15 LOGARITHM OF SULPHUR CAPACITIES AT 1373 K IN $CaO-Na_2O-SiO_2$ MELTS.

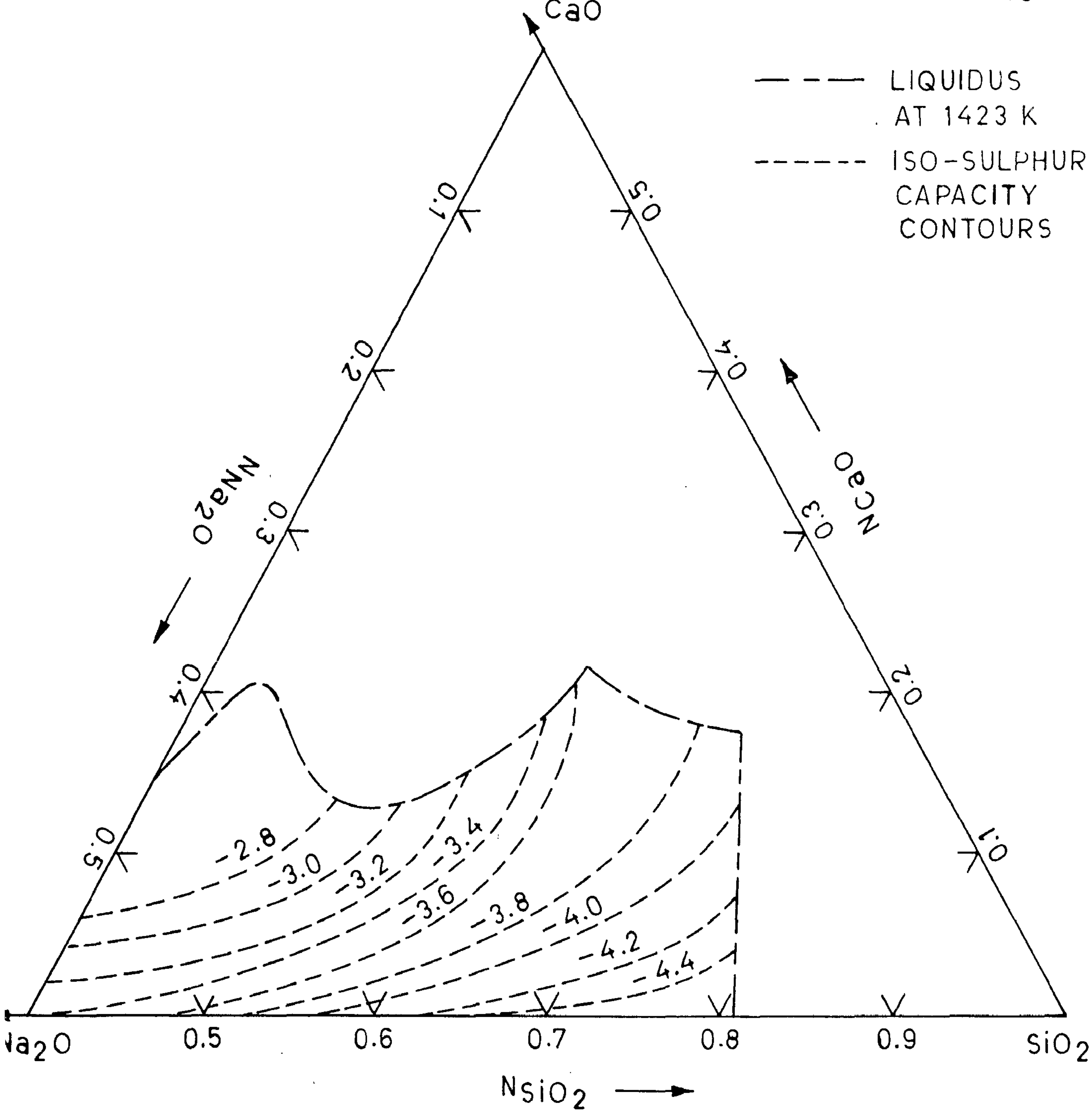


FIG. 4.16 LOGARITHM OF SULPHUR CAPACITIES AT 1423 K IN $CaO-Na_2O-SiO_2$ MELTS.

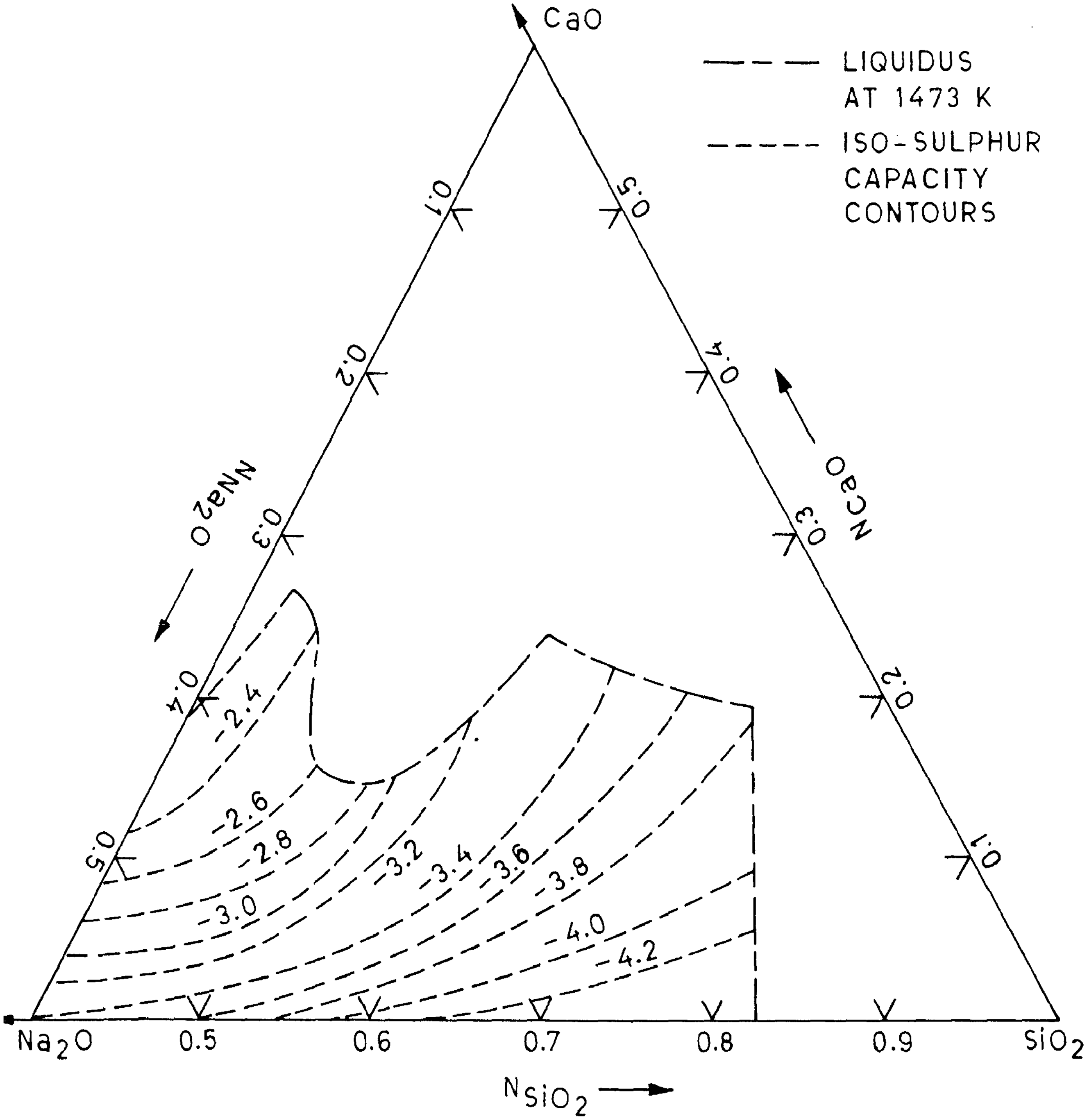


FIG. 4.17 LOGARITHM OF SULPHUR CAPACITIES AT 1473 K IN $CaO-Na_2O-SiO_2$ MELTS.

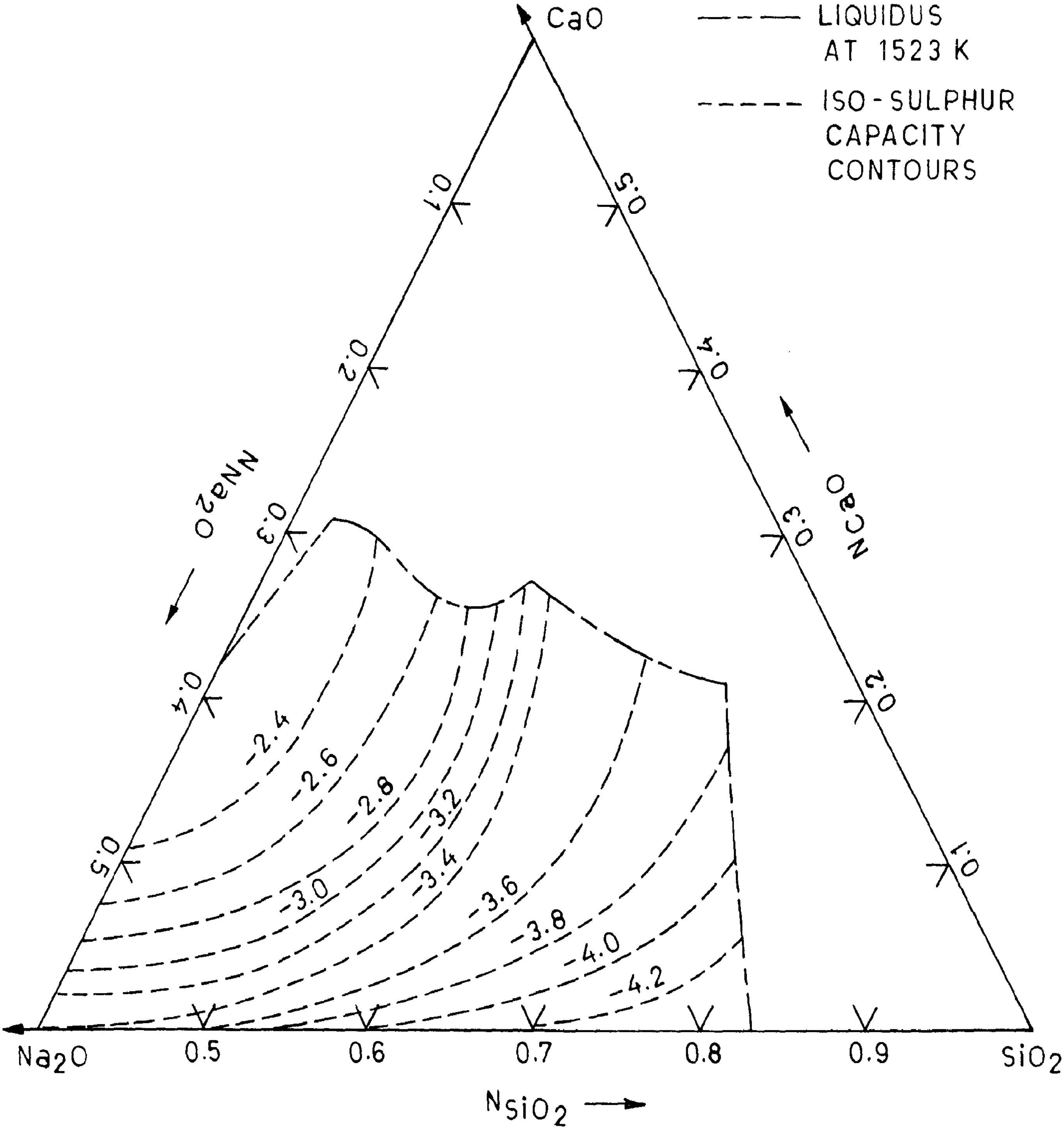


FIG. 4.18 LOGARITHM OF SULPHUR CAPACITIES AT 1523 K IN $CaO - Na_2O - SiO_2$ MELTS.

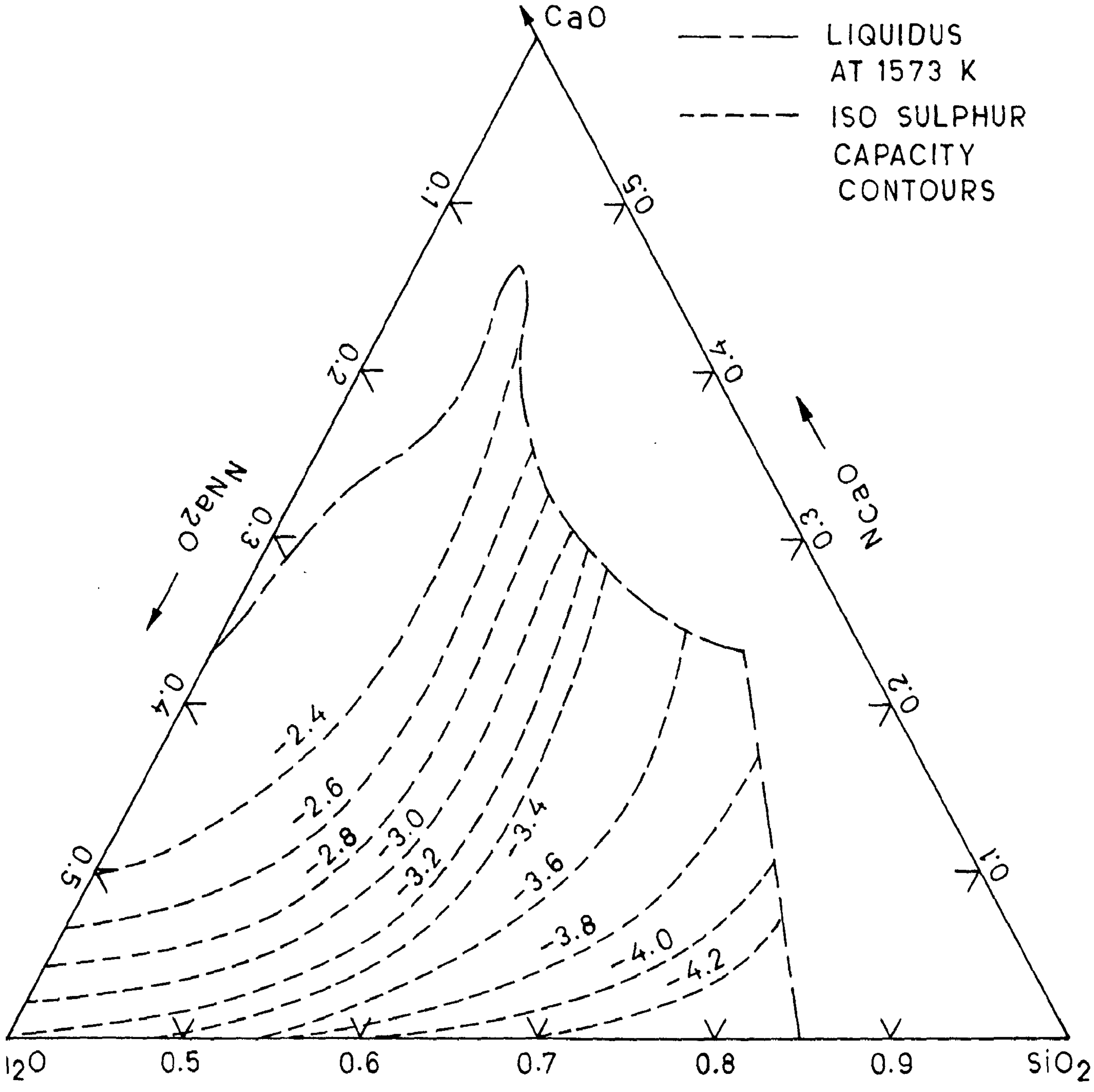


FIG. 4.19 LOGARITHM OF SULPHUR CAPACITIES AT 1573 K IN $CaO-Na_2O-SiO_2$ MELTS.

corner. As we go away from the silica corner, contours of higher log C_S values are observed. At constant lime content, contours of higher sulphur capacity shifts towards Na_2O corner whereas at constant Na_2O concentration it shifts towards lime corner. As is evident from the shifting of contours towards silica corner, it could be emphasised that increasing temperature has a positive effect ons sulphur capacity.

To find out empirical equivalence of lime to soda, log C_S values are plotted against a function of the type

$$\frac{N_{CaO} + Y\, N_{Na_2O}}{N_{SiO_2}}$$

as shown in figs. 4.20-4.22 at temperatures 1373, 1473, and 1573K by giving different integral values to Y. By trial and error, it is observed that a value of Y equal to 1.5 gives a best fit of the experimental data at temperatures of study. Empirical relationship between log C_S and $(N_{CaO} + Y\, N_{Na_2O})/N_{SiO_2}$ could be expressed as follows,

$$\log C_S = 1.233\left(\frac{1.5 N_{Na_2O} + N_{CaO}}{N_{SiO_2}}\right) - 4.943 \qquad \ldots (4.3)$$

$$\log C_S = 1.352\left(\frac{1.5\, N_{Na_2O} + N_{CaO}}{N_{SiO_2}}\right) - 4.933 \qquad \ldots (4.4)$$

and $$\log C_S = 1.163\left(\frac{1.5\, N_{Na_2O} + N_{CaO}}{N_{SiO_2}}\right) - 4.493 \qquad \ldots (4.5)$$

at 1373, 1473 and 1573K respectively. These expressions are

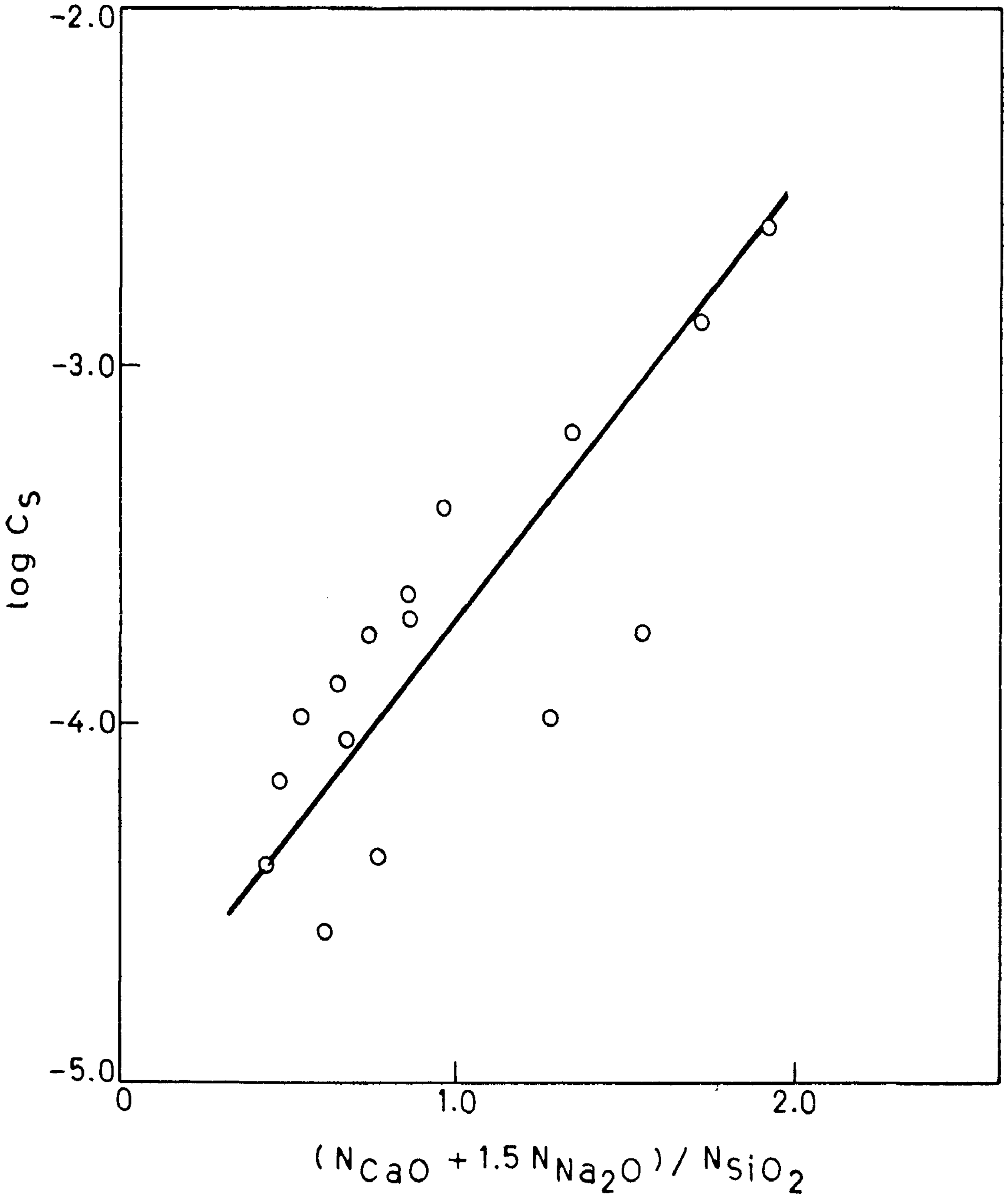


FIG. 4.20 PLOT OF log C_S vs $(N_{CaO} + 1.5\,N_{Na_2O})/N_{SiO_2}$ AT 1373 K.

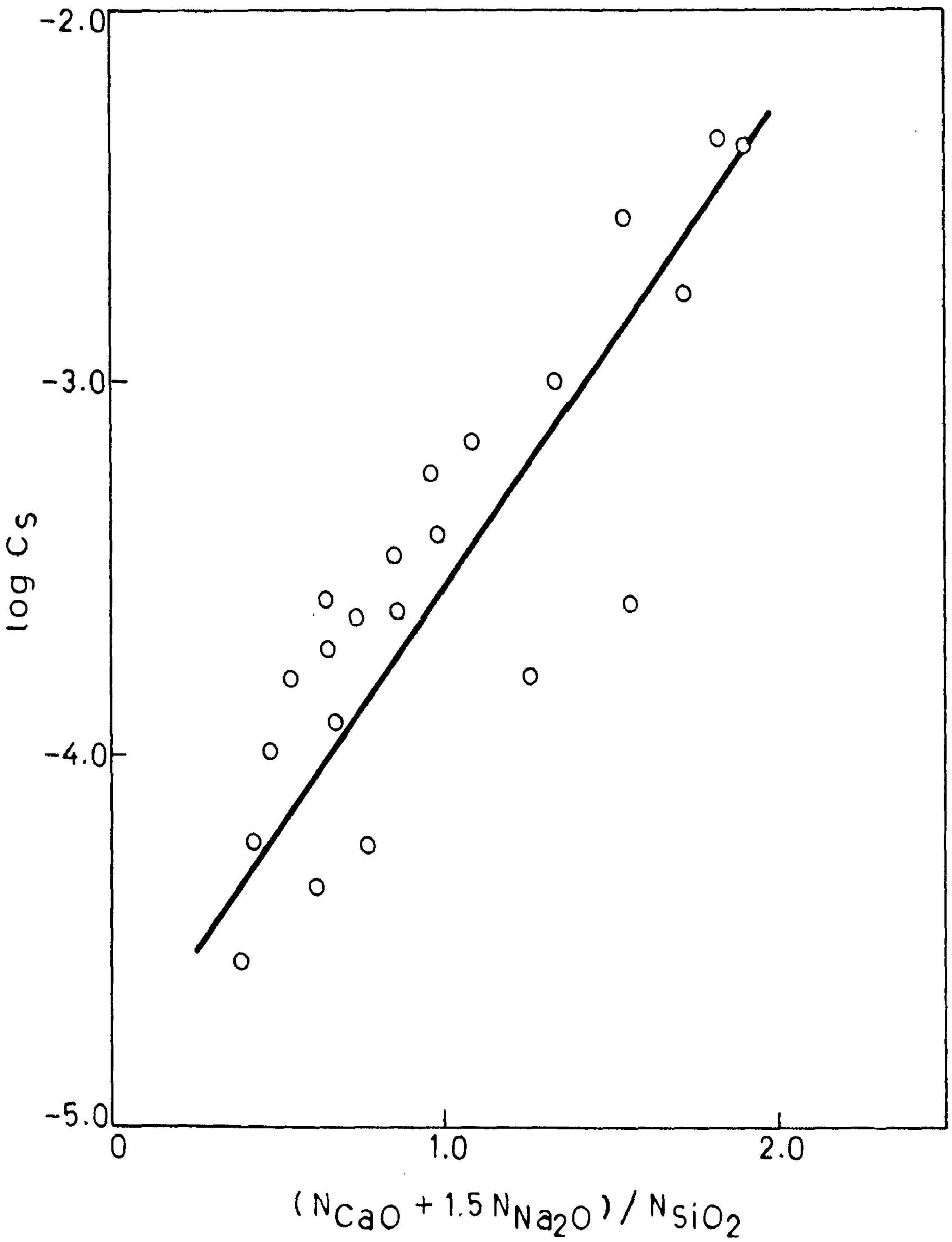


FIG. 4.21 PLOT OF log C_S vs $(N_{CaO} + 1.5 N_{Na_2O})/N_{SiO_2}$ AT 1473 K.

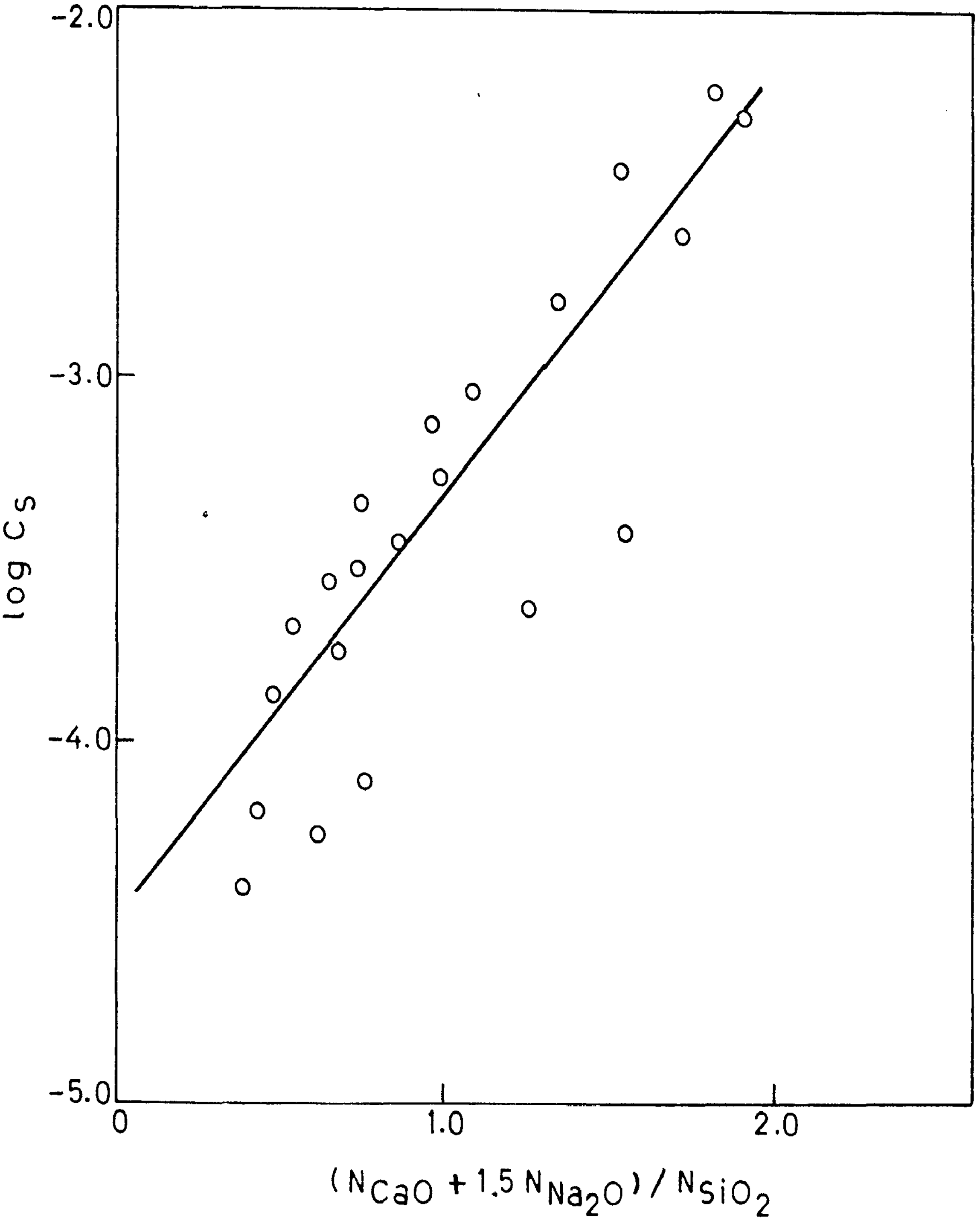


FIG. 4.22 PLOT OF log C_S vs $(N_{CaO} + 1.5\,N_{Na_2O})/N_{SiO_2}$ AT 1573 K.

valid for the system studied in the present investigation. Temperature too affects the sulphur capacity values significantly. However, basic nature of curves remains the same. Increase in temperature of equilibration results into an increase in the sulphur capacity, as shown in figs. 4.23-4.27.

4.4 Comparison with Other Ternary Silicate System

Richardson[12] have shown that for silicate mixtures having different cations and fixed mole fraction of silica, the equilibrium constant, K_9, for sulphur equilibrium between gas and condensed phase can be expressed by the following relationship in terms of molar sulphur capacity C'_S,

$$C'_S = N_{S^{2-}} (p_{O_2}/p_{S_2})^{1/2}$$

$$= \frac{K_9 a_{O^{2-}}}{Y_{S^{2-}}} \qquad \ldots (4.6)$$

which, for a ternary silicate mixture having two different cations X^{2+} and Y^{2+} may be rewritten as,

$$\log C'_S(X^{2+}, Y^{2+}) = N_{X^{2+}} \log C'_S(X^{2+}) + N_{Y^{2+}} \cdot \log C'_S(Y^{2+}) \qquad \ldots (4.6a)$$

$N_{X^{2+}}$ and $N_{Y^{2+}}$ are equal to $(\frac{N_{XO}}{N_{XO} + N_{YO}})$ and $(\frac{N_{YO}}{N_{XO} + N_{YO}})$ respectively and $C'_S(X^{2+})$ is the C'_S for the binary $XO + SiO_2$ etc. at the same mole fraction of SiO_2 as the ternary.

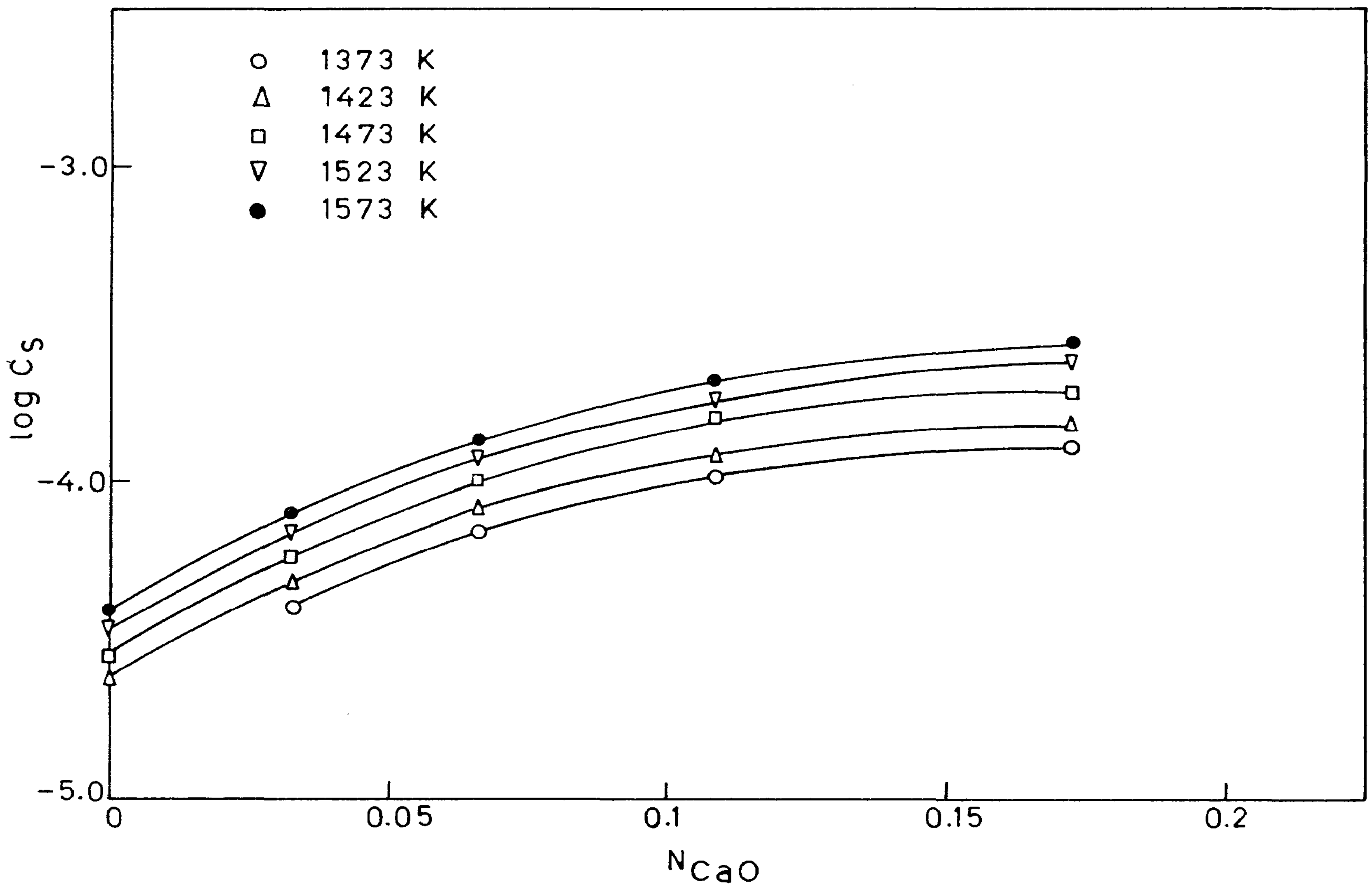


FIG.4.23 VARIATION IN log C_S WITH N_{CaO} FOR SLAGS HAVING N_{Na_2O}/N_{SiO_2} 0.26 AT DIFFERENT TEMPERATURES.

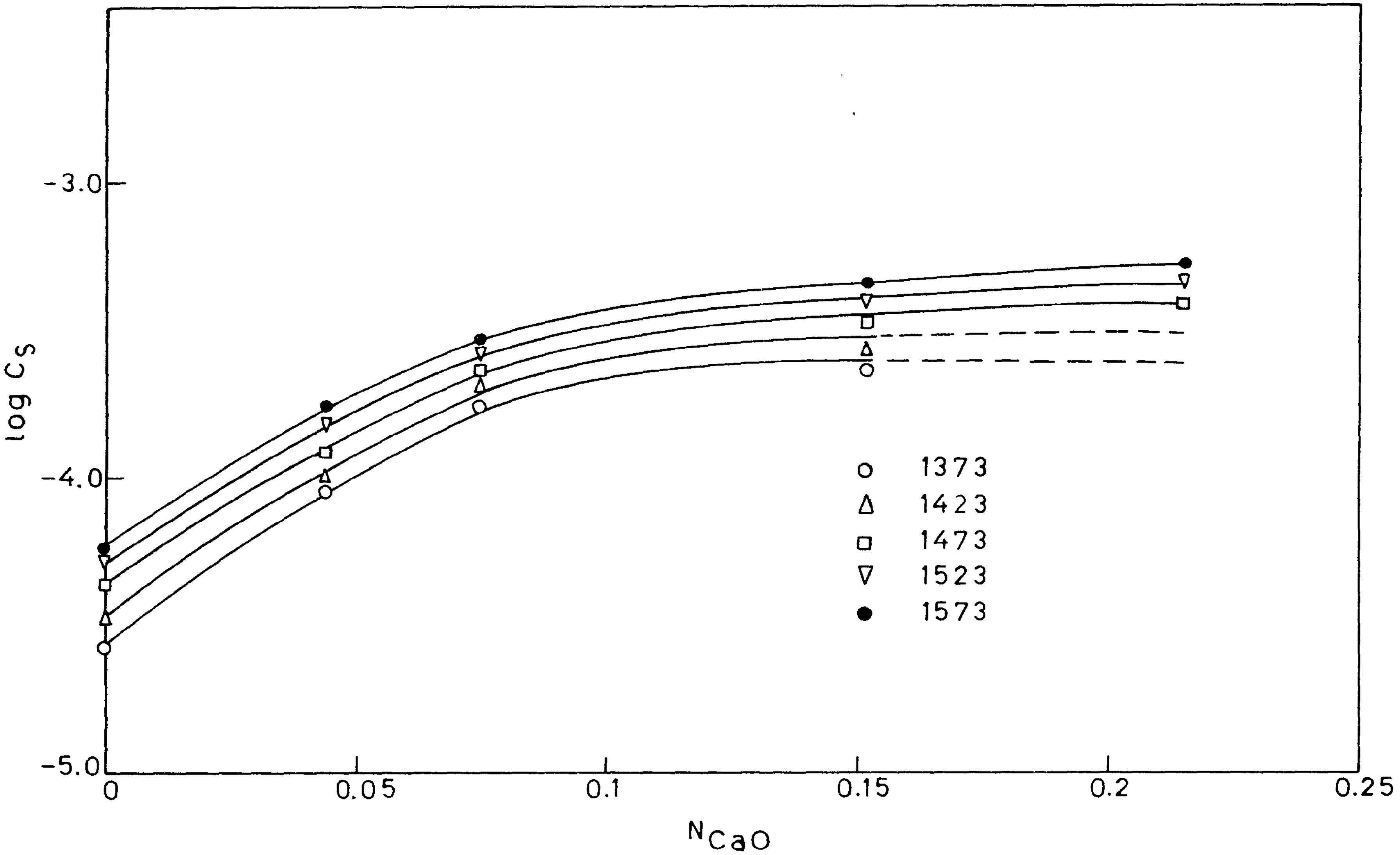


FIG. 4.24 VARIATION IN log C_S WITH N_{CaO} FOR SLAGS HAVING N_{Na_2O} / N_{SiO_2} 0.40 AT DIFFERENT TEMPERATURES.

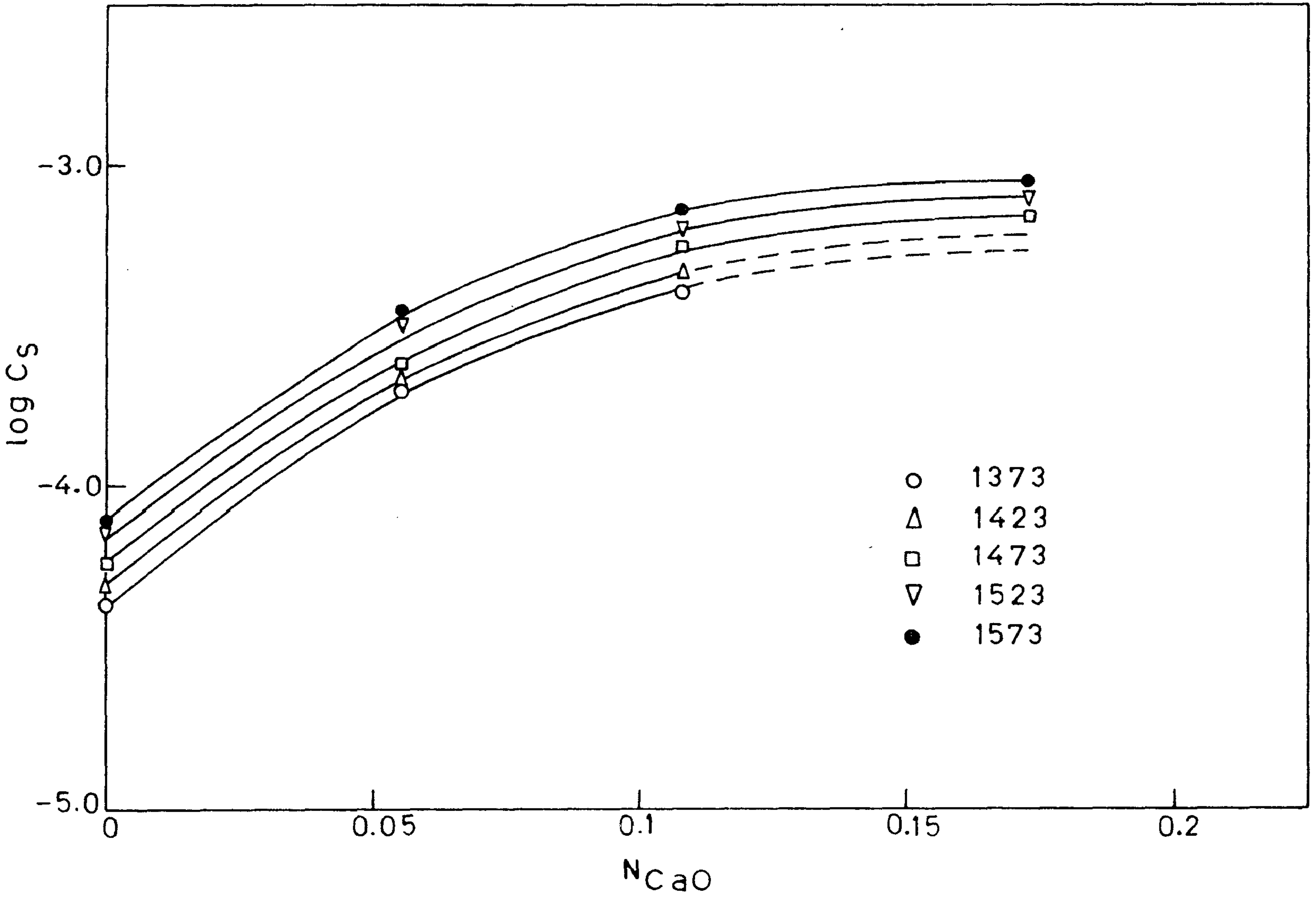


FIG. 4.25 VARIATION IN log C_S WITH N_{CaO} FOR SLAGS HAVING N_{Na_2O}/N_{SiO_2} 0.52 AT DIFFERENT TEMPERATURES.

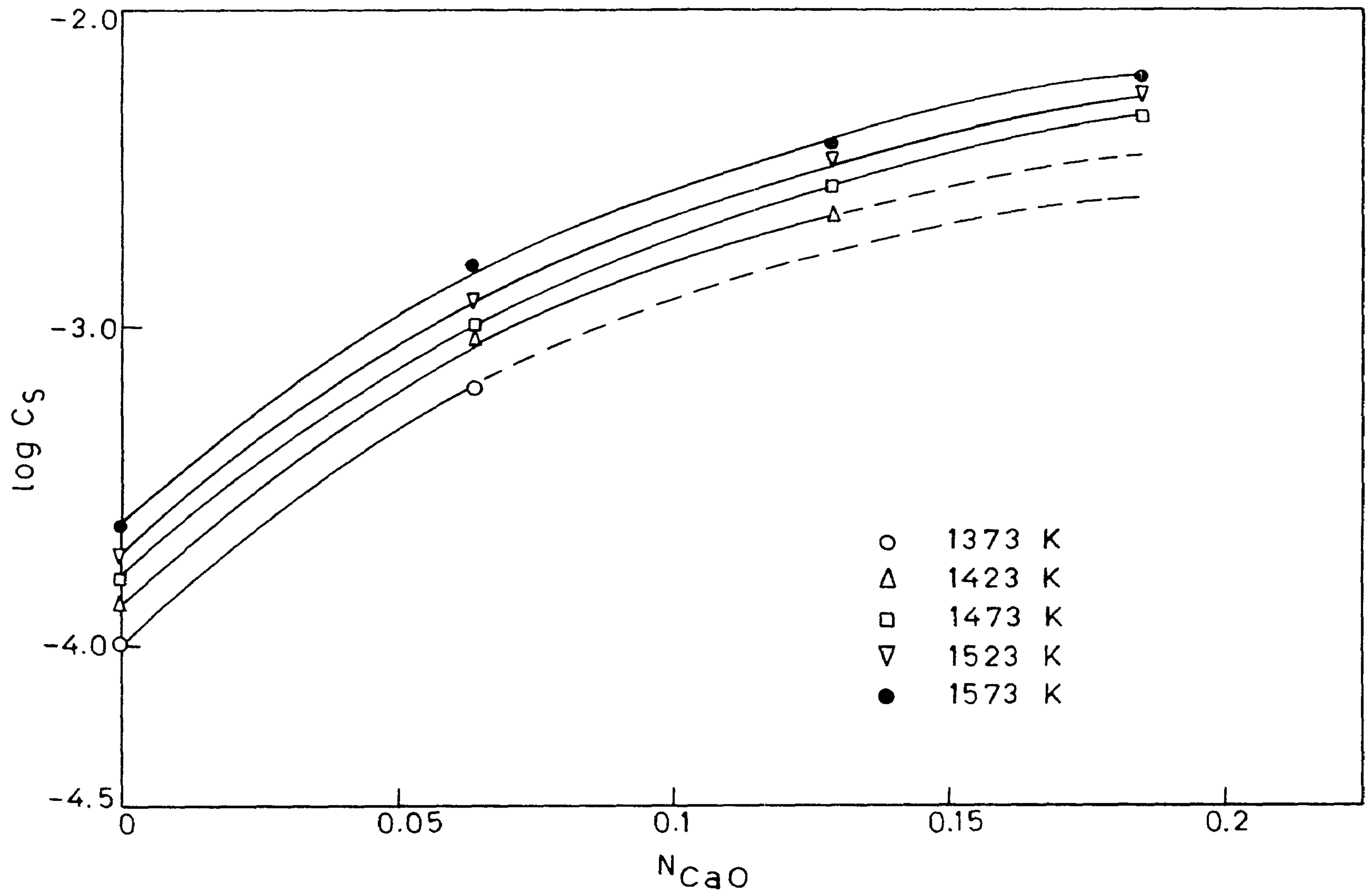


FIG. 4.26 VARIATION IN log C_S WITH N_{CaO} FOR SLAGS HAVING N_{Na_2O}/N_{SiO_2} 0.84 AT DIFFERENT TEMPERATURES.

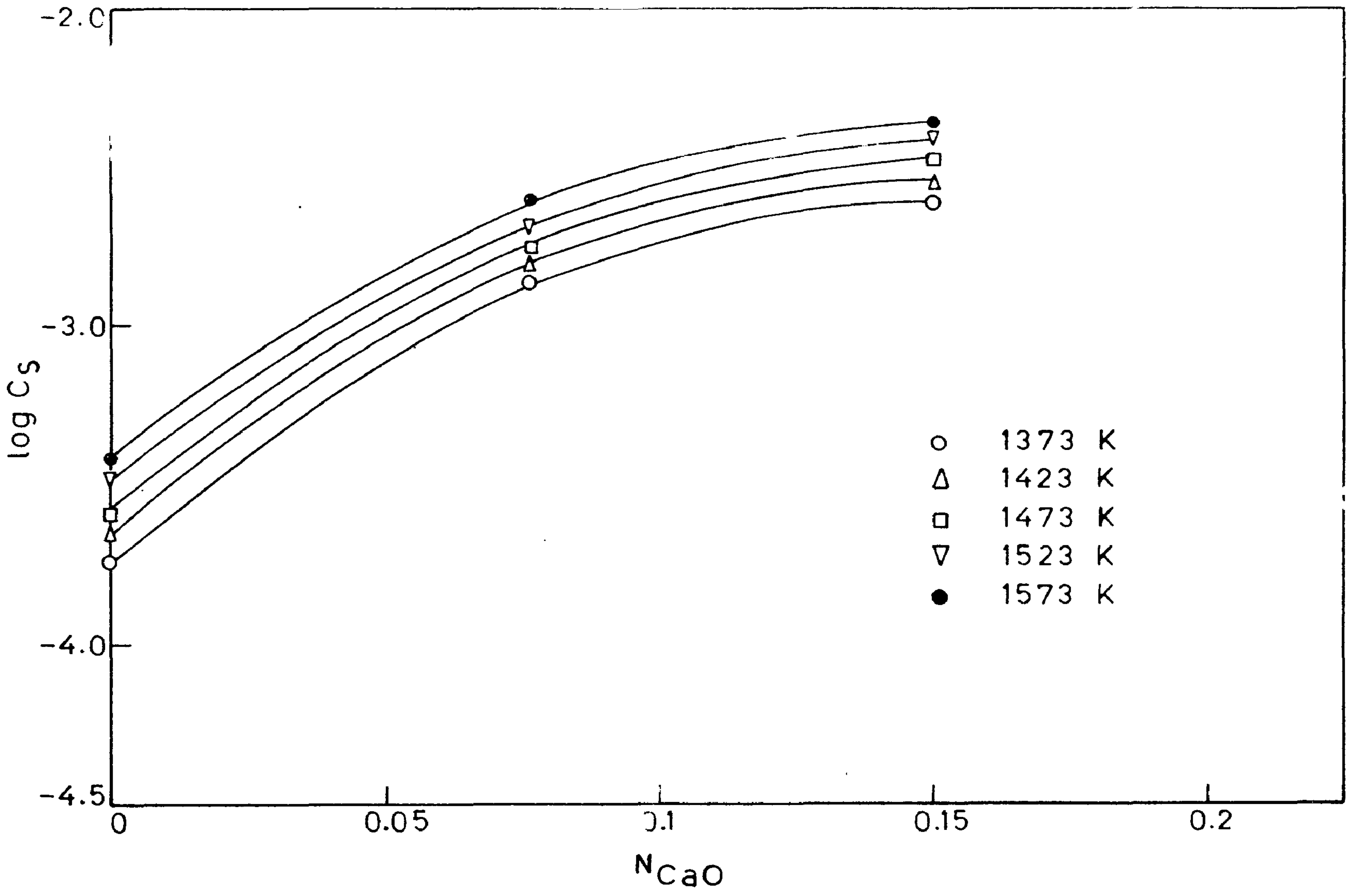


FIG.4.27 VARIATION IN log C_S WITH N_{CaO} FOR SLAGS HAVING N_{Na_2O} / N_{SiO_2} 1.03 AT DIFFERENT TEMPERATURES.

Equation 3.6a shows that, quantitatively, the values of log C_S' of the ternary silicate melts should fall within the log C_S' values of psuedo-binaries XO-SiO_2 and YO-SiO_2 at silica concentration same as the ternary. Richardson et al [98,99] determined sulphur capacity values following this simple relationship (eq.4.6a) at $N_{SiO_2} = 0.5$ for the MnO-MgO-SiO_2, CaO-MnO-SiO_2, CaO-MgO-SiO_2 systems.

In the present system, CaO-Na_2O-SiO_2, however this relationship does not hold good. It has been observed that in the range of composition under consideration, lime additions cause an increase in the C_S value than that of pseudobinary Na_2O-SiO_2, which has higher C_S than CaO-SiO_2 pseudo binary at any silica level. The reason for this variation has already been discussed in the foregoing section.

4.5 COMPARISON WITH PREVIOUS WORK ON LIME-SODA-SILICA SYSTEM

Effect of lime additions on sulphur capacity of soda-silica slags at temperatures in the range of 1250-1350°C has also been studied by Inoue and Suito [84] and Korber and Oelsen [87,88]. Inoue and Suito [84] have studied sulphur transfer between metal and slag by bringing the two phases in equilibrium at temperatures 1250-1350°C and have reported that in the pseudo-binaries, $3Na_2O\cdot 2SiO_2$-$3CaO\cdot 2SiO_2$ and $Na_2O\cdot SiO_2$-$CaO\cdot SiO_2$, log (S) /[S] decreases with increasing CaO concentration. These findings are differing considerably with that of the present investigation. However, the results of present investigation are in good agreement with those of Korber and Oelsen [87,88]. The discrepency in the results with those of Inoue and Suito 84 may be attributed to the magnitude of base equivalence between Na_2O and CaO. Whereas Inoue and Suito [84] have determined 3·33 as CaO equivalence to Na_2O Korber et al 81,88 and in the present work the value is 0·6-0·8 and 1·5 respectively. This observation indicates that CaO shows a positive deviation in solution with Na_2O-SiO_2 melts in the present work whereas Inoue and Suito [84] have inferred a negative deviation which is grossly responsible for the difference. The typical behaviour of ternary slags reported by Inoue and Suito [84] is probably because of considerable amount of magnesia and alumina from refractory lining of crucibles and stirrers made use of by them during the investigation.

Table 4.1 Sulphur equilibration studies in ternary $CaO-Na_2O-SiO_2$ System having $N_{Na_2O}/N_{SiO_2} = 0.26$ at 1373°K

Slag Composition N_{CaO}	Sample Number	Oxygen potential in gas Phase: emf(mV)	Temp. (°K)	pO_2(atm)	pSO_2 (atm)	wt.%. S
0.033	TS_1	550	983	1.68×10^{-10}	0.09	0.165
	TS_2	560	983	2.70×10^{-10}	0.09	0.082
	TS_4	530	983	6.54×10^{-11}	0.094	0.695
0.066	TS_6	537	983	9.11×10^{-11}	0.09	0.702
	TS_7	537	983	9.11×10^{-11}	0.096	0.763
	TS_{10}	541	983	1.10×10^{-10}	0.092	0.546
0.109	TS_{11}	518	993	5.50×10^{-11}	0.08	2.11
	TS_{12}	520	993	6.04×10^{-11}	0.092	1.91
	TS_{13}	520	993	6.04×10^{-11}	0.092	1.93
0.173	TS_{15}	524	993	7.28×10^{-11}	0.086	1.75
	TS_{16}	524	993	7.28×10^{-11}	0.084	1.73
	TS_{18}	528	993	8.78×10^{-11}	0.092	1.44

Table 4.2 Sulphur Equilibration Studies in Ternary CaO-Na_2O-SiO_2 System having N_{Na_2O}/N_{SiO_2} = 0.26 at 1423 °K

Slag Composition N_{CaO}	Sample Number	Oxygen potential in gas Phase			pSO_2 (atm)	wt.% S
		Emf(mV)	Temp(°K)	pO_2(atm)		
0.033	TS_{19}	510	1013	8.18×10^{-11}	0.080	1.61
	TS_{20}	510	1013	8.18×10^{-11}	0.080	1.58
	TS_{21}	514	1013	9.82×10^{-11}	0.086	1.32
0.066	TS_{23}	516	1013	1.08×10^{-10}	0.090	2.04
	TS_{24}	516	1013	1.08×10^{-10}	0.090	1.98
0.109	TS_{25}	516	1013	1.08×10^{-10}	0.094	3.20
	TS_{27}	526	1013	1.70×10^{-10}	0.090	1.46
	TS_{28}	526	1013	1.70×10^{-10}	0.090	1.51
0.173	TS_{30}	518	1013	1.18×10^{-10}	0.090	3.26
	TS_{31}	518	1013	1.18×10^{-10}	0.096	3.54
	TS_{32}	518	1013	1.18×10^{-10}	0.096	3.49

Table 4.3 Sulphur Equilibration Studies in Ternary $CaO-Na_2O-SiO_2$ System having $N_{Na_2O}/N_{SiO_2} = 0.26$ at 1473 °K

Slag Composition N_{CaO}	Sample Number	Oxygen potential in gas phase			pSO_2 (atm)	wt% S
		Emf(mV)	Temp(°K)	pO_2(atm)		
0.033	TS_{34}	538	1033	6.04×10^{-10}	0.090	0.309
	TS_{35}	538	1033	6.04×10^{-10}	0.094	0.312
	TS_{36}	538	1033	6.04×10^{-10}	0.094	0.320
0.066	TS_{38}	541	1033	6.92×10^{-10}	0.094	0.439
	TS_{40}	541	1033	6.92×10^{-10}	0.098	0.483
0.109	TS_{41}	522	1043	4.20×10^{-10}	0.090	1.45
	TS_{43}	528	1043	5.48×10^{-10}	0.090	0.936
	TS_{44}	528	1043	5.48×10^{-10}	0.090	0.941
0.173	TS_{47}	536	1043	7.82×10^{-10}	0.096	0.736
	TS_{48}	536	1043	7.82×10^{-10}	0.096	0.692

Table 4.4 Sulphur Equilibration Studies in Ternary $CaO-Na_2O-Si$
System having N_{Na_2O}/N_{SiO_2} = 0.26 at 1523°K

Slag Composition N_{CaO}	Sample Number	Oxygen potential in gas phase			pSO_2 (atm)	Wt.%S
		Emf(mV)	Temp(K)	pO_2(atm)		
0.033	TS_{49}	528	1053	$7.74x10^{-10}$	0.086	0.630
	TS_{50}	528	1053	$7.74x10^{-10}$	0.086	0.639
	TS_{51}	533	1053	$9.64x10^{-10}$	0.082	0.441
0.066	TS_{52}	533	1053	$9.64x10^{-10}$	0.082	0.793
	TS_{55}	526	1053	$7.09x10^{-10}$	0.086	1.220
	TS_{56}	526	1053	$7.09x10^{-10}$	0.086	1.170
0.109	TS_{57}	526	1053	$7.09x10^{-10}$	0.082	1.690
	TS_{58}	526	1053	$7.09x10^{-10}$	0.082	1.760
	TS_{61}	528	1053	$7.74x10^{-10}$	0.082	1.550
0.173	TS_{63}	528	1053	$7.74x10^{-10}$	0.084	2.100
	TS_{64}	528	1053	$7.74x10^{-10}$	0.084	2.020

Table 4.5- Sulphur Equilibration Studies in Ternary $CaO-Na_2O.SiO_2$ System having N_{Na_2O}/N_{SiO_2} = 0.26 at 1573°K

Slag Composition N_{CaO}	Sample Number	Oxygen potential in gas phase			pSO_2 (atm)	Wt.% S
		Emf(mV)	Temp(°K)	pO_2(atm)		
0.033	TS_{65}	522	1083	1.62×10^{-9}	0.086	0.582
	TS_{67}	528	1083	2.10×10^{-9}	0.080	0.375
	TS_{68}	528	1083	2.10×10^{-9}	0.080	0.368
0.066	TS_{70}	534	1083	2.72×10^{-9}	0.080	0.420
	TS_{71}	534	1083	2.72×10^{-9}	0.088	0.459
	TS_{72}	534	1083	2.72×10^{-9}	0.088	0.454
0.109	TS_{75}	540	1063	1.83×10^{-9}	0.090	1.290
	TS_{76}	540	1063	1.83×10^{-9}	0.090	1.330
0.173	TS_{77}	542	1063	2.00×10^{-9}	0.092	1.570
	TS_{79}	545	1063	2.28×10^{-9}	0.092	1.310
	TS_{80}	545	1063	2.28×10^{-9}	0.092	1.220

Table 4.6- Sulphur Equilibration Studies in Ternary $CaO-Na_2O-SiO_2$ System having N_{Na_2O}/N_{SiO_2} = 0.40 at 1373°K

Slag Composition N_{CaO}	Sample Number	Oxygen potential in gas phase			pSO_2 (atm)	Wt %.S
		Emf.(mV)	Temp (°K)	pO_2(atm)		
0.044	TS_{81}	554	993	2.96×10^{-10}	0.090	0.158
	TS_{83}	560	993	3.92×10^{-10}	0.094	0.108
	TS_{84}	560	993	3.92×10^{-10}	0.094	0.103
0.087	TS_{86}	560	993	3.92×10^{-10}	0.090	0.195
	TS_{87}	562	993	4.30×10^{-10}	0.090	0.178
0.152	TS_{89}	562	993	4.30×10^{-10}	0.098	0.251
	TS_{90}	562	993	4.30×10^{-10}	0.098	0.246
	TS_{91}	550	983	1.68×10^{-10}	0.082	0.851

Table 4.7 Sulphur Equilibration Studies in Ternary $CaO.Na_2O.SiO_2$ System having $N_{Na_2O}/N_{SiO_2} = 0.40$ at 1423°K

Slag Composition N_{CaO}	Sample Number	Oxygen potential in gas phase			pSO_2 (atm)	Wt.%.S
		Emf(mV)	Temp(°K)	pO_2(atm)		
0.044	TS_{93}	540	1023	4.64×10^{-10}	0.090	0.282
	TS_{94}	540	1023	4.64×10^{-10}	0.090	0.286
	TS_{95}	542	1023	5.08×10^{-10}	0.094	0.254
0.087	TS_{97}	553	1023	8.38×10^{-10}	0.100	0.262
	TS_{98}	553	1023	8.38×10^{-10}	0.100	0.257
0.152	TS_{101}	568	993	5.70×10^{-10}	0.096	0.538
	TS_{102}	568	993	5.70×10^{-10}	0.096	0.553
	TS_{103}	574	993	7.54×10^{-10}	0.088	0.334
	TS_{104}	574	993	7.54×10^{-10}	0.088	0.327

Table 4.8- Sulphur Equilibration Studies in Ternary $CaO.Na_2O.SiO_2$ system having $N_{Na_2O}/N_{SiO_2} = 0.4$ at 1473°K

Slagg Composition N_{CaO}	Sample Number	Oxygen potential in gas phase			pSO_2 (atm)	Wt.% S
		Emf(mV)	Temp(°K)	pO_2(atm)		
0.044	TS_{106}	548	1003	3.24×10^{-10}	0.092	1.640
	TS_{107}	552	1003	3.90×10^{-10}	0.092	1.230
	TS_{108}	552	1003	3.90×10^{-10}	0.092	1.290
0.087	TS_{110}	555	1003	4.49×10^{-10}	0.090	1.050
	TS_{111}	567	1003	7.82×10^{-10}	0.088	0.475
	TS_{112}	567	1003	7.82×10^{-10}	0.088	0.464
0.152	TS_{115}	557	993	3.41×10^{-10}	0.082	3.790
	TS_{116}	557	993	3.41×10^{-10}	0.082	3.740
0.215	TS_{117}	557	993	3.41×10^{-10}	0.080	4.240
	TS_{119}	560	993	3.92×10^{-10}	0.080	3.400
	TS_{120}	560	993	3.92×10^{-10}	0.080	3.430

Table 4.9- Sulphur Equilibration Studies in Ternary $CaO.Na_2O.SiO_2$ system having $N_{Na_2O}/N_{SiO_2} = 0.40$ at 1523 °K

Slag Composition N_{CaO}	Sample Number	Oxygen potential in gas phase			pSO_2 (atm)	Wt.%S
		Emf(mV)	Temp(°K)	pO_2(atm)		
0.044	TS_{121}	542	1033	7.23×10^{-10}	0.086	1.56
	TS_{122}	542	1033	7.23×10^{-10}	0.086	1.49
	TS_{123}	544	1033	7.91×10^{-10}	0.082	1.22
0.087	TS_{124}	544	1033	7.91×10^{-10}	0.082	2.20
	TS_{125}	547	1033	9.06×10^{-10}	0.084	1.83
	TS_{127}	548	1033	9.47×10^{-10}	0.084	1.70
0.152	TS_{129}	550	1033	1.04×10^{-9}	0.090	2.37
	TS_{130}	550	1033	1.04×10^{-9}	0.090	2.34
	TS_{131}	544	1033	7.91×10^{-10}	0.084	3.31
0.215	TS_{133}	548	1033	9.47×10^{-10}	0.088	3.11
	TS_{135}	548	1033	9.47×10^{-10}	0.088	3.12

Table 4.10 Sulphur Equilibration Studies in Ternary $CaO-Na_2O-SiO_2$ System having N_{Na_2O}/N_{SiO_2} = 0.40 at 1573 °K

Slag Composition N_{CaO}	Sample Number	Oxygen potential in gas phase			pSO_2 (atm)	Wt.% S
		Emf(mV)	Temp.(°K)	pO_2 (atm)		
0.044	TS_{136}	538	1083	3.22×10^{-9}	0.092	0.497
	TS_{137}	543	1083	4.00×10^{-9}	0.096	0.369
	TS_{138}	543	1083	4.00×10^{-9}	0.096	0.365
0.087	TS_{140}	544	1083	4.17×10^{-9}	0.096	0.602
	TS_{142}	544	1083	4.17×10^{-9}	0.096	0.577
0.152	TS_{145}	546	1083	4.54×10^{-9}	0.090	0.743
	TS_{146}	546	1083	4.54×10^{-9}	0.090	0.731
	TS_{148}	548	1083	4.95×10^{-9}	0.094	0.674
0.215	TS_{150}	552	1083	5.87×10^{-9}	0.094	0.618
	TS_{151}	558	1083	7.60×10^{-9}	0.090	0.395
	TS_{152}	558	1083	7.60×10^{-9}	0.090	0.410

Table 4.11 **Sulphur Equilibration Studies in** Ternary $CaO-Na_2O-SiO_2$ System having $N_{Na_2O}/N_{SiO_2} = 0.52$ at 1373°K

Slag Composition N_{CaO}	Sample Number	Oxygen potential in gas phase			pSO_2 (atm)	Wt.%.S
		Emf(mV)	Temp.(°K)	pO_2(atm)		
0.055	TS_{153}	541	983	1.10×10^{-10}	0.100	1.730
	TS_{154}	544	983	1.27×10^{-10}	0.086	1.140
	TS_{156}	550	983	1.68×10^{-10}	0.080	0.701
0.108	TS_{158}	555	983	2.13×10^{-10}	0.088	1.130
	TS_{159}	560	983	2.70×10^{-10}	0.090	0.789

Table 4.12- Sulphur Equilibration Studies in Ternary $CaO.Na_2O.SiO_2$ System having $N_{Na_2O}/N_{SiO_2} = 0.52$ at 1423°K

Slag Composition	Sample Number	Oxygen potential in gas phase			pSO_2 (atm)	Wt.% S
		Emf(mV)	Temp.(°K)	pO_2(atm)		
0.055	TS_{163}	532	1013	2.24×10^{-10}	0.096	1.84
	TS_{165}	537	1013	2.82×10^{-10}	0.082	1.15
	TS_{166}	537	1013	2.82×10^{-10}	0.082	1.17
0.108	TS_{168}	546	1013	4.26×10^{-10}	0.088	1.45
	TS_{170}	550	1013	5.12×10^{-10}	0.100	1.24
	TS_{171}	550	1013	5.12×10^{-10}	0.096	1.20

Table 4.13- Sulphur Equilibration Studies in Ternary $CaO.Na_2O.SiO_2$ System having N_{Na_2O}/N_{SiO_2} = 0.52 at 1473°K

Slag Composition N_{CaO}	Sample Number	Oxygen potential in gas phase			pSO_2 (atm)	Wt%.S
		Emf(mV)	Temp(°K)	pO_2(atm)		
0.055	TS_{173}	482	1093	4.10×10^{-10}	0.090	2.28
	TS_{174}	482	1093	4.10×10^{-10}	0.090	2.21
	TS_{176}	486	1093	4.86×10^{-10}	0.094	1.76
0.108	TS_{177}	490	1093	5.76×10^{-10}	0.092	3.23
	TS_{179}	490	1093	5.76×10^{-10}	0.100	3.44
0.173	TS_{181}	494	1093	6.82×10^{-10}	0.086	2.88
	TS_{182}	494	1093	6.82×10^{-10}	0.086	2.84
	TS_{183}	497	1093	7.76×10^{-10}	0.094	2.55

Table 4.14- Sulphur Equilibration Studies in Ternary $CaO.Na_2O.SiO_2$ System having N_{Na_2O}/N_{SiO_2} = 0.52 at 1523°K

Slag Composition N_{CaO}	Sample Number	Oxygen potential in gas phase			pSO_2 (atm)	Wt%.S
		Emf(mV)	Temp.(°K)	pO_2(atm)		
0.055	TS_{185}	492	1103	$8.71x10^{-10}$	0.080	2.25
	TS_{186}	492	1103	$8.71x10^{-10}$	0.080	2.19
0.108	TS_{189}	494	1103	$9.47x10^{-10}$	0.082	4.07
	TS_{190}	494	1103	$9.47x10^{-10}$	0.082	4.01
	TS_{192}	495	1103	$9.89x10^{-10}$	0.086	3.92
0.173	TS_{193}	498	1103	$1.12x10^{-9}$	0.080	3.67
	TS_{194}	498	1103	$1.12x10^{-9}$	0.080	3.64
	TS_{195}	498	1103	$1.12x10^{-9}$	0.088	4.01

Table 4.15 Sulphur Equilibration Studies in Ternary $CaO-Na_2O.SiO_2$ System having N_{Na_2O}/N_{SiO_2} = 0.52 at 1573°K

Slag Composition N_{CaO}	Sample Number	Oxygen potential in gas phase			pSO_2 (atm) (atm)	Wt.%S
		Emf(mV)	Temp(°K)	pO_2(atm)		
0.055	TS_{197}	498	1123	2.12×10^{-9}	0.080	1.610
	TS_{199}	498	1123	2.12×10^{-9}	0.076	1.490
	TS_{200}	498	1123	2.12×10^{-9}	0.076	1.520
0.108	TS_{201}	501	1123	2.40×10^{-9}	0.080	2.790
	TS_{202}	501	1123	2.40×10^{-9}	0.080	2.750
	TS_{205}	514	1123	4.10×10^{-9}	0.080	1.230
0.173	TS_{207}	521	1123	5.48×10^{-9}	0.088	1.110
	TS_{208}	521	1123	5.48×10^{-9}	0.088	1.080
	TS_{209}	524	1123	6.20×10^{-9}	0.095	0.949

Table 4.16- Sulphur Equilibration Studies in Ternary $CaO.Na_2O.SiO_2$ System having $N_{Na_2O}/N_{SiO_2} = 0.84$ at 1373°K

Slag Composition N_{CaO}	Sample Number	Oxygen potential in gas phase			pSO_2 (atm)	Wt.%.S
		Emf(mV)	Temp.(°K)	pO_2(atm)		
0.064	TS_{211}	570	993	6.26×10^{-10}	0.08	3.29
	TS_{213}	570	993	6.26×10^{-10}	0.10	4.02
	TS_{214}	570	993	6.26×10^{-10}	0.10	4.11

Table 4.17- Sulphur Equilibration Studies in Ternary $CaO-Na_2O.SiO_2$ System having N_{Na_2O}/N_{SiO_2} = 0.84 at 1423°K

Slag Composition N_{CaO}	Sample Number	Oxygen potential in gas phase			pSO_2 (atm)	Wt.%.S
		Emf(mV)	Temp.(°K)	pO_2(atm)		
0.064	TS_{215}	536	1043	7.82×10^{-10}	0.092	1.210
	TS_{216}	536	1043	7.82×10^{-10}	0.092	1.170
	TS_{217}	540	1043	9.35×10^{-10}	0.084	0.822
0.129	TS_{218}	540	1043	9.35×10^{-10}	0.084	2.050
	TS_{219}	542	1043	1.02×10^{-9}	0.080	1.680
	TS_{220}	542	1043	1.02×10^{-9}	0.080	1.700

Table 4.18 Sulphur Equilibration Studies in Ternary $CaO.Na_2O.SiO_2$ System having N_{Na_2O}/N_{SiO_2} = 0.84 at 1473°K

Slag Composition N_{CaO}	Sample Number	Oxygen potential in gas phase			pSO_2 (atm)	Wt.%.S
		Emf(mV)	Temp(°K)	pO_2(atm)		
0.064	TS_{221}	508	1083	$8.91x10^{-10}$	0.086	3.07
	TS_{223}	508	1083	$8.91x10^{-10}$	0.080	2.28
0.129	TS_{224}	511	1083	$10.16x10^{-10}$	0.076	5.61
	TS_{225}	514	1083	$11.5x10^{-10}$	0.080	4.79
	TS_{226}	514	1083	$11.5x10^{-10}$	0.080	4.76
0.235	TS_{229}	528	1083	$2.1x10^{-9}$	0.080	3.27
	TS_{230}	528	1083	$2.1x10^{-9}$	0.080	3.22

Table 4.19- Sulphur Equilibration Studies in Ternary $CaO-Na_2O-SiO_2$ System having $N_{Na_2O}/N_{SiO_2} = 0.84$ at 1523 °K

Slag Composition N_{CaO}	Sample Number	Oxygen potential in gas phase			pSO_2 (atm)	Wt.% S
		Emf(mV)	Temp(°K)	pO_2(atm)		
0.064	TS_{231}	517	1113	3.42×10^{-9}	0.080	1.160
	TS_{232}	517	1113	3.42×10^{-9}	0.080	1.080
	TS_{233}	517	1113	3.42×10^{-9}	0.070	0.887
0.129	TS_{236}	522	1113	4.20×10^{-9}	0.070	1.970
	TS_{237}	522	1113	4.20×10^{-9}	0.084	2.340
	TS_{238}	522	1113	4.20×10^{-9}	0.084	2.370
0.235	TS_{239}	528	1113	5.40×10^{-9}	0.080	2.400
	TS_{240}	528	1113	5.40×10^{-9}	0.080	2.370

Table 4.20- Sulphur Equilibration Studies in Ternary
$CaO.Na_2O.SiO_2$ System having
$N_{Na_2O}/N_{SiO_2} = 0.84$ at 1573 °K

Slag Composition N_{CaO}	Sample Number	Oxygen potential in gas phase			pSO_2 (atm)	Wt.%.S.
		Emf.(mV)	Temp(°K)	pO_2(atm)		
0.064	TS_{243}	488	1153	3.52×10^{-9}	0.07	3.02
	TS_{244}	488	1153	3.52×10^{-9}	0.07	2.93
	TS_{246}	494	1153	4.48×10^{-9}	0.07	2.07
0.129	TS_{247}	498	1153	5.26×10^{-9}	0.08	4.33
	TS_{248}	498	1153	5.26×10^{-9}	0.08	4.21
0.235	TS_{251}	503	1153	6.44×10^{-9}	0.07	4.49
	TS_{253}	505	1153	6.98×10^{-9}	0.08	4.51

Table 4.21- Sulphur Equilibration Studies in Ternary $CaO.Na_2O.SiO_2$ System having $N_{Na_2O}/N_{SiO_2} = 1.03$ at 1373°K

Slag Composition N_{CaO}	Sample Number	Oxygen potential in gas phase			$pS_{O}2$ (atm)	Wt.%S
		Emf(mV)	Temp(°K)	pO_2(atm)		
0.076	TS_{255}	512	1063	$5.40x10^{-10}$	0.086	0.878
	TS_{256}	512	1063	$5.40x10^{-10}$	0.086	0.899
	TS_{257}	515	1063	$6.16x10^{-10}$	0.080	0.690
0.150	TS_{259}	520	1063	$7.66x10^{-10}$	0.076	0.891
	TS_{260}	520	1063	$7.66x10^{-10}$	0.076	0.824
	TS_{262}	522	1063	$8.36x10^{-10}$	0.082	0.793

Table 4.22 Sulphur Equilibration Studies in Ternary $CaO.Na_2O.SiO_2$ System having $N_{Na_2O}/N_{SiO_2} = 1.03$ at 1423°K

Slag Composition N_{CaO}	Sample Number	Oxygen potential in gas phase			pSO_2 (atm)	Wt.% S.
		Emf(mV)	Temp.(°K)	pO_2 (atm.)		
0.076	TS_{263}	534	1043	7.16×10^{-10}	0.080	2.03
	TS_{264}	534	1043	7.16×10^{-10}	0.080	1.98
	TS_{265}	534	1043	7.16×10^{-10}	0.090	2.19
	TS_{266}	534	1043	7.16×10^{-10}	0.090	2.28
0.150	TS_{269}	539	1043	8.95×10^{-10}	0.090	2.95
	TS_{270}	539	1043	8.95×10^{-10}	0.090	2.93
	TS_{271}	542	1043	10.2×10^{-10}	0.084	2.14

Table 4.23 Sulphur Equilibration Studies in Ternary $CaO.Na_2O.SiO_2$ System having $N_{Na_2O}/N_{SiO_2} = 1.03$ at 1473°K

Slag Composition N_{CaO}	Sample Number	Oxygen potential in gas phase			pSO_2 (atm)	Wt.%S
		Emf(mV)	Temp(°K)	pO_2(atm)		
0.076	TS_{272}	536	1093	$4.06x10^{-9}$	0.086	0.486
	TS_{273}	538	1093	$4.42x10^{-9}$	0.080	0.414
	TS_{274}	538	1093	$4.42x10^{-9}$	0.080	0.401
0.150	TS_{275}	542	1093	$5.24x10^{-9}$	0.082	0.798
	TS_{277}	542	1093	$5.24x10^{-9}$	0.076	0.910

Table 4.24 Sulphur Equilibration Studies in Ternary $CaO.Na_2O.SiO_2$ System having $N_{Na_2O}/N_{SiO_2} = 1.03$ at 1523°K

Slag Composition N_{CaO}	Sample Number	Oxygen Potential in gas phase			pSO_2 (atm)	Wt.%.S.
		Emf(mV)	Temp.(°K)	pO_2(atm)		
0.076	TS_{279}	562	1063	$4.80x10^{-9}$	0.080	1.11
	TS_{280}	562	1063	$4.80x10^{-9}$	0.080	1.04
	TS_{282}	562	1063	$4.80x10^{-9}$	0.074	1.02
0.150	TS_{283}	570	1063	$6.80x10^{-9}$	0.070	1.40
	TS_{285}	574	1063	$8.10x10^{-9}$	0.082	1.22
	TS_{286}	574	1063	$8.10x10^{-9}$	0.082	1.24

Table 4.25- Sulphur Equilibration Studies in Ternary Ca
CaO-$Na_2O.SiO_2$ System having
$N_{Na_2O}/N_{SiO_2} = 1.03$ at 1573°K

Slag Composition N_{CaO}	Sample Number	Oxygen potential in gas phase			pSO_2 (atm)	Wt.%.S
		Emf(mV)	Temp(°K)	pO_2(atm)		
0.076	TS_{287}	542	1093	5.24×10^{-9}	0.08	2.85
	TS_{289}	545	1093	5.96×10^{-9}	0.086	2.43
	TS_{290}	545	1093	5.96×10^{-9}	0.086	2.58
0.150	TS_{293}	552	1093	8.02×10^{-9}	0.08	3.29
	TS_{295}	556	1093	9.50×10^{-9}	0.076	2.40

Table 4.26- Calculated Values of Sulphur Capacity of Ternary CaO-Na_2O-SiO_2 System having $N_{Na_2O}/N_{SiO_2} = 0.26$ at 1373°K

Slag Composition N_{CaO}	Sample Number	pO_2 $(x10^{10})$	p_{S_2}	C_S	Av. C_S	log Av.C_S
0.033	TS_1	1.680	$2.81x10^{-3}$	$4.034x10^{-5}$	$4.025x10^{-5}$	-4.40
	TS_2	2.700	$1.09x10^{-3}$	$4.086x10^{-5}$		
	TS_4	0.654	$2.02x10^{-2}$	$3.955x10^{-5}$		
0.066	TS_6	0.911	$9.55x10^{-3}$	$6.856x10^{-5}$	$6.917x10^{-5}$	-4.16
	TS_7	0.911	$1.09x10^{-2}$	$6.975x10^{-5}$		
	TS_{10}	1.100	$6.85x10^{-3}$	$6.919x10^{-5}$		
0.109	TS_{11}	0.550	$2.07x10^{-2}$	$1.088x10^{-4}$	$1.023 x10^{-4}$	-3.99
	TS_{12}	0.604	$2.27x10^{-2}$	$0.985x10^{-4}$		
	TS_{13}	0.604	$2.27x10^{-2}$	$0.996x10^{-4}$		
0.173	TS_{15}	0.728	$1.37x10^{-2}$	$1.276x10^{-4}$	$1.280x10^{-4}$	-3.89
	TS_{16}	0.728	$1.37x10^{-2}$	$1.261x10^{-4}$		
	TS_{18}	0.878	$1.07x10^{-2}$	$1.304x10^{-4}$		

Table 4.27- Calculated values of Sulphur Capacity of ternary $CaO-Na_2O-SiO_2$ System having $N_{Na_2O}/N_{SiO_2} = 0.26$ at 1423 °K

Slag Composition N_{CaO}	Sample Number	p_{O_2} $x10^{10}$	p_{S_2}	C_S	Av. C_S	log Av.C_S
0.033	TS_{19}	0.818	$8.72x10^{-2}$	$4.931x10^{-5}$	$4.906x10^{-5}$	-4.31
	TS_{20}	0.818	$8.72x10^{-2}$	$4.839x10^{-5}$		
	TS_{21}	0.982	$6.99x10^{-2}$	$4.948x10^{-5}$		
0.066	TS_{23}	1.08	$6.33x10^{-2}$	$8.426x10^{-5}$	$8.302x10^{-5}$	-4.08
	TS_{24}	1.08	$6.33x10^{-2}$	$8.179x10^{-5}$		
0.109	TS_{25}	1.08	$6.90x10^{-2}$	$1.266x10^{-4}$	$1.230x10^{-4}$	-3.91
	TS_{27}	1.70	$2.55x10^{-2}$	$1.192x10^{-4}$		
	TS_{28}	1.70	$2.55x10^{-2}$	$1.233x10^{-4}$		
0.173	TS_{30}	1.18	$5.30x10^{-2}$	$1.538x10^{-4}$	$1.546x10^{-4}$	-3.81
	TS_{31}	1.18	$6.03x10^{-2}$	$1.566x10^{-4}$		
	TS_{32}	1.18	$6.03x10^{-2}$	$1.534x10^{-4}$		

Table 4.28- Calculated Values of Sulphur Capacity of Ternary CaO-Na_2O-SiO_2 System having N_{Na_2O}/N_{SiO_2} = 0.26 at 1473 °K

Slag Composition N_{CaO}	Sample Number	p_{O_2} $(x10^{10})$	p_{S_2}	C_S	Av. C_S	log Av C
0.033	TS_{34}	6.04	$1.62x10^{-2}$	$5.966x10^{-5}$	$5.891x10^{-5}$	-4.23
	TS_{35}	6.04	$1.76x10^{-2}$	$5.780x10^{-5}$		
	TS_{36}	6.04	$1.76x10^{-2}$	$5.928x10^{-5}$		
0.066	TS_{38}	6.92	$1.35x10^{-2}$	$0.994x10^{-4}$	$1.023x10^{-4}$	-3.99
	TS_{40}	6.92	$1.46x10^{-2}$	$1.052x10^{-4}$		
0.109	TS_{41}	4.20	$3.35x10^{-2}$	$1.624x10^{-4}$	$1.585x10^{-4}$	-3.80
	TS_{43}	5.48	$1.97x10^{-2}$	$1.561x10^{-4}$		
	TS_{44}	5.48	$1.97x10^{-2}$	$1.569x10^{-4}$		
0.173	TS_{47}	7.82	$1.10x10^{-2}$	$1.962x10^{-4}$	$1.903x10^{-4}$	-3.72
	TS_{48}	7.82	$1.10x10^{-2}$	$1.845x10^{-4}$		

Table 4.29- Calculated Value of Sulphur Capacity of Ternary $CaO-Na_2O-SiO_2$ System having $N_{Na_2O}/N_{SiO_2} = 0.26$ at 1523 °K

Slag Composition N_{CaO}	Sample Number	p_{O_2} (x10^{10})	p_{S_2}	C_S	Av. C_S	log Av C_S
0.033	TS_{49}	7.74	$6.28x10^{-2}$	$6.994x10^{-4}$		
	TS_{50}	7.74	$6.28x10^{-2}$	$7.094x10^{-4}$	$7.075x10^{-5}$	-4.15
	TS_{51}	9.64	$3.68x10^{-2}$	$7.138x10^{-4}$		
0.066	TS_{52}	9.64	$3.68x10^{-2}$	$1.283x10^{-4}$		
	TS_{55}	7.09	$7.49x10^{-2}$	$1.187x10^{-4}$	$1.203x10^{-4}$	-3.92
	TS_{56}	7.09	$7.49x10^{-2}$	$1.138x10^{-4}$		
0.109	TS_{57}	7.09	$6.81x10^{-2}$	$1.724x10^{-4}$		
	TS_{58}	7.09	$6.81x10^{-2}$	$1.796x10^{-4}$	$1.775x10^{-4}$	-3.75
	TS_{61}	7.74	$5.71x10^{-2}$	$1.805x10^{-4}$		
0.173	TS_{63}	7.74	$5.99x10^{-2}$	$2.387x10^{-4}$	$2.342x10^{-4}$	-3.63
	TS_{64}	7.74	$5.99x10^{-2}$	$2.296x10^{-4}$		

Table 4.30- Calculated values of Sulphur Capacity of Ternary $CaO-Na_2O-SiO_2$ System having $N_{Na_2O}/N_{SiO_2} = 0.26$ at 1573°K

Slag Composition N_{CaO}	Sample Number	p_{O_2} $(x10^{10})$	p_{S_2}	C_S	Av C_S	Log Av C_S
0.033	TS_{65}	16.2	$8.84x10^{-2}$	$7.879x10^{-5}$	$7.947x10^{-5}$	-4.10
	TS_{67}	21.0	$4.55x10^{-2}$	$8.056x10^{-5}$		
	TS_{68}	21.0	$4.55x10^{-2}$	$7.906x10^{-5}$		
0.066	TS_{70}	27.2	$2.72x10^{-2}$	$1.328x10^{-4}$	$1.318x10^{-4}$	-3.88
	TS_{71}	27.2	$3.29x10^{-2}$	$1.320x10^{-4}$		
	TS_{72}	27.2	$3.29x10^{-2}$	$1.305x10^{-4}$		
0.109	TS_{75}	18.3	$7.59x10^{-2}$	$2.003x10^{-4}$	$2.034x10^{-4}$	-3.69
	TS_{76}	18.3	$7.59x10^{-2}$	$2.065x10^{-4}$		
0.173	TS_{77}	20.0	$6.64x10^{-2}$	$2.725x10^{-4}$	$2.690x10^{-4}$	-3.57
	TS_{79}	22.8	$5.11x10^{-2}$	$2.767x10^{-4}$		
	TS_{80}	22.8	$5.11x10^{-2}$	$2.577x10^{-4}$		

Table 4.31. Calculated values of Sulphur Capacity of Ternary CaO-Na_2O-SiO_2 System having $N_{Na_2O}/N_{SiO_2} = 0.40$ at 1373°K

Slag Composition N_{CaO}	Sample Number	p_{O_2} $(\times 10^{10})$	p_{S_2}	C_s	Av. C_s	Log AvC_s
0.044	TS_{81}	2.69	9.05×10^{-4}	9.036×10^{-5}	8.88×10^{-5}	-4.05
	TS_{83}	3.92	5.63×10^{-4}	9.012×10^{-5}		
	TS_{84}	3.92	5.63×10^{-4}	8.595×10^{-5}		
0.087	TS_{86}	3.92	5.16×10^{-4}	1.697×10^{-4}	1.739×10^{-4}	-3.76
	TS_{87}	4.30	4.29×10^{-4}	1.782×10^{-4}		
0.152	TS_{89}	4.30	5.08×10^{-4}	2.309×10^{-4}	2.286×10^{-4}	-3.64
	TS_{90}	4.30	5.08×10^{-4}	2.263×10^{-4}		
	TS_{91}	1.68	2.33×10^{-3}	2.285×10^{-4}		

Table 4.32 Calculated values of Sulphur Capacity of Ternary $CaO-Na_2O-SiO_2$ System having $N_{Na_2O}/N_{SiO_2} = 0.40$ at 1423°K

Slag Composition N_{CaO}	Sample Number	p_{O_2} $(x10^{10})$	p_{S_2}	C_s	Av C_s	log Av C_s
0.044	TS_{93}	4.64	$4.43x10^{-3}$	$1.037x10^{-4}$	$1.038x10^{-4}$	-3.98
	TS_{94}	4.64	$3.43x10^{-3}$	$1.052x10^{-4}$		
	TS_{95}	5.08	$3.12x10^{-3}$	$1.025x10^{-4}$		
0.087	TS_{97}	8.38	$1.30x10^{-3}$	$2.103x10^{-4}$	$2.083x10^{-4}$	-3.68
	TS_{98}	8.38	$1.30x10^{-3}$	$2.063x10^{-4}$		
0.152	TS_{101}	5.70	$2.58x10^{-3}$	$2.529x10^{-4}$	$2.570x10^{-4}$	-3.59
	TS_{102}	5.70	$2.58x10^{-3}$	$2.599x10^{-4}$		
	TS_{103}	7.54	$1.24x10^{-3}$	$2.604x10^{-4}$		
	TS_{104}	7.54	$1.24x10^{-3}$	$2.550x10^{-4}$		

Table 4.33 Calculated Values of Sulphur Capacity of Ternary $CaO-Na_2O-SiO_2$ System having N_{Na_2O} = 0.40 at 1473 °K

Slag Composition N_{CaO}	Sample Number	p_{O_2} $(x10^{10})$	p_{S_2}	C_s	Av. C_s	Log Av C_s
0.044	TS_{106}	3.24	$5.88x10^{-2}$	$1.217x10^{-4}$	$1.229x10^{-4}$	-3.91
	TS_{107}	3.90	$4.06x10^{-2}$	$1.206x10^{-4}$		
	TS_{108}	3.90	$4.06x10^{-2}$	$1.264x10^{-4}$		
0.087	TS_{110}	4.49	$2.93x10^{-2}$	$2.303x10^{-4}$	$2.346x10^{-4}$	-3.63
	TS_{111}	7.82	$9.23x10^{-3}$	$2.384x10^{-4}$		
	TS_{112}	7.82	$9.23x10^{-3}$	$2.352x10^{-4}$		
0.152	TS_{115}	3.41	$4.22x10^{-2}$	$3.407x10^{-4}$	$3.385x10^{-4}$	-3.47
	TS_{116}	3.41	$4.22x10^{-2}$	$3.362x10^{-4}$		
0.215	TS_{117}	3.41	$4.01x10^{-2}$	$3.910x10^{-4}$	$3.893x10^{-4}$	-3.41
	TS_{119}	3.92	$3.03x10^{-2}$	$3.867x10^{-4}$		
	TS_{120}	3.92	$3.03x10^{-2}$	$3.901x10^{-4}$		

Table 4.34 Calculated Values of Sulphur Capacity of Ternary $CaO-Na_2O-SiO_2$ System having $N_{Na_2O}/N_{SiO_2} = 0.40$ at 1523 °K

Slag Composition N_{CaO}	Sample Number	p_{O_2} $(\times 10^{10})$	p_{S_2}	C_s	Av C_s	Log Av C_s
0.044	TS_{121}	7.23	7.2×10^{-2}	1.563×10^{-4}	1.508×10^{-4}	-3.82
	TS_{122}	7.23	7.2×10^{-2}	1.493×10^{-4}		
	TS_{123}	7.91	5.47×10^{-2}	1.467×10^{-4}		
0.087	TS_{124}	7.91	5.47×10^{-2}	2.646×10^{-4}	2.632×10^{-4}	-3.58
	TS_{125}	9.06	4.37×10^{-2}	2.635×10^{-4}		
	TS_{127}	9.47	4.00×10^{-2}	2.616×10^{-4}		
0.152	TS_{129}	10.4	3.81×10^{-2}	3.916×10^{-4}	3.889×10^{-4}	-3.41
	TS_{130}	10.4	3.81×10^{-2}	3.866×10^{-4}		
	TS_{131}	7.91	5.74×10^{-2}	3.886×10^{-4}		
0.215	TS_{133}	9.47	4.39×10^{-2}	4.568×10^{-4}	4.575×10^{-4}	-3.34
	TS_{135}	9.47	4.39×10^{-2}	4.582×10^{-4}		

Table 4.35 Calculated Values of Sulphur Capacity of Ternary $CaO-Na_2O-SiO_2$ System having $N_{Na_2O}/N_{SiO_2} = 0.40$ at 1573°K

Slag Composition N_{CaO}	Sample Number	p_{O_2} $(x10^{10})$	p_{S_2}	C_s	Av C_s	Log Av.C_s
0.044	TS_{136}	32.2	$2.56x10^{-2}$	$1.763x10^{-4}$	$1.738x10^{-4}$	-3.76
	TS_{137}	40.0	$1.81x10^{-2}$	$1.735x10^{-4}$		
	TS_{138}	40.0	$1.81x10^{-2}$	$1.716x10^{-4}$		
0.087	TS_{140}	41.7	$1.66x10^{-2}$	$3.017x10^{-4}$	$2.955x10^{-4}$	-3.53
	TS_{142}	41.7	$1.66x10^{-2}$	$2.892x10^{-4}$		
0.152	TS_{145}	45.4	$1.23x10^{-2}$	$4.514x10^{-4}$	$4.472x10^{-4}$	-3.35
	TS_{146}	45.4	$1.23x10^{-2}$	$4.441x10^{-4}$		
	TS_{148}	49.5	$1.13x10^{-2}$	$4.461x10^{-4}$		
0.215	TS_{150}	58.7	$8.05x10^{-3}$	$5.277x10^{-4}$	$5.285x10^{-4}$	-3.28
	TS_{151}	76.0	$4.40x10^{-3}$	$5.191x10^{-4}$		
	TS_{152}	76.0	$4.40x10^{-3}$	$5.388x10^{-4}$		

Table 4.36- Calculated Values of Sulphur Capacity of Ternary CaO-Na_2O-SiO_2 system having N_{Na_2O}/N_{SiO_2} = 0.52 at 1373°K

Slag Composition N_{CaO}	Sample Number	p_{O_2} ($\times 10^{10}$)	p_{S_2}	C_s	Av C_s	Log AvC_s
0.055	TS_{153}	1.10	8.09×10^{-3}	2.017×10^{-4}	1.973×10^{-4}	-3.70
	TS_{154}	1.27	4.49×10^{-3}	1.917×10^{-4}		
	TS_{156}	1.68	2.22×10^{-3}	1.984×10^{-4}		
0.108	TS_{158}	2.13	1.67×10^{-3}	4.036×10^{-4}	3.982×10^{-4}	-3.40
	TS_{159}	2.70	1.09×10^{-3}	3.927×10^{-4}		

Table 4.37 Calculated Values of Sulphur Capacity of Ternary $CaO-Na_2O-SiO_2$ System having $N_{Na_2O}/N_{SiO_2} = 0.52$ at 1423 °K

Slag Composition N_{CaO}	Sample Number	p_{O_2} ($\times 10^{10}$)	p_{S_2}	C_s	Av C_s	Log Av C_s
0.055	TS_{163}	2.24	1.67×10^{-2}	2.131×10^{-4}		
	TS_{165}	2.82	7.71×10^{-3}	2.199×10^{-4}	2.189×10^{-4}	-3.66
	TS_{166}	2.82	7.71×10^{-3}	2.238×10^{-4}		
0.108	TS_{168}	4.26	3.89×10^{-3}	4.798×10^{-4}		
	TS_{170}	5.12	3.48×10^{-3}	4.756×10^{-4}	4.785×10^{-4}	-3.32
	TS_{171}	5.12	3.20×10^{-3}	4.800×10^{-4}		

Table 4.38 **Calculated** Values of Sulphur Capacity of Ternary $CaO-Na_2O-SiO_2$ System having $N_{Na_2O}/N_{SiO_2} = 0.52$ at 1473 °K

Slag Composition N_{CaO}	Sample Number	p_{O_2} $(x10^{10})$	p_{S_2}	C_s	Av. C_s	LogAvC_s
0.055	TS_{173}	4.10	$3.51x10^{-2}$	$2.464x10^{-4}$	$2.40x10^{-4}$	-3.62
	TS_{174}	4.10	$3.51x10^{-2}$	$2.389x10^{-4}$		
	TS_{176}	4.86	$2.73x10^{-2}$	$2.348x10^{-4}$		
0.108	TS_{177}	5.76	$1.86x10^{-2}$	$5.684x10^{-4}$	$5.625x10^{-4}$	-3.25
	TS_{179}	5.76	$2.20x10^{-2}$	$5.566x10^{-4}$		
0.173	TS_{181}	6.82	$1.16x10^{-2}$	$6.983x10^{-4}$	$6.912x10^{-4}$	-3.16
	TS_{182}	6.82	$1.16x10^{-2}$	$6.886x10^{-4}$		
	TS_{183}	7.76	$1.07x10^{-2}$	$6.867x10^{-4}$		

Table 4.39- Calculated Values of Sulphur Capacity of Ternary $CaO-Na_2O-SiO_2$ system having $N_{Na_2O}/N_{SiO_2} = 0.52$ at 1523 °K

Slag Composition N_{CaO}	Sample Number	p_{O_2} $(x10^{10})$	p_{S_2}	C_s	Av.Cs	LogAv C_s
0.055	TS_{185}	8.71	$4.29x10^{-2}$	$3.206x10^{-4}$	$3.164x10^{-4}$	-3.50
	TS_{186}	8.71	$4.29x10^{-2}$	$3.121x10^{-4}$		
0.108	TS_{189}	9.47	$3.82x10^{-2}$	$6.408x10^{-4}$	$6.343x10^{-4}$	-3.20
	TS_{190}	9.47	$3.82x10^{-2}$	$6.314x10^{-4}$		
	TS_{192}	9.89	$3.84x10^{-2}$	$6.307x10^{-4}$		
0.173	TS_{193}	11.20	$2.60x10^{-2}$	$7.617x10^{-4}$	$7.582x10^{-4}$	-3.12
	TS_{194}	11.20	$2.60x10^{-2}$	$7.555x10^{-4}$		
	TS_{195}	11.20	$3.14x10^{-2}$	$7.573x10^{-4}$		

Table 4.40- Calculated Values of Sulphur Capacity of Ternary CaO-Na_2O-SiO_2 System having $N_{Na_2O}/N_{SiO_2} = 0.52$ at 1573 °K

Slag Composition N_{CaO}	Sample Number	p_{O_2} ($\times 10^{10}$)	p_{S_2}	C_s	Av. C_s	Log Av C_s
0.055	TS_{197}	21.2	4.47×10^{-2}	3.506×10^{-4}	3.467×10^{-4}	-3.46
	TS_{199}	21.2	4.03×10^{-2}	3.417×10^{-4}		
	TS_{200}	21.2	4.03×10^{-2}	3.486×10^{-4}		
0.108	TS_{201}	24.0	3.49×10^{-2}	7.316×10^{-4}	7.254×10^{-4}	-3.14
	TS_{202}	24.0	3.49×10^{-2}	7.211×10^{-4}		
	TS_{205}	41.0	1.20×10^{-2}	7.190×10^{-4}		
0.173	TS_{207}	54.8	8.10×10^{-3}	9.048×10^{-4}	8.878×10^{-4}	-3.05
	TS_{208}	54.8	8.10×10^{-3}	8.883×10^{-4}		
	TS_{209}	62.0	7.37×10^{-3}	8.704×10^{-4}		

Table 4.41 Calculated Values of Sulphur Capacity of Ternary $CaO-Na_2O-SiO_2$ System having $N_{Na_2O}/N_{SiO_2} = 0.84$ at 1373°K

Slag Composition N_{CaO}	Sample Number	p_{O_2} ($\times10^{10}$)	p_{S_2}	C_s	Av. C_s	Log Av. C_s
0.064	TS_{211}	6.26	1.60×10^{-4}	6.508×10^{-4}		
	TS_{213}	6.26	2.50×10^{-4}	6.361×10^{-4}	6.458×10^{-4}	-3.19
	TS_{214}	6.26	2.50×10^{-4}	6.504×10^{-4}		

Table 4.42 Calculated Values of Sulphur Capacity of Ternary $CaO-Na_2O-SiO_2$ System having $N_{Na_2O}/N_{SiO_2} = 0.84$ at 1423 °K

Slag Composition N_{CaO}	Sample Number	p_{O_2} ($\times 10^{10}$)	p_{S_2}	C_s	Av C_s	Log Av C_s
0.064	TS_{215}	7.82	1.26×10^{-3}	9.532×10^{-4}	9.34×10^{-4}	-3.03
	TS_{216}	7.82	1.26×10^{-3}	9.217×10^{-4}		
	TS_{217}	9.35	7.35×10^{-4}	9.271×10^{-4}		
0.129	TS_{218}	9.35	1.05×10^{-3}	1.934×10^{-3}	2.164×10^{-3}	-2.66
	TS_{219}	10.20	5.61×10^{-4}	2.265×10^{-3}		
	TS_{220}	10.20	5.61×10^{-4}	2.292×10^{-3}		

Table 4.43 Calculated Values of Sulphur Capacity of ternary CaO-Na_2O-SiO_2 System having $N_{Na_2O}/N_{SiO_2} = 0.84$ at 1473°K

Slag Composition N_{CaO}	Sample Number	p_{O_2} $(\times 10^{10})$	p_{S_2}	C_s	Av C_s	Log Av C_s
0.064	TS_{221}	8.91	6.79×10^{-3}	1.112×10^{-3}	1.0×10^{-3}	-3.00
	TS_{223}	8.91	5.88×10^{-3}	0.887×10^{-3}		
0.129	TS_{224}	10.16	4.08×10^{-3}	2.799×10^{-3}	2.722×10^{-3}	-2.57
	TS_{225}	11.15	3.53×10^{-3}	2.692×10^{-3}		
	TS_{226}	11.5	3.53×10^{-3}	2.675×10^{-3}		
0.235	TS_{229}	21.0	1.06×10^{-3}	4.603×10^{-3}	4.568×10^{-3}	-2.34
	TS_{230}	21.0	1.06×10^{-3}	4.532×10^{-3}		

Table 4.44 Calculated Values of Sulphur Capacity of Ternary $CaO-Na_2O-SiO_2$ System having $N_{Na_2O}/N_{SiO_2} = 0.84$ at 1523 °K

Slag Composition, N_{CaO}	Sample Number	p_{O_2} $(x10^{10})$	p_{S_2}	C_s	Av C_s	Log Av C_s
0.064	TS_{231}	34.2	$2.78x10^{-3}$	$1.287x10^{-3}$	$1.203x10^{-3}$	-2.92
	TS_{232}	34.2	$2.78x10^{-3}$	$1.198x10^{-3}$		
	TS_{233}	34.2	$2.132x10^{-3}$	$1.123x10^{-3}$		
0.129	TS_{236}	42.0	$1.41x10^{-3}$	$3.400x10^{-3}$	$3.386x10^{-3}$	-2.47
	TS_{237}	42.0	$2.04x10^{-3}$	$3.358x10^{-3}$		
	TS_{238}	42.0	$2.04x10^{-3}$	$3.401x10^{-3}$		
0.235	TS_{239}	54.0	$1.12x10^{-3}$	$5.270x10^{-3}$	$5.237x10^{-3}$	-2.28
	TS_{240}	54.0	$1.12x10^{-3}$	$5.204x10^{-3}$		

Table 4.45 Calculated Values of Sulphur Capacity of Ternary $CaO-Na_2O-SiO_2$ System having $N_{Na_2O}/N_{SiO_2} = 0.84$ at 1573 °K

Slag Composition N_{CaO}	Sample Number	p_{O_2} $(x10^{10})$	p_{S_2}	C_s	Av C_s	Log Av C_s
0.064	TS_{243}	35.2	$1.24x10^{-2}$	$1.609x10^{-3}$	$1.584x10^{-3}$	-2.80
	TS_{244}	35.2	$1.24x10^{-2}$	$1.561x10^{-3}$		
	TS_{246}	44.8	$7.66x10^{-3}$	$1.583x10^{-3}$		
0.129	TS_{247}	52.6	$7.26x10^{-3}$	$3.686x10^{-3}$	$3.635x10^{-3}$	-2.44
	TS_{248}	52.6	$7.26x10^{-3}$	$3.583x10^{-3}$		
0.235	TS_{251}	64.4	$3.71x10^{-3}$	$5.916x10^{-3}$	$5.893x10^{-3}$	-2.23
	TS_{253}	69.8	$4.12x10^{-3}$	$5.870x10^{-3}$		

Table 4.46 Calculated Values of Sulphur Capacity of Ternary $CaO-Na_2O-SiO_2$ System having $N_{Na_2O}/N_{SiO_2} = 1.03$ at 1373 °K

Slag Composition	Sample Number	p_{O_2} (x10^{10})	p_{S_2}	C_s	Av C_s	Log Av C_s
0.076	TS_{255}	5.40	2.48×10^{-4}	1.296×10^{-3}	1.319×10^{-3}	-2.88
	TS_{256}	5.40	2.48×10^{-4}	1.327×10^{-3}		
	TS_{257}	6.16	1.65×10^{-4}	1.333×10^{-3}		
0.150	TS_{259}	7.66	9.64×10^{-5}	2.512×10^{-3}	2.399×10^{-3}	-2.62
	TS_{260}	7.66	9.64×10^{-5}	2.323×10^{-3}		
	TS_{262}	8.36	9.42×10^{-5}	2.362×10^{-3}		

Table 4.47 Calculated Values of Sulphur Capacity of Ternary $CaO-Na_2O-SiO_2$ System having $N_{Na_2O}/N_{SiO_2} = 1.03$ at 1423 °K

Slag Composition N_{CaO}	Sample Number	p_{O_2} $(x10^{10})$	p_{S_2}	C_s	Av C_s	Log Av C_s
0.076	TS_{263}	7.16	$1.14x10^{-3}$	$1.609x10^{-3}$	$1.583x10^{-3}$	-2.80
	TS_{264}	7.16	$1.14x10^{-3}$	$1.569x10^{-3}$		
	TS_{265}	7.16	$1.44x10^{-3}$	$1.544x10^{-3}$		
	TS_{266}	7.16	$1.44x10^{-3}$	$1.608x10^{-3}$		
0.150	TS_{269}	8.95	$9.22x10^{-4}$	$2.906x10^{-3}$	$2.814x10^{-3}$	-2.55
	TS_{270}	8.95	$9.22x10^{-4}$	$2.788x10^{-3}$		
	TS_{271}	10.20	$6.18x10^{-4}$	$2.749x10^{-3}$		

Table 4·48 Calculated values of Sulphur Capacity of Ternary $CaO-Na_2O-SiO_2$ System having $N_{Na_2O}/N_{SiO_2} = 1{\cdot}03$ at 1473 °K

Slag Composition N_{CaO}	Sample Number	p_{O_2} $(\times10^{10})$	p_{S_2}	C_s	Av. C_s	Log Av. C_s
0·076	TS_{272}	40·6	$3{\cdot}27\times10^{-4}$	$1{\cdot}712\times10^{-3}$	$1{\cdot}739\times10^{-3}$	-2·76
	TS_{273}	44·2	$2{\cdot}39\times10^{-4}$	$1{\cdot}780\times10^{-3}$		
	TS_{274}	44·2	$2{\cdot}39\times10^{-4}$	$1{\cdot}724\times10^{-3}$		
0·150	TS_{275}	52·4	$1{\cdot}78\times10^{-4}$	$4{\cdot}330\times10^{-3}$	$4{\cdot}273\times10^{-3}$	-2·37
	TS_{277}	52·4	$2{\cdot}44\times10^{-4}$	$4{\cdot}217\times10^{-3}$		

Table 4.49 Calculated Values of Sulphur Capacity of Ternary $CaO-Na_2O-SiO_2$ system having $N_{Na_2O}/N_{SiO_2} = 1.03$ at 1523 °K

Slag Composition	Sample Number	p_{O_2} $(\times 10^{10})$	p_{S_2}	C_s	Av C_s	Log Av C_s
0.076	TS_{279}	48.0	1.41×10^{-3}	2.048×10^{-3}	2.000×10^{-3}	-2.70
	TS_{280}	48.0	1.41×10^{-3}	1.919×10^{-3}		
	TS_{282}	48.0	1.21×10^{-3}	2.032×10^{-3}		
~~0.150~~	TS_{283}	~~68.0~~	~~5.39×10^{-4}~~	4.973×10^{-3}	4.888×10^{-3}	-2.31
	TS_{285}	81.0	5.22×10^{-4}	4.806×10^{-3}		
	TS_{286}	81.0	5.22×10^{-4}	4.885×10^{-3}		

Table 4.50 Calculated Values of Sulphur Capacity of Ternary $CaO-Na_2O-SiO_2$ System having $N_{Na_2O}/N_{SiO_2} = 1.03$ at 1573 °K

Slag Composition N_{CaO}	Sample Number	p_{O_2} ($\times 10^{10}$)	p_{S_2}	C_s	Av C_s	Log Av C_s
0.076	TS_{287}	52.4	7.32×10^{-3}	2.411×10^{-3}	2.399×10^{-3}	-2.62
	TS_{289}	59.6	6.53×10^{-3}	2.322×10^{-3}		
	TS_{290}	59.6	6.53×10^{-3}	2.465×10^{-3}		
0.150	TS_{293}	80.2	3.12×10^{-3}	5.275×10^{-3}	5.247×10^{-3}	-2.28
	TS_{295}	95.0	2.01×10^{-3}	5.218×10^{-3}		

CHAPTER - 5

SUMMARY AND CONCLUSIONS

In this chapter the experimental results on sulphur capacity of soda base binary and ternary slag systems have been summarised and concluded.

5.1 SUMMARY

Sulphur capacities of binary soda-silica slags having molar ratios, 0.26, 0.40, 0.52, 0.84 and 1.03 at temperatures, 1373, 1473 and 1573 K are presented in table 5.1 whereas, those for ternary lime soda-silica slags having Na_2O/SiO_2 molar ratios 0.26, 0.52 and 1.03 at above stated temperatures are in table 5.2.

5.2 CONCLUSIONS

On the basis of the analysis of the present data, the conclusions drawn for binary and ternary slag systems are enumerated as follows.

5.2.1 Binary Soda-Silica Slag

(i) Logarithm of sulphur capacity varied linearly with N_{Na_2O}/N_{SiO_2} ratio at all temperatures of investigation. A relationship between log C_S and molar ratio of Na_2O/SiO_2 at 1473 is expressed as,

$$\log C_S = -1.314(N_{Na_2O}/N_{SiO_2}) + 4894 \qquad \ldots (5.1)$$

value of $d(\log C_S)/d(N_{Na_2O}/N_{SiO_2})$ is practically identical, however, log C_S increases with temperature.

(ii) Variation of logarithmic sulphur capacity with reciprocal of absolute temperature is linear and is expressed in the following form,

$$\log C_S = \frac{3647.06}{T} + 1.776 \qquad \ldots (5.2)$$

at $N_{Na_2O}/N_{SiO_2} = 0.5$. Plots for all molar ratio are parallel.

(iii) Sulphur capacity of soda-silica system lies in between those of $CaO-SiO_2$ and $CaO-CaF_2$.

5.2.2 Ternary Lime-Soda-Silica System

(i) With lime additions there is sharp initial increase in sulphur capacity which is less pronounced afterwards upto around 25 mole per cent of lime.

(ii) At constant lime concentrations, sulphur capacity increased with N_{Na_2O}/N_{SiO_2} ratio.

(iii) At constant silica levels, sulphur capacity decreased with decreased lime concentrations.

(iv) Iso-sulphur capacity contours showed higher logarithmic sulphur capacity values away from silica end.

(v) Empirical equivalence between lime and soda has been established. A representative relationship at 1573 between log C_S and mole fractions of lime, soda and silica, is found to be as,

$$\log C_S = \frac{(1.715 N_{Na_2O} + 1.163\, N_{CaO} - 4.493 N_{SiO_2})}{N_{SiO_2}} \qquad \ldots (5.3)$$

(vi) Temperature has been found to cause a significant positive effect on sulphur capacities.

Table 5·1- Sulphur Capacity of Binary Soda-Silica Slags

Temperature	Sulphur Capacity x 10^5				
	Na_2O/SiO_2 molar ratio				
	0·26	0·40	0·52	0·84	1·03
1373 K	-	2·620	4·275	10·22	17·76
1473 K	2·809	4·464	5·782	16·22	25·67
1573 K	3·894	5·507	7·767	22·9	37·18

Table 5.2 Sulphur Capacity of Ternary Lime-Soda Silica Slags

Temperature	Sulphur Capacity x 10^5								
	Slag Composition								
	$Na_2O/SiO_2 = 0.26$				$Na_2O/SiO_2 = 0.52$			$Na_2O/SiO_2 = 1.03$	
	N_{CaO}				N_{CaO}			N_{CaO}	
	0.033	0.066	0.109	0.173	0.055	0.108	0.173	0.076	0.150
1373K	3.981	6.918	10.23	12.88	19.5	39.81	-	131.8	240.0
1473	5.888	10.23	15.85	19.05	24.0	56.23	69.18	173.8	426.6
1573	7.943	13.18	20.42	26.92	34.67	72.44	89.13	239.9	524.8

SUGGESTIONS FOR FUTURE RESEARCH PROGRAMMES

1. Experimental studies may be carried out to determine sulphur capacity of soda-alumina, soda-sillimanite systems also, as alumina is an important constituent of slags.

2. Other alkali based systems e.g. potassium **oxide** lithium oxide in combinations with silica and alumina could be the subject of interest in the field of desulphurisation as they are likely to perform better in refining owing to their lower enthalpy values for silicate formation, lower activation energy requirements for ionic conduction and lower ion oxygen attraction in comparison to other basic oxides.

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