THERMODYNAMICS OF DILUTE SOLUTION OF SULPHUR IN MULTICOMPONENT MOLTEN ALLOY SYSTEMS

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BY

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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled, 'THERMODYNAMICS OF DILUTE SOLUTION OF SULPHUR IN MULTICOMPONENT MOLTEN ALLOY SYSTEMS' 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 July, 1975 to February, 1981 under the supervision of Dr. M.L. Kapoor, Professor of Extractive Metallurgy and Head of the Department.

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

(Girish Chandra Kaushal)
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This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

Date: February 12 , 1981.

(Dr. M.L. Kapoor)
Signature of Supervisor

ABSTRACT

Studies on the properties of pure sulphides, interactions between different sulphides or the different gas-sulphide or liquid-sulphide systems and also the behaviour of sulphur in molten as well as solid metals and alloys have been, for a long time, of particular concern to the geologists, chemists, metallurgists and material scientists for a better understanding of the formation and characteristics of mineral deposits, extraction and refining of pure metalsfrom sulphur-bearing raw-materials and development of new metallic materials for specific applications. A critical study of the published work indicated that although extensive work has been done on the properties of pure sulphides and their mixtures,yet only few studies have been conducted on the behaviour of sulphur in the dilute solution range. Here again most of the work reported has been carried out on the behaviour of sulphur in ferrous-systems only. Thus little is known on the behaviour of sulphur in non-ferrous metals and their alloys, although many important metals of this group are recovered from their sulphide deposits occurring in nature.

The present work has, therefore, been taken up to systematically study the behaviour of sulphur in non-ferrous metallic systems. Three pure metals namely lead, silver and copper and their binary and ternary alloys of different compositions have been used for the experimental studies at

different temperatures for dissolution of sulphur from the gaseous phase of known sulphur potentials in equilibrium with the molten metallic solvents. Further, for a quantitative interpretation of the experimental data so obtained, several statistical thermodynamic solution models based on free-volume theory have been developed. The entire work reported in this dissertation has been spread over five chapters.

Chapter-I deals with the review of the available literature on different studies made on sulphide systems and methods employed for this purpose, different theoretical thermodynamic models developed to interpret properties of actual solutions and finally the formulation of the problem.

Chapter-II describes the experimental set-up, materials and methods used for carrying out the equilibria runs and for chemical analysis for sulphur in the equilibrated metal-alloy samples.

Chapter-III presents the results of experimentation in tabular forms and also the different thermodynamic properties of sulphur computed from these, namely, the equilibrium constants, interaction parameters, free energy, enthalpy and entropy for the dissolution reaction equilibria at different temperatures for pure metallic solvents and their binary and ternary alloys of different compositions. The results obtained in the present work have also been compared with the available data obtained by others workers.

In Chapter-IV, for interpretation of the experimental data, presented in Chapter-III, eight different thermodynamic models for multicomponent substitutional solutions have been developed based on free volume theory and different simplifying assumptions. Expressions for the free energy of dissolution of sulphur in binary, ternary and multicomponent solvents have been derived assuming linear and non-linear forms of energy and free volume and also preferential and random distribution of solute and solvent atoms. Calculated values of the thermodynamic parameters, based on the different expressions derived, have been plotted and compared with the experimental values to ascertain and establish the applicability of the theoretical solution models developed.

Chapter-V summarizes the different results obtained and conclusions drawn from the present work.

Finally, suggestions for further work in this direction have been incorporated.

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Kaushal

Roorkee
February 12 , 1981.

(Girish Chandra Kaushal)

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NOMENCLATURE

$(\text{at.\% S})_A$	atomic percent sulphur dissolved in A.
$(\text{at.\% S})_{(A-B)}$	atomic percent sulphur dissolved in(A-B).
a_S	activity of sulphur in solution with pure hypothetical liquid sulphur as standard state.
E_i	energy of the system in i^{th} state.
E_{max}	value of energy in the maximum term
E_A^o	total energy of all n_A^{ijo} atoms
E_A^1	total energy of all n_A^{kdl} atoms.
E_C^1	total energy of all n_C^{uvl} atoms
E_S	energy of solute (sulphur) atoms.
E	total energy of the system
E_P^o	total energy of all n_P^{xyo} atoms
E_P^1	energy of all n_P^{pql} atoms
E_C^o	total energy of all n_C^{rto} atoms
$f_{S_2}^o$	fugacity of sulphur
$f_{S(x)}$	Henrian activity coefficient of sulphur in x
$f_{S(A-B)}^S$	self-interaction coefficient of sulphur in (A-B)
f_S^B	interaction coefficient of effect of B on sulphur

$\Delta G^o_{HS(x)}$	free-energy for equilibrium reaction H_2S-H_2-$\underline{S}(x)$, where x represents pure metal-lead, silver or copper
$\Delta G^o_{HS(A-B)}$	free-energy for equilibrium reaction H_2S-H_2-$\underline{S}(A-B)$, where (A-B) represents binary alloys of metals-lead, silver and copper.
$\Delta G^o_{HS(A-B-C)}$	free-energy for equilibrium reaction H_2S-H_2-$\underline{S}(A-B-C)$, where (A-B-C) represents ternary alloys of metals-lead, silver and copper.
$\Delta G^o_{S(Pb)}$	free-energy for $\underline{S}(Pb)$-S_2 equilibrium
$\Delta G^o_{S(Ag)}$	free-energy for $\underline{S}(Ag)$-S_2 equilibrium
$\Delta G^o_{S(Cu)}$	free-energy for $\underline{S}(Cu)$-S_2 equilibrium
$\Delta G^o_{S(Pb-Cu)}$	free-energy for $\underline{S}(Pb-Cu)$-S_2 equilibrium
$\Delta G^o_{S(Pb-Ag)}$	free-energy for $\underline{S}(Pb-Ag)$-S_2 equilibrium
$\Delta G^o_{S(Cu-Ag)}$	free-energy for $\underline{S}(Cu-Ag)$-S_2 equilibrium
$\Delta G^o_{S(Pb-Ag-Cu)}$	free-energy for $\underline{S}(Pb-Ag-Cu)$-S_2 equilibrium
$\Delta \bar{G}^{ex,\infty}_{S(A+B)}$	excess partial molar free-energy of sulphur in (A+B) at infinite dilution where A and B are two component metals of the solution
ΔG^o	free-energy for H_2S-H_2 equilibrium reaction
$\Delta G^o_1(T)$	free-energy for S_2-S(l) equilibrium at T^oK
ΔG_2	free-energy for S(l)-$\underline{S}$ equilibrium

ΔG_2^{id}	free-energy for Raoultian behaviour of sulphur in melt.
ΔG_2^{H}	free-energy for S(1)-$\underline{S}$ equilibria for Henrian behaviour
$\Delta\bar{G}^{ex,\infty}_{S(A+P+C)}$	excess partial molar free energy of sulphur in (A+P+C) at infinite dilution.
$\Delta G^{o}_{S(A+P+C)}$	free energy of sulphur at infinite dilution in (A+P+C) determined experimentally
$\Delta G^{ex}_{mix(A+P+C)}$	excess free energy of mixing of solution containing (A+P+C) where A stands for silver, P for lead and C for copper.
$\Delta\bar{G}^{ex,\infty}_{S(A)}$	excess partial molar free energy of sulphur in A, (Silver), at infinite dilution.
$\Delta\bar{G}^{ex,\infty}_{S(P)}$	excess partial molar free-energy of sulphur in P, (lead), at infinite dilution.
$\Delta\bar{G}^{ex,\infty}_{S(C)}$	excess partial molar free-energy of sulphur in C, (copper), at infinite dilution.
$\Delta\bar{G}^{ex}_{A(A+P+C)}$	excess partial molar free-energy of silver in ternary silver-lead-copper alloy
$\Delta\bar{G}^{ex.}_{P(A+P+C)}$	excess partial molar free-energy of lead in ternary silver-lead-copper alloy
$\Delta\bar{G}^{ex.}_{C(A+P+C)}$	excess partial molar free-energy of copper in ternary silver-lead-copper alloy.

g_{max}	number of distinguishable states in the maximum term
$g(E_i)$	number of distinguishable states of the system having same total energy E_i
h_S	Henrian activity of sulphur in solution
$h(n_A, n_P, n_C, n_S)$	normalizing factor
$\Delta H^o_{S(Pb-Ag)}$	enthalpy of reaction equilibria $\underline{S}(Pb-Ag)-S_2$
$\Delta H^o_{S(Pb-Cu)}$	enthalpy of reaction equilibria $\underline{S}(Pb-Cu)-S_2$
$\Delta H^o_{S(Ag-Cu)}$	enthalpy of reaction equilibria $\underline{S}(Ag-Cu)-S_2$
K_A, K_P, K_C	functions as defined by equations (IV.202a), (IV.202b) and (IV.202c) respectively or equations (IV.164), (IV.165), and (IV.166) respectively
k	Boltzmann constant
K	equilibrium constant
K_{HS}	equilibrium constant of $H_2-H_2S-\underline{S}$ equilibrium
$K_{S(Pb)}$	equilibrium constant for $\underline{S}(Pb)-S_2$ equilibrium reaction
$K_{S(Ag)}$	equilibrium constant for $\underline{S}(Ag)-S_2$ equilibrium reaction
$K_{S(Cu)}$	equilibrium constant for $\underline{S}(Cu)-S_2$ equilibrium reaction
$K_{HS(Pb-Ag)}$	equilibrium constant for $H_2S-H_2-\underline{S}(Pb-Ag)$ equilibria.

$K_{HS(Pb-Cu)}$	equilibrium constant for $H_2S-H_2-\underline{S}(Pb-Cu)$ equilibria
$K_{HS(Ag-Cu)}$	equilibrium constant for $H_2S-H_2-\underline{S}(Ag-Cu)$ equilibria
$K_{HS(Pb-Cu-Ag)}$	equilibrium constant for reaction equilibria $\underline{S}(Pb-Cu-Ag)-H_2S-H_2$
$K_{HS(A-B-C)}$	equilibrium constant for reaction equilibria $\underline{S}(A-B-C)-H_2S-H_2$
$\ln \alpha_A, \ln\alpha_P,$ $\ln\alpha_C, \ln\alpha_S$	lagrangian multipliers
$\ln K_{HS(A-B)}$	logarithm of equilibrium constant for $H_2S-H_2-\underline{S}(A-B)$ equilibria where A-B stands for a binary alloy of A and B
$\ln K_{HS(A)}$	logarithm of equilibrium constant for H_2S-H_2-A equilibria where A is a pure metallic solvent
n_A^{ijo}	number of atoms of Ag having i atoms of Pb and j atoms of Cu in first coordination shell.
n_A^{kdl}	number of atoms of Ag having k atoms of Pb , d atoms of Cu and one atom of sulphur in the first coordination shell.
n_P^{pql}	number of atoms of Pb having p atoms of Cu, q atoms of Ag and one atom of S in the first coordination shell.

n_P^{xyo}	number of lead atoms having x copper atoms, y silver atoms and no sulphur atom in their first coordination shell.
n_C^{rto}	number of Cu atoms having r-Ag atoms, t-Pb atoms and no S atom in their first coordination shell.
n_C^{uvl}	number of Cu atoms having u-Ag atoms, v-Pb atoms and no S atom in their first coordination shell.
n_A^{*ijo}	number of Ag atoms having i-Pb atoms,j-Cu atoms and no S atom around them-all randomly distributed.
n_A^{*kdl}	number of Ag atoms having k atoms of Pb and d atoms of Cu and one atom of sulphur-all randomly distributed
n_P^{*xyo}	number of Pb atoms having x-Cu atoms, y-Ag atoms and no S atom in the first coordination shell-all randomly distributed.
n_P^{*pql}	number of Pb atoms having p-Cu atoms, q-Ag atoms and one S atom in the first coordination shell-all randomly distributed
n_C^{*rto}	number of Cu atoms having r-Ag atoms, t-Pb atoms and no S atom in the first coordination shell-all randomly distributed
n_C^{*uvl}	number of Cu atoms having u-Ag atoms, v-Pb atoms and one S atom in the first coordination shell - all randomly distributed

n_S^{*mw}	number of S atoms having m-Ag atoms, s-Pb atoms and rest Cu-atoms in the first coordination shell-all randomly distributed.
n_S^{mw}	number of S atoms having m-Ag atoms and w-Pb atoms in their first coordination shell.
n_A^o	total number of n_A^{ijo} atoms
n_A^l	total number of n_A^{kdl} atoms
N_S^{id}	mole fraction of S in melt for Raoultian standard state
N_S^H	mole fraction of S in melt with resepect to infinite dilution (Henrian behaviour)
n_x	number of atoms of any component x
n_A	number of atoms of Ag or component A
n_P	number of atoms of Pb
n_C	number of atoms of Cu
n_S	number of atoms of S
N	Avogadro's number
N_A^1	a function defined as $N_A^1 = \frac{n_A^1}{zn_S}$
N_P^1	a function defined as $N_P^1 = \frac{n_P^1}{zn_S}$
N_C^1	a function defined as $N_C^1 = \frac{n_C^1}{zn_C}$
N_A	atom fraction of component Ag or component A

N_P	atom fraction of component Pb
N_C	atom fraction of component Cu
n_A^{*1}	number of Ag atoms having one S atom in the first coordination shell-all randomly distributed.
n_P^{*1}	number of Pb atoms having one S atom in the first coordination shell-all randomly distributed.
n_C^{*1}	number of Cu atoms having one S atom in the first coordination shell-all randomly distributed.
n_A^{*o}	number of Ag atoms having no S atom in the first coordination shell-all randomly distributed.
n_P^{*o}	number of Pb atoms having no S atom in the first coordination shell-all randomly distributed.
n_C^{*o}	number of Cu atoms having no S atoms in the first coordination shell-all randomly distributed.
n_C^1	total number of n_C^{uv1} atoms
n_C^o	total number of n_C^{rto} atoms
n_P^1	total number of n_P^{pq1} atoms
n_P^o	total number of n_P^{xyo} atoms
p_{S_2}	partial pressure of sulphur
R	universal gas constant
$\underline{S}$	sulphur dissolved in solution
$\underline{S}(i)$	sulphur dissolved in 'i', where i may be Pb, Cu or Ag or their binary or ternary alloys

$S(l)$	pure liquid sulphur
S_2	pure gaseous sulphur
$\Delta S^{o}_{S(A-B)}$	entropy of reaction equilibria $\underline{S}(A-B) = S_2$ where (A-B) stands for binary alloys Pb-Cu, Pb-Ag or Ag-Cu.
T	temperature in °K
v_i	free-volume of i^{th} atom
v_A^{ijo}	free-volume of Ag atoms having i-Pb atoms, j-Cu atoms and no S atom in their first coordination shell
v_A^{kdl}	free-volume of Ag atoms having k-Pb atoms, d-Cu atoms and one S atom in their first coordination shell
v_P^{xyo}	free-volume of Pb atoms having x-Cu atoms, y-Ag atoms and no S atom in their first coordination shell
v_P^{pql}	free-volume of Pb atoms having p-Cu atoms, q-Ag atoms and one S atom in their first coordination shell
v_C^{rto}	free-volume of Cu atoms having r-Ag atoms, t-Pb atoms and no S atom in their first coordination shell
v_C^{uvl}	free-volume of Cu atoms having u-Ag atoms, v-Pb atoms and one S atom in their first coordination shell

v_S^{mw}	free-volume of S atoms having m-Ag atoms, w-Pb atoms and rest Cu-atoms in their first coordination shell
W_A^{ijo}	energy of n_A^{ijo} atoms
W_A^{kdl}	energy of n_A^{kdl} atoms
W_C^{uvl}	energy of n_C^{uvl} atoms
W_C^{rto}	energy of n_C^{rto} atoms
W_P^{xyo}	energy of n_P^{xyo} atoms
W_P^{pql}	energy of n_P^{pql} atoms
W_S^{mw}	energy of n_S^{mw} atoms
z	coordination number
ε_S^S	self-interaction parameter of S
ε_S^B	interaction parameter for effect of B on S.
$\varepsilon_{S(j)}^i$	interaction parameter for effect of 'i' on sulphur in component 'j' where 'i' and 'j' stand for metals Pb, Ag or Cu.
$\varepsilon_{S(A-B)}^S$	self-interaction parameter of sulphur in binary alloy (A-B)
$\varepsilon_{S(A-B-C)}^S$	self-interaction parameter of sulphur in ternary alloy (A-B-C).
γ^o	Henry's law constant
μ_S	chemical potential of sulphur

Ω	configurational partition function
Ξ	semi-grand partition function
$\pi_1, \pi_2, \pi_3,$ π_4, π_5, π_6	lagrangian multipliers

CHAPTER - I

GENERAL

I.1 Introduction

Sulphur has been considered to be an element of great significance by metallurgists and material scientists for a long time. It generally tends to seggregate in the metallic systems, invariably along the grain boundaries when present in concentrations in excess of the solubility limits in the parent phase or phases present. Thus, as a general rule, its effects on the physical, mechanical and other engineering properties of metals and alloys are undesirable. Some of its deleterious effects include introduction of hot shortness, increase in hardness, electrical resistance and reduction in ductility, toughness, electrical conductivity, corrosion resistance etc., of both ferrous and non-ferrous metallic materials. However, in one case, this seggregation is advantageously used e.g. in the production of alloys with high machinability such as free machining steels, brasses etc.

Because of the adverse effects of sulphur, on properties of materials, from the view point of alloy development or development of new metallic materials suitable for specific service requirements and production of high-purity metals from their primary sources (e.g. ores, minerals, marine water or sediments etc.) or secondary sources (viz. scrap, slags, fumes etc.), metallurgists and other scientists have concentrated their efforts to minimise the contents of this harmful element in the metallic materials and hence have conducted several studies on systems containing this element in past few years.

The position of sulphur in the Periodic Table, in the sixth group below oxygen, reflects to its chemical reactivity and all naturally occurring ores and minerals especially those of common base metals are of the 'sulphide type' and are invariably associated with a large number of other elements as 'impurity', only a few of which have by-product value. The run of mine (R.O.M.) ore, therefore, contains invariably a large proportion of the country rock and other gangue minerals and hence in the first stage of extraction of metals from these - namely the mineral beneficiation,using differences between the physical or physico-chemical properties of 'values' and the 'gangue', most of the mechanically associated impurities are eliminated. For the second stage, i.e. chemical separation of impurities from the metallic values, generally achieved by simple chemical or electrochemical reduction reactions, any of the three-pyrometallurgical,hydrometallurgical or electrometallurgical paths are adopted. Of the three paths, named above, pyrometallurgical path is commonly adopted one, especially in case of common base metals, because of several technical and economical advantages over other two types, of which high production capacity, productivity and applicability are most significant.

The different unit processes adopted in pyrometallurgical techniques include agglomeration by sintering or pelletization, roasting, calcining, reduction or matte-smelting, converting, fire-refining by preferential oxidation and slagging, or special techniques such as distillation, thermal dissociation, zone refining etc. to obtain high purity metals from their sources. These processes have advantages of improved feasibility and enhanced reaction rates due to higher temperatures used in such chemically reactive systems using, solid, liquid and/or gaseous reactants including charge materials, fuels, fluxes, reductants or oxidising agents etc. Further, such systems involve one or more of the solid-solid, solid-liquid, solid-gas, liquid-liquid, liquid-gas reacting systems. Thus both chemical reactions and diffusion or mass transport rates control the rate and efficiency of the chemical reactions involving condensed phases, whereas in gaseous phase reactions, due to complete mixing, primarily chemical reaction rates control the process. In both cases higher temperatures, used during these processes, favour both the reaction feasibility and kinetics. The ultimate chemical efficiency of the process adopted and purity of the products obtained essentially depend upon the phase-equilibria considerations.

Sulphur may enter the reacting systems in any of these pyrometallurgical operations from various input materials either as sulphide, sulphatic or organic sulphur and is removed invariably either in the slag, fumes, vapours or gases emerging out of the furnaces used for these pyrometallurgical unit-processes as a result of partition between different condensed or gaseous phases present. The residual sulphur in the refined metallic phase is generally present as a dilute solution because of its low concentrations. Importance of physico-chemical properties of sulphur such as its activity in the condensed phases and partial pressure and chemical potential in the gaseous phase, therefore, cannot be over-emphasised for perfecting the processes of extraction and refining and production of high purity metals. Laboratory scale studies on the thermodynamic properties of sulphur in metallic solutions and other metallic systems including studies on metal sulphides, metal-metal sulphide equilibria etc. have therefore, been exclusively conducted using a variety of methods. These will be reviewed in the next section. However, as will be seen in this section, most of these have been restricted in the ferrous systems and only a few are reported on nonferrous metals or metal sulphide systems.

I.2 Literature Survey

Having realised the importance of thermodynamic data on metal-sulphides and sulphur dissolved in metals and alloys both in the solid and liquid states for a better understanding and control of different pyrometallurgical processes and alloy-design especially in the ferrous systems, a large number of thermodynamic studies have been carried out. The different studies made may broadly be classified in the following three categories:

i) Properties of pure metal sulphides.

ii) Studies on metal-metal sulphide equilibria, and,

iii) Properties of dilute solutions of sulphur in metals and alloys.

Extensive reliable thermodynamic data have been obtained, by a large number of investigators, on solid as well as molten metal sulphides on their melting points, boiling points, heats and entropies of fusion, free energies of formation etc. and presented in tabulated and other forms [1,2,3] for ready reference. The existing data is also corrected or replaced by more reliable data as and when obtained by using more accurate modern research techniques.

It has long been felt that the data available on pure sulphides is insufficient to analyse and control smelting of sulphide ores or concentrates because of the presence of several other sulphides in the matte which interact among each other, and also in presence of air or oxygen, with the slag, to obtain the final product. For example, in matte - smelting of chalcopyrite, the roasted charge, fed to the smelting furnace, may contain Cu_2S, FeS, NiS, Ag_2S, Sb_2S_3, As_2S_3 etc., together with some oxides of the impurity metals, and those present in the copper concentrates as the gangue constituents. Therefore, for a better understanding of the physico-chemical principles, governing such smelting and/or converting processes, extensive reliable data on all such systems, analysing also the effects of the interaction of other constituents present in the system, is required.

Schuhmann [4] has reviewed the available thermodynamic data applicable to copper smelting and presented it in a tabulated form. The important gaps in the thermodynamic data have been pointed out for further investigations and experimental research programme proposed to supply the missing data that appear most essential for a better quantitative understanding of physical chemistry of copper smelting. Rosenqvist [5] reviewed the data available on the different phase equilibria that are of importance in the roasting and smelting of certain important sulphide ores. Experimental techniques used to study such systems have also been discussed.

Schuhmann et al [6] have reviewed the available thermodynamic data on Pb-S-O system. Thermodynamic properties of Pb-S liquid solutions have been critically reviewed and a thermodynamic model proposed for a continuous process of converting galena concentrates to a crude lead product.

Friedrich and Leroux [7] carried out thermal and microscopic measurements on Pb-PbS system to determine the liquidus temperatures and compositions and reported that no miscibility gap exists in this system. Melting point of PbS was estimated to be 1103°C. Guertler et al [8] and Leitgebel et al.[9], in their investigations, reported complete miscibility and their data corroborate the earlier work [7]. Miller and Komarek [10] used DTA technique to measure the solubility of PbS in lead, between 10.03 at.% and 50 at.%S, and found no miscibility gap. Kohlmeyer [11] concluded from his investigations that a miscibility gap existed above 1040°C and between 2wt% and 12wt%S. Kullerud [12] claimed immiscibility in the composition range 4.8 wt% and 6.95 wt%S. Measurements by him were made by using DTA and quench test techniques. Recent investigations by Esdaile [13] also suggested the existence of miscibility gap in the temperature range between 1041-1058°C by critically reviewing the data available on Pb-PbS system and carrying out calculations using Margules' equation. Esin and Sryvalin [14] conducted studies on Pb-PbS system by using emf method and claimed immiscibility region in the composition range of 4.0 to 8.5 wt%S. They also determined the activity coefficient of sulphur and lead at 1180°C.

Blank and Willis [15] determined solubility of sulphur in lead in equilibrium with lead sulphide over the comparatively large range of temperature from 427 to 923°C ensuring that equilibrium was approached from both high and low sulphur contents. The equilibrium constant for the reaction,

$$Pb + H_2S = PbS + H_2 \qquad \ldots (I.1)$$

may be expressed as ,

$$\ln K = \frac{664}{T} - 2.59 \qquad \ldots (I.2)$$

Stubbles and Birchenall [16] measured the equilibrium H_2S/H_2 ratio in gaseous mixture under equilibrium with lead-

lead sulphide mixture at temperatures between 585-920°C and arrived at the following expression for the free energy of formation of PbS in the above temperature range,

$$\Delta G^{o} = - 77280 + 41.3\ T \text{ cals} \qquad \ldots (I.3)$$

for the reaction,

$$2Pb(l) + S_2(g) = 2\ PbS \qquad \ldots (I.4)$$

As reported in this investigation, equilibrated lead samples were not analysed for sulphur and only gas-mixture was analysed. Kellog [17] critically reviewed the work by Stubbles and Birchenall [16] and commented upon the straight line correlation of $\log(p_{H_2S}/p_{H_2})$ Vs. $(1/T)$ and further on the calculation of ΔG^{o} and its applicability even when extrapolated to low temperatures (427°C). The results of Blanks and Willis [15] and Stubbles and Birchenall [16] have been found to be in good agreement.

Studies conducted on Pb-PbS system in the liquid region by different investigators show very contradicting results which suggests the necessity of carrying out further work on the system, to obtain concurrent and reliable data.

Ag-Ag_2S portion of the silver-sulphur system has been studied by Rosenqvist [18] and also by Yazawa et al.[19]. Rosenqvist [18] determined the activity of sulphur in Ag-S melts by measuring equilibrium H_2S/H_2 ratio of the gaseous mixture, circulating over the sample, by using buoyancy balance in the temperature range of 400-1300°C; established the phase relationships in the liquid region and showed a big miscibility gap between the silver - rich liquid and sulphur-rich liquid and further used the data obtained for calculating the enthalpy, entropy and free energy changes for the metal-metal sulphide reaction. Yazawa et al. [19] used S_2-N_2 mixtures of known partial pressures of sulphur for attaining Ag-Ag_2S-S_2 equilibria at temperatures 1000 , 1100 and 1200°C, determined the values of activities of silver and silver sulphide and found that a miscibility gap existed in the liquid region as reported by Rosenqvist [18]. Further standard free energy changes for the formation of Ag_2S at 1000°C and 1105°C were calculated and found to be equal to -10410 and - 9480 cal/mole respectively. The results obtained in this study were in agreement with those reported by Rosenqvist [18].

Cox et al. [20] studied the Cu-S equilibria in the liquid region by using different H_2S/H_2 gaseous mixtures in the temperature range of 1150 to 1350°C and used the data obtained to calculate the free energy of formation of Cu_2S. Schuhmann et al. [21] carried out extensive studies on Cu-S system by equilibrating molten Cu_2S with H_2S/H_2 gaseous mixtures at different temperatures. At equilibrium, the relation between temperature and partial pressure of sulphur was found to be as follows;

$$\log p_{S_2} = -\frac{14360}{T} + 3.721 \qquad \ldots \text{(I.5)}$$

for the liquid copper sulphide melts ranging in composition from saturation concentration of copper to about 21.5%S.

Solubility of sulphur in these Cu_2S melts was found to be 19.4, 19.6 and 19.8 wt% respectively at 1150 , 1250 and 1350°C temperatures. The equilibrium partial pressure measurements by Schuhmann et al. [21] for the system containing liquid copper and liquid Cu_2S at different temperatures were represented by the following expression.,

$$\log p_{S_2} = - \frac{15505}{T} + 4.56 \qquad \ldots \quad (I.6)$$

Nagamori et al. [22] determined the equilibrium solubility of sulphur in liquid Cu-S melts to be about 20.34 wt% by equilibrating N_2-S_2 gaseous mixtures with the melts at 1200°C. Johannsen and Vollmer [23] reported 19.52 wt%S solubility for copper saturated compositions of molten copper sulphide at 1200°C. Bourgon et al [24] determined the sulphur content of molten Cu_2S saturated with copper at 1170°C and 1250°C to be 20.75 wt%S and 20.66 wt%S respectively. Bale et al. [25] have carried out an extensive thermodynamic study of Cu-S system and have established phase relationships in the liquid region upto 35 at.%S. Equilibrium p_{S_2} values have also been determined in the copper-rich liquid, in the two-phase region and in the sulphur-rich liquid. A large miscibility gap has been reported. Solubility of sulphur in copper-saturated Cu_2S melt has been reported to be about 19.4wt% at 1200°C. A comparative study of the data obtained by different researchers reveals that the results of Bale et al. [25], Schuhmann et al. [21] and Johannsen et al. [23] are in good agreement, whereas those of Nagamori et al.[22] and

Bourgon et al.[24] are quite close to each other but appreciably different from those of the above mentioned workers.

Hirakoso and Tanaka [26] have studied Cu-S system at three different temperatures viz. 1145 , 1196 and 1247°C by equilibrating copper with H_2S-H_2 gaseous mixture and determined the maximum solubility of sulphur in copper rich liquid respectively as 0.97, 1.06 and 1.22 wt% at above temperatures. Esin et al.[14] carried out investigations to determine the activity coefficient of sulphur in molten Cu-S system at two different temperatures viz. 1200°C and 1300°C in the melts with compositions ranging from 0.0022 to 0.318 atom fraction of sulphur. Values of the activity coefficients of sulphur were determined as 2.0 and 1.3 respectively at these temperatures.

Bale et al. [25] have studied Fe-S system at 1200°C with liquid sulphide and γ-iron in equilibrium with H_2S-H_2 gaseous mixture. Activity of γ-Fe, dissolved in the sulphide melt, was determined and value of the free energy of formation of Fe-S calculated. Cox et al.[20] studied Fe-S system in the temperature range of 770 -1275°C and derived a relationship between partial pressure of sulphur and temperature for the formation of FeS as follows,

$$\log p_{S_2} = -\frac{17810}{T} + 7.51 \qquad \ldots (I.7)$$

Lin et al.[27], determined the activity of sulphur in pyrrhotite by equilibrating it with H_2S-H_2 gaseous mixture at 1073°K.

The results obtained are in good agreement with those of Rosenqvist [28] in the temperature range of 400 - 1200°C.

As Cu-Fe-S system constitutes the matte obtained in copper smelting process, investigations have been carried out by many researchers on this system. Krivsky et al.[29] measured the ratio of H_2S/H_2 in mixtures of these gases in equilibrium with Cu-Fe-S systems of varying compositions at temperatures 1150 , 1250 and 1350°C. From the experimental measurements of activity of sulphur , various other thermodynamic properties of matte were calculated. Activities of the different constituents of the matte viz. Cu_2S and FeS and also of copper and iron were calculated as a function of its composition by using different alternative forms of Gibbs-Duhem equation. Bale et al. [25) studied Cu-Fe-S system at 1200°C at mole fraction ratios, expressed by the parameter , $(\frac{N_{Fe}}{N_{Fe}+N_{Cu}})$, ranging from 0.232 to 0.856. The interpolated values of solubility of sulphur at different values of P_{S_2} compare well with the results of Krivsky et al. [29] who found that the Cu_2S-FeS pseudo-binary system exhibited small negative deviation from ideality.

Yoshiyuki and Tozawa [30] have studied the Cu-Fe-S systems at 1200 and 1250°C for determination of activity of iron as a function of composition and concluded that the sulphur content in the melt decreases with an increase in its iron content at the same sulphur potential of the gaseous phase in equilibrium with the melt. These workers [31] further examined the effect of other elements such as nickel, silver, and tin also on the activity coefficients of sulphur dissolved in copper in equilibrium with the molten Cu_2S, and reported that it increases with an increase in the concentration of above elements in the system. Hagiwara [32] carried out investigations on the reactions between copper and sulphur in lead to study the thermodynamics of refining of pig lead. Removal of copper from lead-copper alloys is one of the important reactions in lead refining from the metallurgical viewpoint [33]. Studies were made to measure the equilibrium constant for the displacement reaction,

$$Cu_2S(s)+Pb(l) = 2\,Cu(\text{in l-Pb})+PbS\,(s) \qquad \ldots (I.8)$$

in the temperature range of 420 to 800°C, under two different conditions, (i) when the two phases of Cu_2S and PbS existed in the melt, for which,

$$\log K = -\frac{2910.4}{T} + 2.28 \qquad \ldots (I.9)$$

and,(ii) when the melt was saturated with Cu_2S and PbS remained in the melt, for which the equilibrium constant was derived as,

$$\log K = -\frac{4442.8}{T} + 3.378 \qquad \ldots (I.10)$$

Wagner and Wagner [34] determined the free energy change for the following displacement reaction,

$$2Cu(s) + PbS(s) = Cu_2S(s) + Pb(s,l) \qquad \ldots (I.11)$$

in the temperature range 250 - 350°C by emf measurements of the following cell,

$$Cu/(CuBr\ /Cu_{1.98}S)/(Cu_{1.98}S,\ PbS)/(PbCl_2{+}1\%\ KCl)/Pb$$

and calculated the value of standard free energy of formation of Cu_2S at 300°C to be equal to - 22607 cal.

Investigations carried out by different researchers to understand the thermodynamics of smelting of copper and lead from their sulphide values are not very systematic and sufficiently detailed, except that by Bale et al. [25] and Schuhmann et al. [21]. The data reported so far on the behaviour of systems involved in copper and lead smelting at the smelting temperatures are quite meagre. Detailed investigations are necessary to obtain more reliable data on such systems.

In recovery of values in a state of high purity, from sulphide ores or concentrates using matte-smelting, converting and/or fire-refining, the sulphur content continuously decreases during processing till the refining stage, when it is present in very small concentrations forming very dilute solutions. A knowledge of the properties of dilute solutions of sulphur is therefore essential for a proper analysis and control of such processes. Also behaviour of sulphur in iron and its alloys in dilute solution range is of great importance for making quality steels, with very low sulphur content. Therefore, for producing ferrous as well as non-ferrous metals and alloys with extra-low sulphur content in the finished product, large number of investigations have been carried out on the thermodynamic properties of sulphur in molten metals and alloys in the dilute solution range.

White and Skelly [35] determined the solubility of sulphur in iron in the temperature range 1555 - 1600°C, using H_2S-H_2 gaseous mixture of known composition in equilibrium with molten iron. Activity of sulphur was determined and the equilibrium constant for the dissolution reaction was represented as a function of temperature by the following relationship,

$$\log K = -\frac{4526}{T} - 0.20 \qquad \ldots (I.12)$$

Ban-ya and Chipman [36] studied the following equilibrium reaction,

$$\underline{S}\ (\text{in Fe}) + H_2 = H_2S \qquad \ldots (I.13)$$

at three different temperatures viz. 1500 , 1550 and 1600°C and for sulphur concentrations upto 7.2 wt% and found from the thermodynamic treatment of data employing composition variable $z_S = \frac{n_S}{(n_{Fe}-n_S)}$ and activity coefficient, defined as $\Psi_S = a'_S/z_S$, the following relationship to hold good for correlation of composition with the activity coefficient,

$$\log \Psi_S = -2.3\, z_S \qquad \ldots (I.14)$$

The standard free energy change for the above reaction was also expressed as a function of the temperature by the following relationship ,

$$\Delta G^{o} = - 32,280 + 13.65\ T \qquad \ldots\ (I.15)$$

Sherman et al.[37] also investigated the thermodynamic properties of sulphur dissolved in molten iron by equilibrium method using H_2S-H_2 gaseous mixture in the temperature range of 1530 -1730°C and sulphur concentrations upto 4.8 wt%. The free energy change for the reaction,

$$H_2(g) + \underline{S} = H_2S(g) \qquad \ldots\ (I.16)$$

was studied as a function of temperature and was found to follow the following relationship,

$$\Delta G^{o} = 9840 + 6.54\ T \qquad \ldots\ (I.17)$$

Values of activity coefficient of sulphur were also determined and using the data of Morris et al. [38], the effect of silicon on activity coefficient of sulphur were computed to conclude that the experimental results were in good agreement with the computed values. Chipman [39] critically reviewed the then existing data on activity of sulphur in iron alloys mainly due to Morris and Williams [38], Morris and Buehl [40] and Sherman and Chipman [41] and concluded that aluminium, silicon, carbon and phosphorus increase the activity coefficient of sulphur in iron alloys whereas manganese, copper and sulphur (by self-interaction) decrease it. Cordier's [42] work, who also studied the activity of sulphur in iron-nickel alloys over the entire composition range and concluded that the interaction parameter $e_S^{Ni} = 0$ has also been quoted by Chipman [39]. Similarly effects of other alloying elements, j, on activity of sulphur have also been reported in terms of the interaction parameters, e_S^j , as presented in Table I.1 below :

TABLE-I.1 : Interaction parameters of different elements on sulphur in iron.

element j	e_S^j
Carbon	+ 0.11
silicon	+ 0.065
Phosphorus	+ 0.042
Manganese	- 0.025
Aluminium	+ 0.055
Copper	- 0.012
Nickel	0.000.

Ohtani et al.[43] have determined the self-interaction parameter of sulphur in iron as well as the effect of other elements such as carbon, nitrogen, oxygen, aluminium, silicon etc., on the activity coefficient of sulphur in molten iron. Rosenqvist et al.[44] found that small amounts of copper lowered the activity of sulphur in steel. Griffing and Healy [45] studied the effect of chromium on activity of sulphur in Cr-Fe-S melts and concluded that chromium has a pronounced negative effect on the activity coefficient , f_S^{Cr}, of sulphur which upto about 20% Cr may be represented by the following expression ,

$$\log f_S^{Cr} = -0.019\ [\%\ Cr] \qquad \ldots\ (I.18)$$

It was also found that the influence of chromium on the activity of sulphur was unaltered even in presence of appreciable amounts of carbon and silicon. Fishel et al.[46], in their investigations have shown that titanium has a positive effect on desulphurisation of steel since it reacts with sulphur in preference to carbon and separates it out as a second phase. Alcock and Cheng [47] studied the thermodynamic behaviour of sulphur in dilute solution range in iron, cobalt, nickel and their binary alloys by equilibrating small beads of metals with gaseous H_2S-H_2 mixtures of controlled ratios. Partial molar free energy of dissolution of sulphur in individual metal has also been determined and it has been shown that whereas the behaviour of sulphur departs appreciably from Henry's law in dilute solution range in liquid iron, the solutions in liquid nickel and cobalt conform to this law upto a sulphur content of 6 at.% and 1 at.% respectively. Venal and Geiger [48] determined the thermodynamic properties of dilute solutions of sulphur in pure nickel and its alloys with iron, chromium, molybdenum, silicon and aluminium at temperatures 1500, 1550 and 1575°C and for sulphur concentrations upto 0.7 wt %. With the assumption of 1 wt % standard state for sulphur, the equilibrium constant for the reaction,

$$H_2(g) + \underline{S}\ (\text{in liquid Ni}) = H_2S(g) \qquad \ldots\ (I.19)$$

was expressed as a function of temperature by the following relationship,

$$\log K = -\frac{1469}{T} - 1.772 \qquad \ldots \text{(I.20)}$$

Activity coefficient of sulphur at 1575°C in the dilute solution range in nickel was similarly represented as a function of the sulphur content of the metallic phase by the following relationship,

$$\log f_S = -0.035\ [\%S] \qquad \ldots \text{(I.21)}$$

Effect of alloying elements on the activity coefficient of sulphur in liquid nickel were also determined by calculating the corresponding interaction parameters, values of which are presented below in Table-I.2

TABLE-I.2 : Interaction parameters of different elements on sulphur in nickel.

element (j)	Interaction parameter (e_S^j)
Iron	+ 0.005
Chromium	+ 0.03
Molybdenum	+ 0.053
Silicon	+ 0.16
Aluminium	+ 0.133

It is to be noted that results of Alcock and Cheng [47] showed Henrian behaviour of sulphur upto 6 at% S whereas the results obtained by Venal et al. [48] showed deviation from Henrian behaviour.

These studies contributed positively to a better understanding of the behaviour of sulphur in iron and steel making processes.

Hirakoso et al.[49] studied the behaviour of sulphur in dilute solution range in molten copper at three temperatures viz., 1145°, 1196° and 1247°C by equilibrating molten copper with H_2S-H_2 gaseous mixture and determined the free energy of dissolution of sulphur in copper. Bale et al.[25] also determined the solubility of sulphur in dilute solution range in molten copper at three temperatures viz., 1100°, 1150° and 1200°C and showed that sulphur does not obey Henry's law in the solution and instead shows a negative deviation.

Alcock and Richardson [50] determined the activity coefficient of sulphur in molten pure copper and binary alloys of copper with gold, silicon, platinum, cobalt, iron and nickel at temperatures between 1100°C and 1500°C and showed that platinum and gold increase the activity coefficient of sulphur whereas nickel and iron decrease it.

Rosenqvist [18] determined the solubility of sulphur in molten silver and using the solubility data in the dilute solution range calculated the free energy of dissolution of sulphur from the following expression,

$$\Delta G^{o} = - 16400 + 1.0T \qquad \ldots (I.22)$$

Grant and Russell [51] studied the thermodynamic properties of sulphur in dilute solution range in lead by using a closed-gas circulation system and H_2-H_2S gaseous mixture in the temperature range 600 - 900°C. For the equilibria

$$\underline{S}\ (\text{at\% in Pb}) + H_2 = H_2S \qquad \ldots (I.23)$$

equilibrium constant, K, was found to vary with temperature, T, according to the following relationship,

$$\log K = -\frac{273.9}{T} - 1.707 \qquad \ldots (I.24)$$

Further, maximum solubility of sulphur in lead at 600°C was calculated to be 0.46 at% and variation of the activity coefficient of sulphur, γ_S^o, referred to a pure hypothetical liquid sulphur as standard state, with temperature, T, was found to obey the following relationship,

$$\log \gamma_S^o = -0.1228 - \frac{2371}{T} \qquad \ldots (I.25)$$

They also determined the effect of copper on sulphur dissolved in liquid lead and arrived at the following relationship for the temperature dependence of the Cu-S interaction coefficient in lead in the dilute solution range,

$$\log(-\varepsilon_S^{Cu}) = \frac{2070.9}{T} - 0.558 \qquad \ldots (I.26)$$

Maximum solubility of sulphur in lead, calculated from the expressions derived was found to be 0.47 at.%. Gerlach and Grigel [52] also determined solubility of sulphur in molten lead by equilibrating with H_2S/H_2 mixture at saturation and sub-saturation levels. The equilibrium constant for the reaction

$$\underline{S} + H_2(g) = H_2S\,(g) \qquad \ldots (I.27)$$

was expressed as a function of temperature by the following expression,

$$\log K = -\frac{461}{T} - 1.53 \qquad \ldots (I.28)$$

in the temperature range of 700 to 950°C. Alcock and Cheng [53] carried out studies on thermodynamic behaviour of sulphur in lead and tin in the temperature range 500 to 680°C by using radiochemical methods for analysis of the equilibrated H_2S-H_2 gaseous mixture and sulphur dissolved in the metal beads, to derive expression for equilibrium constant K and ΔG^o as functions of temperature for the reaction

$$\underline{S}\ (\text{in Pb or Sn}) + H_2(g) \rightarrow H_2S(g). \qquad (I.29)$$

as

$$\log K_{Sn} = -\frac{735}{T} - 1.461 \qquad \ldots (I.30)$$

$$\Delta G^o_{Sn} = 3362 + 6.68T \text{ Cal/mole} \qquad \ldots. (I.31)$$

$$\log K_{Pb} = -\frac{342}{T} - 1.578 \qquad \ldots (I.32)$$

$$\Delta G^o_{Pb} = 1564 + 7.22\ T \text{ Cal/mole} \qquad \ldots (I.33)$$

They further reported that the maximum solubility of sulphur in lead was about 0.42 at% at 600°C and also found that sulphur in lead and tin in dilute solution range obeyed Henry's law. Hagiwara [54] studied the equilibrium between H_2S-H_2 gaseous mixture and molten lead in the temperature range between 800° to 950°C and expressed the standard free energy change, ΔG^o, for dissolution of sulphur in lead as a function of temperature given by the following expression,

$$\Delta G^{o} = 10,285 - 1.565\ T \qquad \ldots (I.34)$$

Hagiwara [55], using the similar technique determined the solubility of sulphur in tin in the temperature range of 800°-950°C and expressed free energy of dissolution of sulphur in molten tin by the following expression

$$\Delta G^{o} = 11,058 - 2.544\ T \qquad \ldots (I.35)$$

Equilibria measurements were also made for Pb-Sn alloys with mixtures of H_2S-H_2 at 800°C and it was inferred that the activity of sulphur in molten lead was increased by presence of tin but this effect was very small. Hagiwara [56] studied the effect of different alloying elements viz. silver, copper, bismuth and tin on the activity coefficient of sulphur in liquid lead by equilibrium method using H_2S-H_2 gaseous mixture in the temperature range 800°-900°C and concluded that the value of the activity coefficient of sulphur in liquid lead was increased by the presence of silver, antimony and bismuth but decreased by that of copper. Hagiwara [57] further investigated the behaviour of sulphur in multi-component metallic alloys of lead, silver, copper, bismuth and antimony by equilibrating the melts with H_2S-H_2 gaseous mixture and found the following expressions to hold good for determining the activity coefficient of sulphur in liquid lead alloys,

$$\log f_S = \log f_S^x + \log f_S^y + \ldots \qquad \ldots (I.36)$$

where, the symbols f_S, f_S^x, f_S^y etc. represent respectively

the activity coefficients of sulphur in liquid Pb-S-x-y-...,
Pb-S-x, Pb-S-y,... etc. alloy melts.

Twidwell and Larson [58] studied the effect of different elements such as gold, silver, antimony, bismuth, tin and copper on the activity coefficient of sulphur in liquid lead at 600°C by circulating H_2S-H_2 gaseous mixture over different melts and computed the interaction parameters, presented in Table-I.3, to quantify the effect of different elements present.

TABLE-I.3 : Interaction Parameters of elements on sulphur in lead.

Element (j)	Interaction parameter ε_S^j
Gold	+ 5.4
Silver	+ 3.3
Antimony	0.0
Bismuth	0.0
Tin	0.0
Copper	-55.0

Maximum solubility of sulphur in lead at 600°C was precisely measured to be 0.46 at. %.

Solubility of sulphur was also measured in multicomponent alloys. Interaction parameters determined in the investigation were used to predict the activity coefficient of sulphur in multicomponent alloys by using Wagner's interpolation formula [59] and the calculated values were compared with the empirical values.

The results obtained by Grant and Russell [51] compare well with those of Alcock and Cheng [53], Twidwell and Larson [58] and Gerlach and Grigel [52] but differ considerably with those obtained by Hagiwara [54], Blank and Willis [15], Miller and Komarek [10] and Stubbles and Birchenall[16]. The results of these two groups of workers differ considerably. Mohapatra and Frohberg [60] determined solubility of sulphur in liquid silver-lead and silver-tin alloys at temperatures 827 and 950°C using the gas-metal equilibria technique incorporating quartz twin capsules and calculated the activity coefficient of sulphur in these alloys.

I.3 Methods of Thermodynamic Study

Systematic thermodynamic studies on metallic systems at temperatures above 1000°C started largely from the early 1930's but were seldom carried out above 1650°C till about 1945. The different techniques [61,62] used for determining the physico-chemical properties of metallic systems at high temperatures may be classified as follows:

i) calorimetry
ii) emf measurements
iii) vapour pressure measurements, and,
iv) chemical equilibria.

These techniques will be very briefly reviewed below.

I.3.1 Calorimetry

Calorimetry may be defined as the measurement of energy in the form of heat. Calorimetric techniques measure changes in enthalpy or heat content of a substance or a system associated with, (a) changes in its temperature (b) changes in its state, such as on melting, boiling or phase transformation or (c) changes in chemical combinations, such as interaction of one constituent with the other in chemically reacting systems, alloying or dissolution in non-reactive systems.

Different types of calorimeters have been used, and a wide ranging application of these calorimeters has been established. The different calorimetric techniques, adopted in practice, may be grouped keeping in view the factors common to them and classified as follows:

i) Reaction calorimetry
ii) Bomb calorimetry, and ,
iii) Specific heat calorimetry

In reaction calorimetry, variety of modifications have been developed depending upon the type of substance under study and therefore the technique can be subclassified further as follows:

a) Reaction calorimetry with low temperature environment.
b) annealing calorimetry, and,

c) solution calorimetry, further sub-classified as,
  i) Aqueous solution calorimetry , and ,
  ii) Liquid-metal solution calorimetry

In reaction calorimetry, two methods viz. the direct and indirect methods are generally used to determine the thermodynamic properties. The direct method offers an advantage over the indirect method in that the quantity measured depends directly on the accuracy of the method of measurement. However, this method suffers from the uncertainty in the final state of the system and in some cases from the difficulties in the measurement of first and last part of the reaction. This is particularly true in cases where the kinetics of reaction are being investigated. The temperatures, to which the measured reaction energy refers, are not always clearly defined with direct measurement methods, and it is not possible to measure heats of reactions at low temperatures directly.

Indirect methods clearly define the initial and final states of the sample, but the energy change of interest may be a small difference between two large quantities with the consequent need for high precision in the measurement techniques adopted. The temperature to which a measured reaction energy refers is well-defined and it is possible to measure indirectly the heats of reaction at or below room temperatures. Kinetic studies are, however, tedius in this case.

In bomb calorimeters, combustion is carried out with a gas as one of the reactants. Basically the calorimeter compares the amount of heat liberated from the combustion of a sample with a known amount of electrical energy. This may involve use of an intermediate substance e.g., a material which has been calibrated. Values of the heats of combustion, when converted to heats of formation and then combined with entropies obtained from heat capacity data, provide free energy data which are otherwise most difficult to obtain in any other way. In fact, values of entropy can frequently be estimated in this manner with considerable accuracy if experimental determinations are not possible otherwise. This is specially true of reactions in the condensed state where entropy changes are small. Different kinds of bomb calorimeters used for the determination of thermodynamic data may be classified as follows:

i) Static bomb in isothermal jacket
ii) Static bomb in adiabatic jacket , and ,
iii) Rotating bomb.

one of the most important considerations in calorimetry involving combustion reactions is the identification of the specific reaction or reactions responsible for the measured heat.

Sources of error in calorimetry are many e.g., due to improper temperature measurements or computation of energy equivalents, ignition energy, presence of impurities and side reactions initiated by them, incomplete reactions etc.

These, if not taken care of with precision, may yield unreliable and non-reproducible results.

I.3.2 Vapour Pressure Measurements

Vapour pressure measurements of pure metals and alloys provide direct information on the thermodynamic properties of the systems under study as the data on vapour pressure as a function of temperature are used to compute the standard free energy and entropy of vaporisation. Further, rate of vaporisation, activities of components in an alloy, bonding of oxide or sulphide molecules etc. may also be determined by vapour pressure techniques. Method , employed in any particular case is dependent on the vapour pressures encountered and on the need for absolute or relative measurements of pressure. For metals with relatively high vapour pressures, the entrainment method has been extensively used to provide absolute values of pressure for the liquids. An inert gas, generally hydrogen, is swept over the specimen at a steady measured rate at constant temperature. Under equilibrium conditions of flow, the carrier gas must be saturated with the metallic vapour and this vapour content is analysed by condensation or absorption in the cooler portion of the experimental set-up. Several determinations are carried out at different steady rates of flow of the carrier gas and the criterion for saturation is in the constancy of the concentration of metallic vapour with varying flow rates. The entrainment method has been used in the pressure range from about 0.2 to 200 mm Hg.

With proper precautions taken against thermal diffusion, the method is quite reliable and is often the only absolute method which can be used, especially for the more volatile metals.

Vapour equilibration techniques, or the isopiestic techniques have been used extensively for determination of the comparative vapour pressures. In this method, samples are partially equilibrated through the vapour state so that they display a common vapour pressure of a particular component. Analysis of these samples then provides the necessary information to describe the system.

Knudsen effusion technique can be used only in cases where the vapour pressures are quite low. The rate at which a gas or vapour escapes through a small orifice into vacuum is measured and is used to compute the vapour pressure of the substance under study.

The different conditions to be satisfied in the use of Knudsen method may be briefly mentioned as follows: (i) the mean free path of the vapour inside the cell must be several times longer than the orifice diameter,,(ii) the effective sample area must be very large compared will the orifice area, and,(iii) orifice temperature must be the same as that of the other portions of the cell. Provided these simple conditions are satisfied, the method is very reliable.

For measurement of very low vapour pressures, the free-evaporation method of Langmuir offers interesting possibilities in that it allows measurement of pressures as low as 10^{-7}mm Hg. In this method, the rate of evaporation of a heated specimen in vacuum is measured. All evaporating vapours must be condensed, and in addition to a good initial vacuum, the method of heating must be such as to ensure that the temperature of the specimen is considerably higher than that of the surrounding walls. Considerable care in surface preparation must be taken in order to obtain dependable results.

These effusion methods can only be employed when the vapour species effusing is simple or chemically well-defined. This is because the molecular weight of the vapour species must be known in order to calculate the vapour pressure from the effusing mass. However, where the vapour has a complex composition, application of these simple methods can be extremely difficult. The mass spectrometer offers a valuable method for the identification of vapour species in a complex vapour. It is also useful in the determination of vapour pressure and heat of vaporisation of refractory elements and compounds whose low vapour pressures make it necessary to work at high temperatures. Further, the reversibility of mass spectrometer makes it possible to detect the presence of minor species. Finally the mass spectrometer permits the study of vapour pressures of a particular species without fear of interference by impurities.

I.3.3 e.m.f. Measurements

Measurement of the e.m.f. of a cell is one of the most useful methods of determination of thermodynamic data. However, the main difficulty in designing an electrochemical experiment for high temperature studies is in securing a suitable material of construction for the cells, which does not react with the melt and in most cases which should be an electric insulator. Below 1000°C, a variety of stable refractory materials are available, and measurements can be made with sufficient accuracy but above this temperature, only a few materials are inert and accuracy may be considerably reduced. For accurate measurements of the e.m.f. of the cell due to the reaction under study a number of precautions, enumerated below must be observed:

i) The cell reaction must be thermodynamically reversible.

ii) Thermoelectric and/or eddy-current potentials must either be avoided or compensated.

iii) The cell must be allowed to attain equilibrium.

iv) Unless a redox system is being studied, ions in the electrolyte must not be present in different valence state.

v) The electrolyte must exhibit ionic conduction only and no electronic conductance.

vi) Secondary reactions must not be allowed to take place in the cell at the electrodes and it must be established that the e.m.f. generated and measured is only due to the cell reaction under study and no other reaction.

A number of thermodynamic studies on metallic and oxidised (silicate) systems using both liquid and solid electrolytes have been conducted by several investigators.

I.3.4 Chemical Equilibria Technique

Gas-condensed phase equilibria techniques have been extensively used to determine the chemical potential of the species under study in a number of systems such as solid-gas molten metal-gas, molten slags or salts-gas systems etc. In studies involving reactions between a gaseous and a condensed phase at elevated temperatures, the chemical potential of the reacting species is readily controlled by an appropriate choice of the gaseous mixtures used and bringing them into equilibrium with the condensed phase. Alternatively, gases may be made to attain equilibrium with substantial quantities of condensed phases of the desired composition and chemical potentials may then be measured by analysing the gases. The type of gaseous mixtures used for controlling the chemical potentials of certain species are not unlimited. Various possible gaseous mixtures used and potentials established [62] are given in Table-I.4.

TABLE-I.4 : Gaseous mixtures 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_2-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
$H2-H_2O-SiO$	Si

The choice of gaseous mixture to be used in any specific case depends on a large number of factors. Besides the specific chemical potential required, it also depends on the ease of developing the gaseous mixture and simple apparatus design as well as the capability of transporting the reacting species at a reasonable rate so as to attain equilibrium in a reasonable period of time. Different techniques have been used for establishing the gaseous mixtures of definite chemical potentials of the desired species. Constant pressure head flowmeters have been used for multicomponent gaseous mixtures which are formed by mixing the gases obtained from cylinders. This method was first developed by Johnston and Walker [63] and was later modified by Darken and Gurry [64].

Mixing of gases is not always the convenient way of establishing the chemical potentials of the reacting species. The chemical potentials of certain gaseous species can best be controlled more readily by reacting a suitable gaseous mixture with a particular condensed phase (or phases). The gaseous-mixture of definite composition, thus obtained is then allowed to react with the system under study. There are many ways of establishing the chemical potential in the reacting systems. The different techniques used may be classified into three categories.

i) Open circuit experiments
ii) Closed circuit experiments , and,
iii) Static atmosphere experiments

In open circuit experiments, a gas is passed over a particular condensed phase to saturate it with the desired vapour species, and then allowed to react with another condensed phase contained in the same reaction vessel. An example of this includes gas-mixtures used for definite phosphorus and oxygen potentials or those for the definite silicon potential etc.

In closed circuit experiments, the reacting species are transferred from one condensed phase at any temperature T_1 to other condensed phase at a different temperature T_2 via a suitable circulating gas.

Experiments in a static gas atmosphere can be carried out only in special cases, e.g., a single component gas or encapsulated gaseous mixtures under isothermal conditions. A sealed capsule technique is often employed in the study of reactiohs between condensed phases, since matter is transferred from one condensed phase to another via the gaseous phase.

In these equilibrium techniques, one of the most important problems faced is the 'thermal diffusion'. This occurs because a gaseous mixture is held in an apparatus, one part of which is kept at higher temperature and the other at lower temperature and hence the components of low molecular weights in the gaseous phase tend to seggregate in the high temperature parts and the heavier ones in the low temperature parts. The degree of seggregation increases with increasing differences between the temperatures of the cold and hot zones of the apparatus and also by a larger difference between the molecular weights and the sizes of the constituent species in the gaseous mixture. In such experimental set-ups, therefore, flow of the gaseous mixtures should be sufficiently high enough to keep this thermal seggregation to the minimum.

For establishing the sulphur potential in the gaseous phase, both the above mentioned techniques have been used by different investigators. The required sulphur potential, over a wide range, may be obtained by mixing hydrogen and hydrogen sulphide gases. This technique was used by Rosenqvist and Dunicz [65]. However, it is not every much suited for establishing very low potentials of sulphur. Yazawa et al.,[19] have used N_2-S_2 mixture for developing the required sulphur potential for thermodynamic studies of solution of sulphur in condensed phase. By closed-circuit circulation of mixtures of H_2S-H_2 gases, number of investigators have carried out equilibria studies [18,47,58]. Mohapatra et al.,[60] have used encapsulated metal and metal-metal sulphide mixtures in their investigations. Of these, the H_2S-H_2 gaseous mixture equilibria technique has been most widely used. These methods differ only in one respect, i.e. the technique of analysis of the gaseous mixture wherein Buoyancy balance [28], thermogravimetric balance [25], radiochemical techniques [53], etc. have been used to establish and measure the equilibrium conditions in the systems studied by different research workers.

I.4 Theoretical Studies-Thermodynamic Models

Extensive empirical data obtained on the thermodynamic properties of metallic solutions by different investigators have been summarized, analysed and compiled by Hultgren et al.[66]. Wilson [67] also compiled experimental data on several physical and physico-chemical properties of pure liquid metals and indicated qualitative and empirical relationships amongst them.

In the past few years, considerable theoretical work has been done by a large number of workers-to name a few Kubaschewski, Ansara, Bonnier, Mathieu, Hildebrandt, Fowler, Bethe, Guggenheim, Wagner, Lupis, Elloit, Frohberg, Kapoor etc. Several thermodynamic models developed by these workers have been critically reviewed by Kapoor [68].

Theoretical analysis of metallic solutions has been done using both classical as well as statistical thermodynamic approaches. In the latter approach, the different models proposed are based on the 'quasi-crystalline lattice concepts'. The solute atom can occupy either a lattice site substituting for the solvent atom (substitutional solutions), or an interstitical position between the solvent atoms (interstitial solutions). The formation of solution results in breakage of some bonds between the like atoms (of solvent) and making of some new bonds between unlike atoms (solvent and solute). It is this phenomenon which is considered, in different models proposed, to be responsible for the thermodynamic behaviour of the system on mixing. The changes on mixing are explained to different degrees of accuracy in terms of regular solution model, quasi-chemical theory and central-(or surrounded-)

atom model, developed primarily for binary solutions and then extended to ternary and other multicomponent systems.

The basic assumptions, on which the different models have been developed, alongwith their limitations are briefly reviewed below:

The word 'regular solution' was coined by Hildebrandt [69] for binary substitutional solutions having their excess entropy of mixing as zero and the enthalpy of mixing $\Delta H_M = W.N_A.N_B$, where W is a system dependent constant but independent of temperature and composition of the solution and N_A and N_B are respectively the mole fractions of components A and B of the binary solution (A-B). In the statistical thermodynamic analysis, these solutions are assumed to have ,(i) random distribution of atoms in the lattice, (ii) total energy of any state equal to the sum of the bond energies and each bond (like or unlike type) having the same fixed energy, and,(iii) the volume or internal partition function of the system does not change on mixing. This model only qualitatively explained the properties of solutions because of the above assumptions. To overcome its limitations, Hardy [70] proposed an empirical 'semi-regular solution' model and explained the assymetrical behaviour of some metallic solutions.

Quasi-chemical theory was next developed jointly by Fowler [71,72], Bethe [73], Rushbrooke [74] and Guggenheim[75], primarily to explain the thermodynamic properties of simple and polymer organic solutions. This takes into account the preferential distribution of atoms, arising from the different interaction energies of like and unlike atoms. The nearest neighbours of an atom are assumed not to be present in the first coordination shell of each other. The other assumptions of regular solution model have been taken to be valid for this model also. The model explained the properties of solutions in a manner slightly better than the first model but still could not explain assymetric behaviour of the solutions.

Central-(surrounded-) atom model, simultaneously developed by Lupis and Elliot [76] (as the central-atom model) and by Mathieu et al. [77,78](as the surrounded atom model) differs from the previous approaches in that it treats the atom as the basic unit rather than the bonds. Hence energy and partition function are both functions of the central atoms and their nearest neighbours and therefore, both, energy and internal partition function, are assumed to change on mixing. Energy and internal partition function may either be assumed as linear or parabolic functions of the atoms present in the solution. Thus, the different expressions developed in this treatment explained the assymetric behaviour of the binary and the ternary systems. Wagner [79], Blander [80] and Kapoor [81], have extended this approach to explain the thermodynamic properties of dilute solutions.

Recently kapoor [82] developed a new model based on the free volume theory using lattice concept with additional assumptions that the energy and free volumes of any atoms are functions of both number and types of the nearest neighbours i.e. in the first coordination shell and has derived semi-empirical relationships for the energies and free volumes of atoms present in the binary solution and, from these, for the thermodynamic properties of the solutions. The expressions derived in this treatment have been applied to a very large number of binary substitutional solutions to test their applicability.

The brief discussion above, thus shows that a unified approach for theoretical treatment of the thermodynamic behaviour of multicomponent dilute solutions is yet to be developed.

I.5 Formulation of the Problem

In sections (I.2) - (I.4), it has been amply demonstrated that although several studies have been made on solutions of sulphur in metallic systems, in general, the data obtained by different workers differ substantially. Further, explanations of the empirical data on the basis of theoretical models have also been inadequate.

In the present investigation, therefore, properties of sulphur in dilute solution range in copper, silver and lead as solvents and in their binary and ternary alloys will be studied experimentally. Mixtures of hydrogen sulphide and hydrogen gases of different known sulphur potentials will be equilibrated with the above metals and their binary and ternary alloys of varying compositions at different temperatures to arrive at the values of thermodynamic properties of sulphur in such solutions.

Further, theoretical models based on free volume theory and statistical thermodynamic concepts will be developed and the available data from the present investigation and, if possible, of other workers will be used to test the validity of the different expressions developed for the thermodynamic properties of sulphur. For development of theoretical models, the quasi-crystalline lattice concept of the solution and both linear and quadratic forms of energy and free volumes of atoms in relation to their positions and also both random and preferential distributions of solute and solvent atoms will be assumed. Attempts will also be made to generalise, the different expressions so developed, for multi-component solvent systems and also to predict the properties of solute in solvents of known compositions.

CHAPTER - II

MATERIALS AND METHODS USED

Of the various techniques used for the study of behaviour of sulphur in metallic phases as briefly described in the previous chapter, the gas-condensed phase equilibria using closed circuit technique has been employed for the present investigation, to study the thermodynamic properties of sulphur in pure lead, silver and copper solvents and also in their binary and ternary alloys. The different materials and methods used are briefly presented in this chapter.

II.1 Experimental Set-up

The apparatus used in the present investigation is schematically shown in Fig. II.1 and consists essentially of two resistance tubular furnaces, mercury manometer, flowmeter, an all-glass gas-circulating pump and moisture traps. The gas purifying train which constitutes a part of the experimental set-up is not shown in this diagram. Recrystallised alumina tubes of 25 mm internal diameter were used as the reaction tubes in the two furnaces and both ends of these refractory tubes were cemented to standard B-36 pyrex glass-joints with the help of araldite. The ends of these tubes were also water-cooled by using appropriately designed water-jackets made of copper. In one furnace, to be referred to as 'metal furnace' later in the text, metal beads, kept in a high alumina boat, were placed. In the other furnace, termed

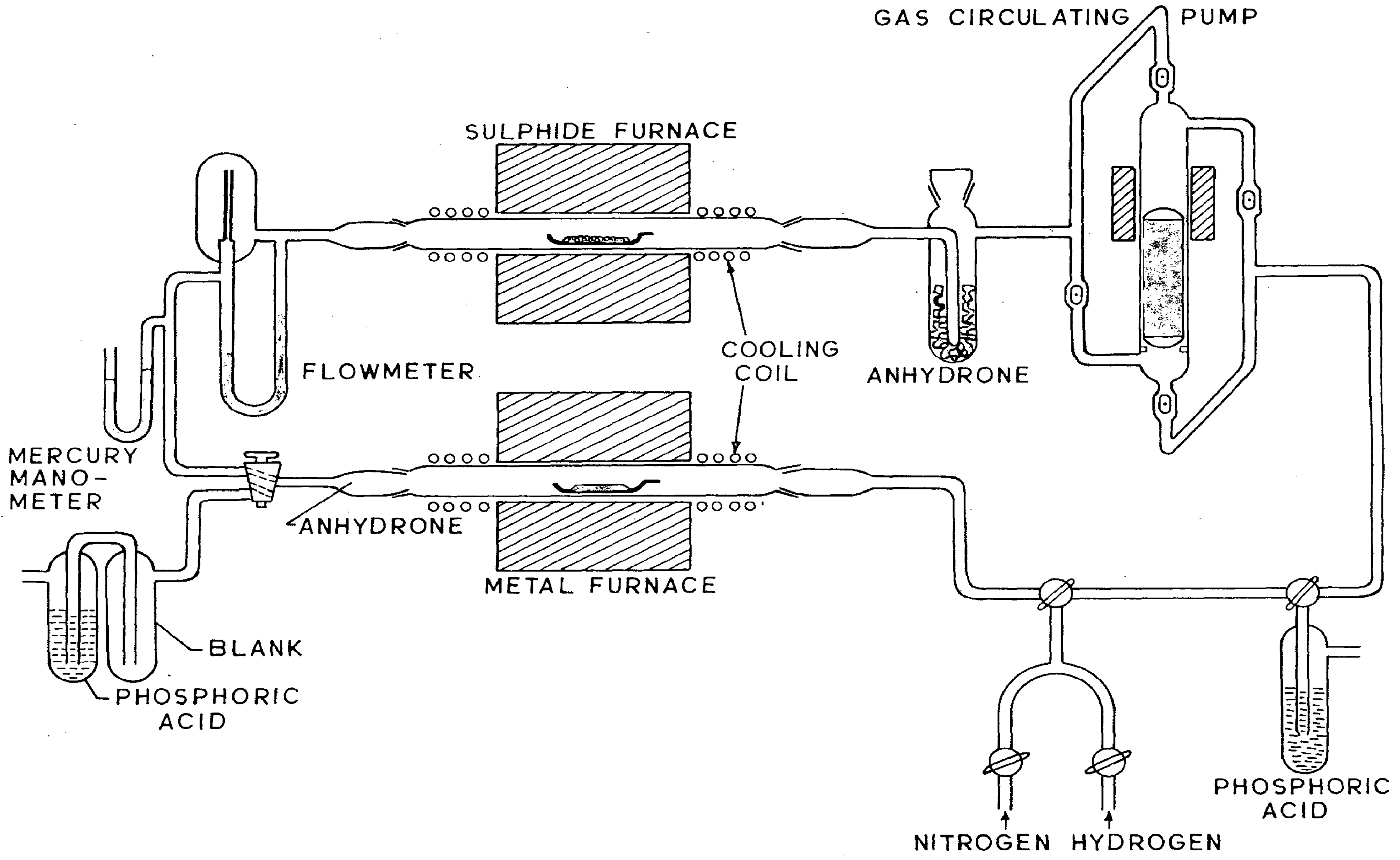

FIG.II.1 SCHEMATIC DIAGRAM OF EXPERIMENTAL SET-UP. (WITHOUT GAS-PURIFYING TRAIN) similarly as the 'sulphide furnace', a well-mixed powder of copper and cuprous sulphide, kept in a similar boat, was placed. Each furnace was provided with two thermocouples, one for controlling and the other for accurate measurement of temperature using OSAW make (Oriental Scientific Apparatus Workshop, Ambala, India) portable potentiometer. For measurement and control of temperatures upto 973°K, alumel-chromel thermocouples were used but for higher temperatures, platinum-platinum 13% rhodium thermocouples were used. Temperature of each furnace was automatically controlled with an 'on and off' type temperature controller of APLAB make (Applied Electronics, Thana, India). Power was supplied to the furnaces through an automatic solid-state voltage stabilizer (NELCO-Indian make 7.5 KVA, 230V output, 175/260 V input) and auto-transformers (15A,260V). The uniform high temperature zone of each furnace was sufficiently long as to cover the entire length of the boats referred to above and containing the reacting materials. Temperature of this high temperature even zone of both the furnaces could be controlled within ± 2°C. Mercury manometer and flowmeter using dibutyl-phthalate were used to measure respectively the pressure and rate of flow of gaseous mixture in the apparatus. Magnesium perchlorate was kept near the ends of the reaction tubes as well as in a wash bottle to absorb any moisture, if present, in any part of the apparatus. The double-acting all-glass gas circulating, pump, designed and fabricated locally, consisted of four non-return valves. A single solenoid coil, supplied with 30V, 3 amp. D.C. power (AFFCOSET, Indian-make, IC regulated power supply), was used to actuate the piston which fell under its own weight, on its return downward stroke. The piston armature was a piece of iron contained in a perspex sheath, carefully matched with the internal diameter of the glass tube, to slide comfortably within the glass tube of the pump assembly. In the lower portion of the glass tube, small rubber tubing was connected to act as a shock absorber for the falling piston. A relay-operated circuit energized the solenoid at a controlled rate resulting in a reciprocating speed of the piston varying from 60 to 130 strokes per minute— a range at which the pump was found to circulate gaseous mixture at a flow rate of 100 - 200 ml/min. in the apparatus. The apparatus, therefore, consisted of no other metallic surface exposed to the flowing gaseous mixture except the reactants under study.

The gas purifying train consisted of two furnaces. In one furnace, porous alumina balls were packed in the even temperature zone and in other, copper chips were placed. In between these two furnaces, a bubbler containing concentrated sulphuric acid was incorporated. Alkaline pyrogallol and concentrated sulphuric acid in bubblers and magnesium perchlorate in wash bottle were connected, in the sequence mentioned, next to the furnace containing the copper chips. A photograph of all the components of the experimental set-up is shown in Fig. II.2.

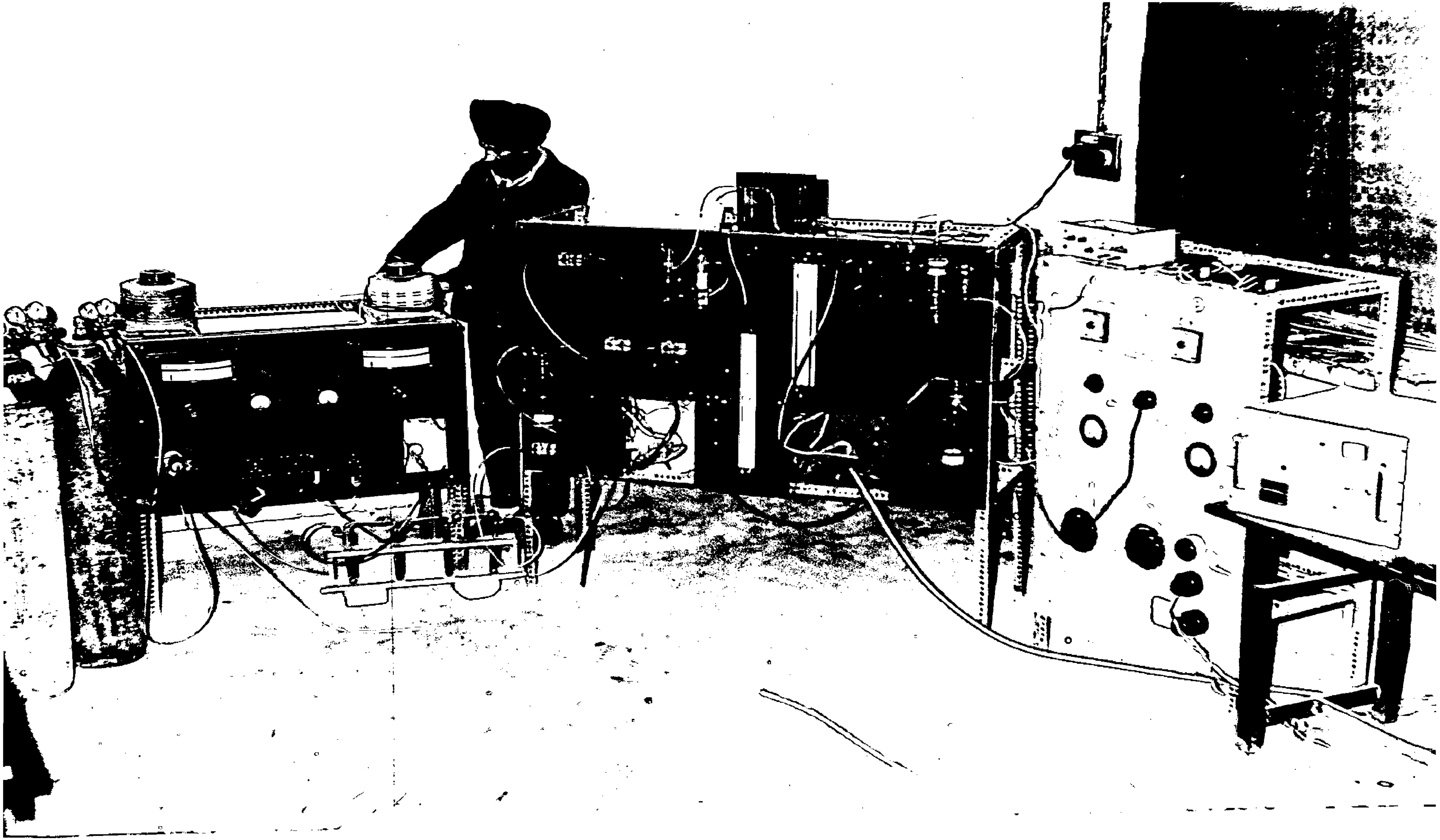

FIG.II.2 OVER-ALL VIEW OF THE EXPERIMENTAL SET-UP SHOWING ESSENTIAL COMPONENTS.

II.2 Preparation of Materials

II.2.1 Pure Metals and Alloy Preparation

Analytical grade pure metals - lead, silver and copper (+ 99.9% purity) were further purified by melting them under a stream of hydrogen. These were kept in molten state for about three hours and cooled to room temperature under hydrogen flow to remove any traces of oxygen present. The binary and ternary alloys of these metals were also prepared in refractory boats in the hydrogen atmosphere.

II. 2.2 Preparation of Sulphides

For preparation of cuprous sulphide, cupric sulphide was precipitated from aqueous solution of cupric sulphate (Analar-grade) by passing hydrogen sulphide. The precipitated cupric sulphide was filtered, washed with distilled water containing some dissolved hydrogen sulphide gas. This precipitate was then dried and mixed with pure sulphur (recrystallised with carbon-di-sulphide). This mixture was then charged in a porcelain crucible and heated for about 15 minutes in a stream of hydrogen, in the tube furnace, first at lower temperature (730°K) and then at a high temperature (1050°K) for few minutes. The excess sulphur was finally driven-off by heating the above mixture at about 900°K in the stream of hydrogen for about an hour. Lead sulphide was similarly prepared using Analar grade reagents.

II. 2.3 Purification of Gases

High purity hydrogen and nitrogen gases, both supplied in cylinders(by Indian Oxygen Limited, Poona) were further purified to render them oxygen-free by first passing them over alumina balls heated to a temperature of about 823°K and then consecutively bubbling through concentrated sulphuric acid, passing over copper chips kept at 873°K, again bubbling through alkaline pyrogallol and concentrated sulphuric acid and finally passing through anhydrone to remove the last traces of moisture.

II. 3 Experimental Procedure

II. 3.1 Flushing and Drying of the Assembly

The apparatus was first flushed with nitrogen and temperatures of both the furnaces were raised between 723 - 773°K. Flow of nitrogen was then stopped and the apparatus was sealed to the atmosphere by operating the appropriate stop-cocks and the gas-circulating pump was started. This continued for about 20 hours and helped eliminate moisture completely from the apparatus. Removal of moisture was indicated by drop of pressure which maintained at a constant level when moisture was completely removed.

II. 3.2 Equilibria Runs

To start the equilibria runs, metal or alloy beads (approx. 1 gm in weight) and about 10 gm weight of either

$Cu-Cu_2S$ mixture or Pb-PbS mixture, both kept in dried high alumina refractory boats, were quickly inserted in the respective furnaces. The ends of the tubes were closed and the apparatus was flushed with purified hydrogen. As the flushing operation continued, temperatures of both the furnaces were slowly raised to the desired levels. Flushing with hydrogen was then stopped and the apparatus was sealed to the atmosphere. The gas-circulating pump was then switched on and its speed adjusted. This circulation of hydrogen gas, in the sulphide and metal furnaces resulted in transfer of sulphur from $Cu-Cu_2S$ (or Pb-PbS) mixture kept in 'sulphide furnace' to the metallic bead in the 'metal furnace'. This is because at the temperature of $Cu-Cu_2S$ (or Pb-PbS) mixture, gaseous hydrogen reacts with the metal-sulphide mixture to produce a H_2-H_2S mixture of specific sulphur potential depending upon the temperature of the 'sulphide furnace'. This gaseous mixture as it passes over the metallic beads transfers sulphur to the later in the 'metal furnace'. To avoid error introduced due to the thermal diffusion phenomenon, the speed of the pump was adjusted between 120 - 150 ml/min. After the stipulated period of time, depending upon the temperature of the 'metal furnace', the gas circulating pump was stopped and the 'metal furnace' was disconnected from the 'sulphide furnace' and flushed with nitrogen for about 15 to 20 minutes. The alumina boat containing the metal beads was then taken out and cooled rapidly in a stream of nitrogen. Trial-runs were carried out to determine the minimum time of equilibration of metal beads with the reacting H_2-H_2S gaseous mixture. To ascertain the attainment of equilibrium between the metal beads and sulphur - bearing gas in these runs, samples were taken out at different intervals of time for which the metal beads were exposed to the reacting H_2-H_2S mixture of known sulphur potential. These exposed samples were analysed for their sulphur content by evolution and spectrophotometric method. It was observed that the sulphur content of the metal beads did not change after about 16 hours exposure to the reacting sulphur-bearing gas.

Although equilibrium was reached in about 16 hours time as indicated by trial-runs, yet all experimental runs for equilibrium of different solvent samples with sulphur in gaseous-mixture were carried out for a period of twenty hours or more.

II. 4 Chemical Analysis

Different methods have been used for determination of sulphur in metals and alloys. The evolution method used by Twidwell and Larson [58] was tried but was found unsuitable as complete dissolution of the alloys containing silver could not be attained. In the present work, therefore, the evolution of H_2S was accomplished by using hydriodic-hypophosphorus acid mixture [83] and the evolved gas was absorbed in zinc acetate solution. The quantity of sulphur in the zinc acetate solution was determined spectrophotometrically using p-aminodimethylaniline [84]. The procedure adopted for analysis is outlined below.

II. 4.1 Apparatus Used

Apparatus used for analysis of sulphur in metals - lead, copper, silver and their alloys consisted of the following:

i) Evolution apparatus, and,
ii) Spectrophotometer.

The distillation or evolution apparatus, shown in Fig. II.3 consisted of a thick-walled corning glass round bottom flask of 50 ml capacity fitted with a 29/32 ground glass socket. The corresponding cone of the socket carried, (i) an inlet tube for the carrier-gas (nitrogen) which reached almost upto the bottom of the flask and (ii) a horizontal outlet tube, which was attached via a ground glass joint to a right angled tube leading to a 50 ml volumetric flask acting as receiver. Bausch and Lamb spectrophotometer (spectronic-20) was used for determining the absorbance of the solution samples prepared.

II. 4.2 Reagents Used

Following reagents of Analar grade purity were used in the analysis.

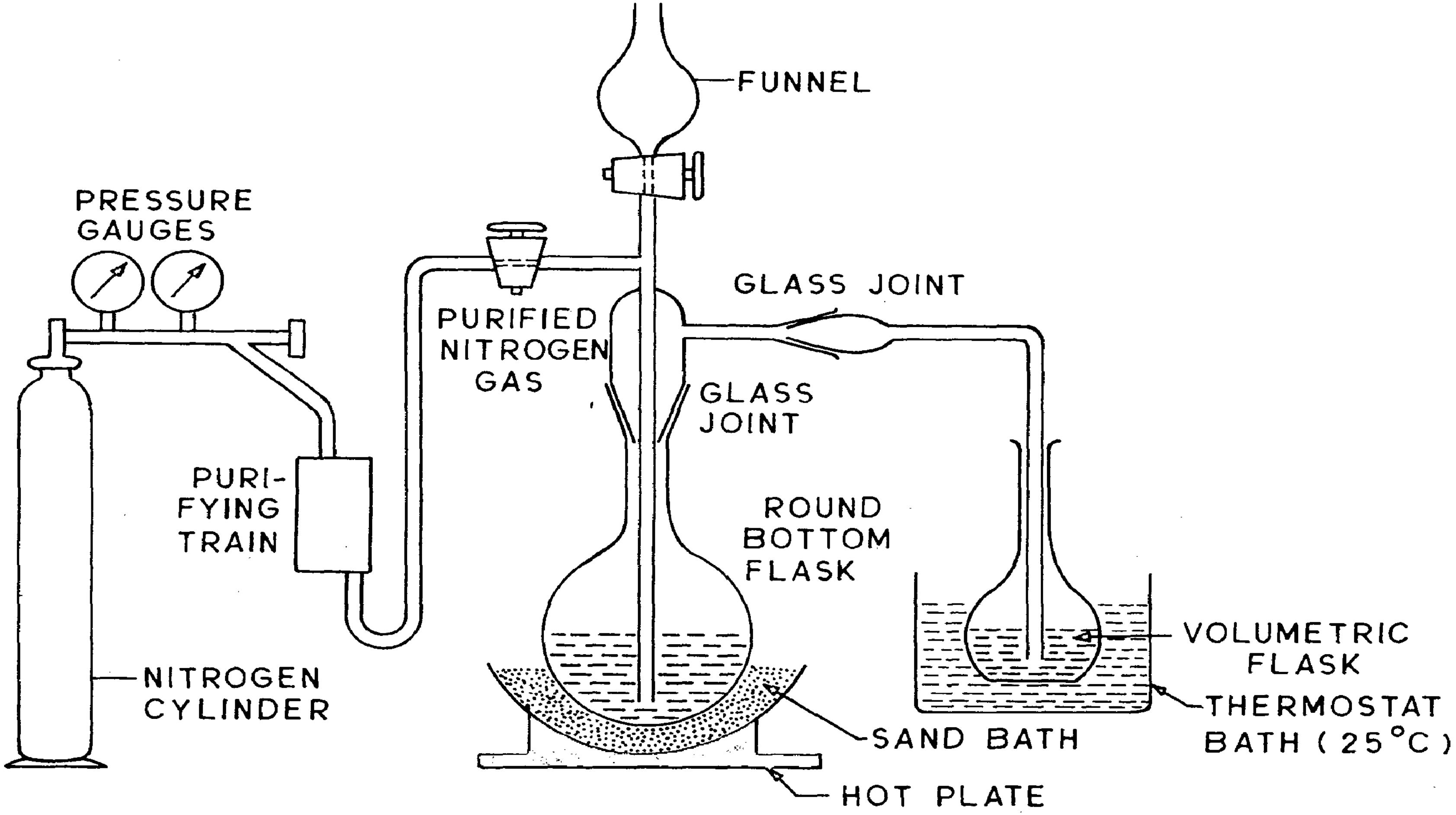

FIG.II.3 SCHEMATIC DIAGRAM OF EVOLUTION APPARATUS FOR ESTIMATION OF SULPHUR.

i) Standard potassium sulphate solution - 1 ml of this solution corresponded to 5 μ gm of sulphur.

ii) Redistilled hydrochloric acid

iii) Redistilled nitric acid.

iv) Redistilled formic acid.

v) Hydriodic-hypophosphorus acid mixture of volumetric ratio 4:1 e.g. containing 100 ml HI and 25 ml H_2PO_3,

vi) p-aminodimethylaniline (0.7% w/v prepared in 1:1 sulphuric acid).

vii) Zinc acetate (2% aqueous solution) , and ,

viii) Ferric chloride (10% aqueous solution).

II. 4.3 Procedure

Analysis of sulphur in the metallic samples makes use of the absorbance of zinc acetate solution containing absorbed H_2S, in which a methyline blue colour is developed using p-aminodimethylaniline and ferric-chloride solutions. For the correspondence of absorbance of the solution with the sulphur content, standard curve was plotted between absorbance and amount of sulphur using potassium sulphate solution. For this purpose 0, 2, 4.... ml of standard potassium sulphate solution from a burrette were taken in 50 ml round bottom corning flask and evaporated to dryness over a bunsen flame taking due care that no sulphurous fumes were around the place of this analytical work.

The dried sample was cooled to room temperature and 5 ml of redistilled hydrochloric acid and 15 ml of hydriodic-hypophosphorus acid mixture were added making sure that a drop or two fell on the ground glass joints also so that latter was wet enough to eliminate any leakage of vapours through it during subsequent distillation and flushing operations. The flask was stoppered at once with the cone and the horizontal tube-arm was dipped into 35 ml of 2% zinc acetate aqueous solution kept in a 50 ml capacity volumetric flask. The round bottom flask was placed on a sand bath, temperature of which was maintained at 185 ± 5°C. Flow of nitrogen in this assembly was started at a constant rate, 200 ml/min, to get reproducible results. The distillation operation was carried out for 30 minutes after which the flow of nitrogen gas was stopped and the volumetric flask was detatched from the evolution apparatus and kept for a period of about 30 minutes in the thermostat bath at 25°C. 1.5 ml of p-aminodimethylaniline solution was added slowly down the wall with a 2 ml pippette to the contents of this volumetric flask, followed by addition of 0.5 ml of ferric chloride aqueous solution. The flask was vigorously shaken for about 2 minutes and a methylene blue colour developed. It was further kept at 25°C for another 15 minutes in the thermostat bath. The solution was then made up to the mark in the volumetric flask by addition of distilled water and its absorbance was measured at 660 nm

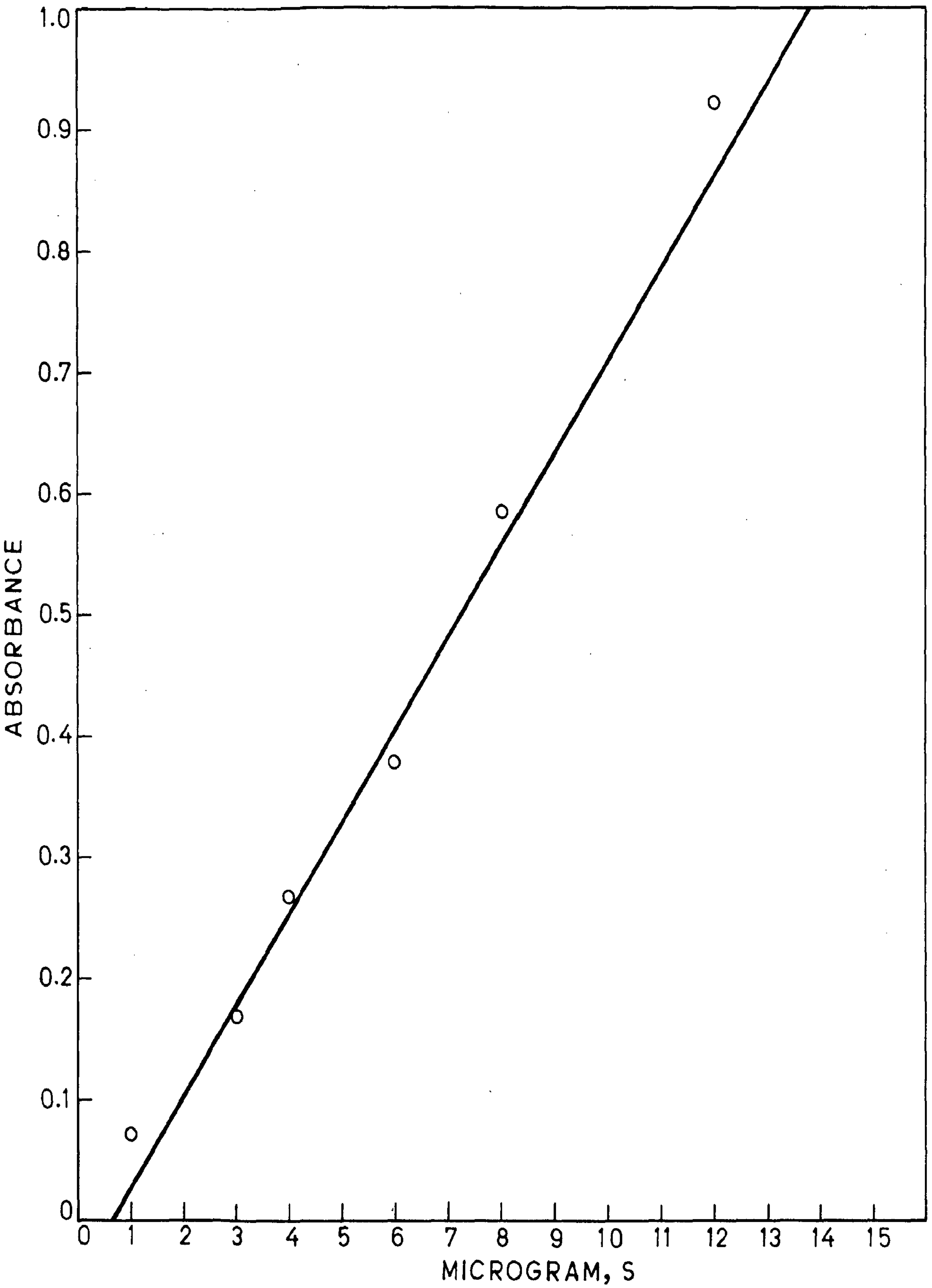

FIG. II.4 STANDARDISATION PLOT BETWEEN ABSORBANCE AND MICROGRAM OF SULPHUR.

against a blank run. A standard curve shown in Fig. II.4 was thus prepared by plotting microgram of sulphur against absorbance by adopting the same procedure for all other samples of the standard potassium sulphate, referred to above.

II. 4.4 Analysis of Metallic Beads

For analysis of equilibrated metallic samples, about 0.2 to 0.5 gm of sample weight, varying with the type of material, was taken and dissolved in redistilled nitric acid or a mixture of hydrochloric acid and nitric acid. In case of the samples containing silver, after dissolution in nitric acid, silver was completely precipitated by adding sufficient quantity of hydrochloric acid and the solution was decanted into a 50 ml distillation flask. The precipitate was washed twice by decantation using 3 ml portions of hydrochloric acid. The decanted solution and the washings were boiled down to 15 ml volume. To this solution, redistilled formic acid was added to destroy nitric acid. The solution was then boiled down to 1 to 2 ml volume on bunsen flame to expel formic acid. To this, 10 ml HCl was added and boiled down to 5 ml. This solution was then allowed to cool down to room temperature and analysis of sulphur present in it carried out using hydriodic-hypophosphorus acid mixture as in case of standard samples.

In case of samples of lead, dissolution was achieved in nitric acid with gentle heating and the solution so obtained was boiled down to 1 ml. 15 ml of HCl was added to this solution which was treated with formic acid to destroy nitrates on heating. The solution was boiled down to 5 ml and further addition of 15 ml of HCl was made. This solution was then analysed for its sulphur content using hydriodic-hypophosphorous acid mixture as in case of other samples. Lead-copper alloys were dissolved in a mixture of hydrochloric acid and nitric acid. However, pure copper was dissolved in nitric acid.

CHAPTER - III

RESULTS AND DISCUSSION

III. 1 Results

The results of equilibria runs of H_2S - H_2 gaseous mixture with pure lead, copper, silver and their binary and ternary alloys are given in Tables III.1 - III.33.

TABLE-III.1 : Amount of sulphur dissolved in pure lead at different $\frac{p_{H_2S}}{p_{H_2}}$ ratios and temperatures.

Sample No.	Temp °K.	$\frac{p_{H_2S}}{p_{H_2}} \times 10^4$	at % S	$\ln\left(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{at\%S}\right)$
P_3	723	0.2857	0.073	-7.8458
P_4		0.333	0.091	-7.913
P_5		0.4872	0.125	-7.85
P_7		0.572	0.147	-7.85
P_9	773	0.3342	0.0565	-7.433
P_{12}		0.4138	0.0701	-7.4334
P_{13}		0.5667	0.096	-7.435
P_{15}		0.7486	0.127	-7.4363
P_{16}	823	0.409	0.048	-7.068
P_{21}		0.5117	0.06	-7.067
P_{22}		0.7006	0.082	-7.066
P_{24}		0.9405	0.11	-7.0644
P_{25}	873	0.4289	0.0375	-6.773
P_{27}		0.527	0.046	-6.77
P_{28}		0.7286	0.0634	-6.768
P_{30}		0.957	0.083	-6.7685
P_{32}	923	0.4868	0.032	-6.4882
P_{33}		0.5948	0.039	-6.4856
P_{34}		0.8202	0.0535	-6.48
P_{36}		1.08	0.07	-6.474

TABLE-III.2 : Amount of sulphur dissolved in pure copper at different p_{H_2S}/p_{H_2} ratios and temperatures.

Sample No.	Temp. °K	$\frac{p_{H_2S}}{p_{H_2}} \times 10^4$	at % S	$\ln\left(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{at \% S}\right)$
C_6	1423	2.88	0.145	-6.22
C_7		7.047	0.337	-6.17
C_9		12.457	0.65	-6.25
C_{10}		16.947	1.02	-6.40
C_{12}		26.33	1.70	-6.47
C_{14}		28.57	2.275	-6.680
C_{15}	1473	2.974	0.12	-6.00
C_{16}		6.794	0.30	-6.09
C_{18}		13.59	0.65	-6.17
C_{21}		25.835	1.325	-6.24
C_{22}		31.84	1.95	-6.442
C_{23}	1523	10.59	0.425	-5.995
C_{24}		24.86	1.25	-6.22
C_{25}		34.90	1.79	-6.40
C_{27}		38.70	2.40	-6.43

TABLE-III.3 : Amount of sulphur dissolved in pure silver at different p_{H_2S}/p_{H_2} ratios and temperatures.

Sample No.	Temp. °K	$\frac{p_{H_2S}}{p_{H_2}} \times 10^4$	at % S	$\ln(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{\text{at \%S}})$
A_3	1273	0.4887	0.0014	-3.356
A_5		1.234	0.00355	-3.359
A_6		2.136	0.0062	-3.368
A_7		3.276	0.00937	-3.353
A_8		4.401	0.0129	-3.378
A_9	1323	0.352	0.0011	-3.442
A_{10}		0.648	0.0020	-3.429
A_{12}		1.988	0.00635	-3.464
A_{13}		3.296	0.0102	-3.432
A_{14}		4.15	0.0132	-3.459
A_{15}	1373	0.4008	0.00137	-3.531
A_{16}		1.482	0.0049	-3.498
A_{18}		1.97	0.0067	-3.526
A_{19}		2.874	0.00973	-3.522
A_{20}		3.17	0.0106	-3.5097.

TABLE-III.4 : Amount of sulphur dissolved in binary Pb-Ag alloy(N_{Pb}0.92, N_{Ag}0.18)at different p_{H_2S} / p_{H_2} ratios and temperatures.

Sample No.	Temp°K	$\frac{p_{H_2S}}{p_{H_2}} \times 10^4$	at % S	$\ln(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{\text{at \% S}})$
PA_1	1273	4.711	0.056	-4.778
PA_3		9.86	0.115	-4.759
PA_4		16.079	0.184	-4.74
PA_5		21.54	0.234	-4.688
PA_6	1323	5.778	0.068	-4.768
PA_7		10.9148	0.130	-4.78
PA_9		17.19	0.189	-4.70
PA_{12}		21.01	0.231	-4.70
PA_{13}		27.263	0.288	-4.66
PA_{14}	1373	4.2577	0.047	-4.704
PA_{15}		10.9132	0.113	-4.64
PA_{16}		15.8386	0.164	-4.64
PA_{17}		24.6904	0.236	-4.56
PA_{18}		40.1203	0.354	-4.48

TABLE-III.5 : Amount of sulphur dissolved in binary Pb-Ag alloy(N_{Pb}, 0.824, N_{Ag} 0.176) at different p_{H_2S}/p_{H_2} ratios and temperatures.

Sample No.	Temp ^oK	$\frac{p_{H_2S}}{p_{H_2}} \times 10^4$	at % S	$\ln(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{at\ \%\ S})$
PA_{19}	1273	3.27	0.028	-4.450
PA_{20}		7.057	0.058	-4.409
PA_{21}		10.71	0.089	-4.42
PA_{22}		15.59	0.1245	-4.38
PA_{23}	1323	5.4825	0.054	-4.59
PA_{24}		12.4693	0.118	-4.55
PA_{27}		19.5323	0.187	-4.54
PA_{28}		29.8359	0.274	-4.52
PA_{30}		37.8534	0.3575	-4.548
PA_{31}	1373	6.46	0.057	-4.48
PA_{32}		11.48	0.0966	-4.433
PA_{34}		16.2061	0.132	-4.40
PA_{35}		24.858	0.198	-4.378
PA_{36}		31.0754	0.236	-4.33

TABLE-III.6 : Amount of sulphur dissolved in binary Pb-Ag alloy(N_{Pb}.0.61,N_{Ag}0.39) at different p_{H_2S}/p_{H_2} ratios and temperatures.

Sample No.	Temp °K	$\frac{p_{H_2S}}{p_{H_2}} \times 10^4$	at % S	$\ln(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{\text{at \%S}})$
PA_{40}	1273	3.9	0.018	-3.832
PA_{41}		9.716	0.044	-3.813
PA_{42}		14.40	0.067	-3.84
PA_{45}		19.412	0.088	-3.814
PA_{46}		24.858	0.116	-3.843
PA_{48}	1323	7.1903	0.047	-4.18
PA_{49}		17.9487	0.115	-4.16
PA_{50}		27.3286	0.1744	-4.156
PA_{52}		40.6940	0.266	-4.18
PA_{54}		55.8499	0.368	-4.188
PA_{56}	1373	10.613	0.068	-4.16
PA_{57}		18.764	0.113	-4.098
PA_{59}		24.03	0.145	-4.10
PA_{60}		33.787	0.192	-4.04
PA_{61}		43.687	0.239	-4.002

TABLE-III.7 : Amount of sulphur dissolved in binary Pb-Ag alloy (N_{Pb} 0.438, N_{Ag} 0.562) at different p_{H_2S}/p_{H_2} ratios and temperatures.

Sample No.	Temp°K	$\frac{p_{H_2S}}{p_{H_2}} \times 10^4$	at % S	$\ln\left(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{at\%S}\right)$
PA_{62}	1273	7.327	0.026	-3.569
PA_{63}		11.48	0.053	-3.60
PA_{65}		22.18	0.082	-3.61
PA_{66}		28.96	0.106	-3.60
PA_{68}		35.178	0.134	-3.64
PA_{69}	1323	11.2226	0.056	-3.91
PA_{72}		26.186	0.136	-3.95
PA_{73}		38.108	0.194	-3.93
PA_{75}		50.053	0.266	-3.973
PA_{77}		62.378	0.344	-4.01
PA_{79}	1373	9.9033	0.053	-3.98
PA_{81}		14.1014	0.07309	-3.948
PA_{82}		26.1701	0.128	-3.89
PA_{83}		30.687	0.148	-3.88
PA_{84}		50.4978	0.228	-3.81

TABLE-III.8 : Amount of sulphur dissolved in binary Pb-Ag alloy ($N_{Pb.}$ 0.283, N_{Ag} 0.717) at different p_{H_2S}/p_{H_2} ratios and temperatures.

Sample No.	Temp °K	$\frac{p_{H_2S}}{p_{H_2}} \times 10^7$	at % S	$\ln\left(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{\text{at } \% S}\right)$
PA_{86}	1273	10.474	0.034	-3.48
PA_{87}		19.75	0.067	-3.524
PA_{88}		27.879	0.094	-3.518
PA_{90}		46.457	0.165	-3.57
PA_{91}	1323	16.6111	0.075	-3.81
PA_{93}		24.6078	0.110	-3.80
PA_{94}		30.6870	0.138	-3.806
PA_{95}		38.285	0.176	-3.878
PA_{96}		44.2197	0.212	-3.87
PA_{99}	1373	10.474	0.0476	-3.818
PA_{100}		14.1041	0.064	-3.815
PA_{102}		22.18	0.966	-3.774
PA_{103}		27.3651	0.118	-3.764
PA_{104}		43.3303	0.1788	-3.72

TABLE-III.9 : Amount of sulphur dissolved in binary Pb-Ag alloy (N_{Pb} 0.148, N_{Ag} 0.852) at different p_{H_2S}/p_{H_2} ratios and temperatures.

Sample No.	Temp °K	$\frac{p_{H_2S}}{p_{H_2}} \times 10^4$	at % S	$\ln(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{at\ \%S})$
PA_{105}	1273	4.168	0.013	-3.44
PA_{106}		14.428	0.046	-3.462
PA_{107}		23.625	0.076	-3.471
PA_{109}		33.27	0.108	-3.48
PA_{110}		36.736	0.123	-3.511
PA_{111}	1323	13.38	0.052	-3.66
PA_{112}		22.3812	0.089	-3.683
PA_{114}		31.504	0.1301	-3.72
PA_{115}		42.03	0.1702	-3.70
PA_{116}		48.652	0.2101	-3.765
PA_{118}		55.335	0.236	-3.753
PA_{119}	1373	9.3949	0.038	-3.70
PA_{120}		18.583	0.072	-3.657
PA_{122}		27.1391	0.104	-3.646
PA_{124}		39.425	0.144	-3.598
PA_{126}		49.1991	0.173	-3.56

TABLE-III.10 : Amount of sulphur dissolved in binary Pb-Cu alloys (N_{Pb}0.92, N_{Cu}0.18) at different p_{H_2S}/p_{H_2} ratios and temperatures.

Sample No.	Temp°K	$\frac{p_{H_2S}}{p_{H_2}} \times 10^4$	at % S	$\ln(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{at\ \%S})$
PC_4	1273	3.837	0.108	-5.64
PC_5		8.8997	0.248	-5.63
PC_6		15.681	0.414	-5.576
PC_7		22.484	0.596	-5.58
PC_8		29.803	0.744	-5.52
PC_9	1323	4.573	0.13	-5.65
PC_{10}		12.338	0.335	-5.604
PC_{12}		18.759	0.528	-5.64
PC_{13}		26.216	0.704	-5.593
PC_{16}	1373	10.337	0.274	-5.58
PC_{18}		15.421	0.38	-5.507
PC_{19}		22.051	0.556	-5.53
PC_{21}		29.536	0.707	-5.478

TABLE-III.11 : Amount of sulphur dissolved in binary Pb-Cu alloys (N_{Pb}0.734, N_{Cu}0.266) at different p_{H_2S}/p_{H_2} ratios and temperatures.

Sample No.	Temp °K	$\frac{p_{H_2S}}{p_{H_2}} \times 10^4$	at % S	$\ln(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{\text{at } \% S})$
PC_{22}	1273	1.8149	0.106	-6.37
PC_{24}		4.28	0.250	-6.37
PC_{26}		7.3126	0.412	-6.334
PC_{27}		9.269	0.536	-6.36
PC_{28}		12.167	0.676	-6.32
PC_{29}	1323	2.967	0.184	-6.43
PC_{30}		5.586	0.343	-6.42
PC_{32}		8.109	0.492	-6.408
PC_{34}		10.846	0.67	-6.426
PC_{36}	1373	3.067	0.196	-6.46
PC_{38}		6.288	0.39	-6.43
PC_{42}		9.435	0.584	-6.428
PC_{45}		14.279	0.868	-6.41

TABLE-III.12 : Amount of sulphur dissolved in Pb-Cu binary alloy (N_{Pb}0.417, N_{Cu}0.583) at different p_{H_2S}/p_{H_2} ratios and temperatures.

Sample No.	Temp°K	$\frac{p_{H_2S}}{p_{H_2}} \times 10^4$	at % S	$\ln(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{\text{at \%S}})$
PC_{46}	1273	1.1078	0.09	-6.70
PC_{47}		3.101	0.254	-6.708
PC_{49}		4.681	0.388	-6.720
PC_{50}		6.421	0.55	-6.753
PC_{52}		8.329	0.736	-6.784
PC_{53}	1323	1.264	0.092	-6.59
PC_{54}		3.387	0.254	-6.62
PC_{57}		5.926	0.448	-6.628
PC_{58}		8.363	0.666	-6.68
PC_{59}		10.906	0.894	-6.709
PC_{60}	1373	1.524	0.108	-6.63
PC_{61}		3.45	0.272	-6.67
PC_{62}		5.557	0.456	-6.71
PC_{63}		8.284	0.673	-6.70
PC_{65}		10.703	0.896	-6.73

TABLE-III.13 : Amount of sulphur dissolved in binary Pb-Cu alloy (N_{Pb}0.28, N_{Cu}0.72) at different p_{H_2S}/p_{H_2} ratios and temperatures.

Sample No.	Temp. °K	$\frac{p_{H_2S}}{p_{H_2}} \times 10^4$	at % S	$\ln(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{at\ \%S})$
PC_{66}	1273	1.332	0.104	-6.66
PC_{69}		2.913	0.232	-6.68
PC_{70}		4.621	0.368	-6.68
PC_{72}		6.354	0.508	-6.684
PC_{73}		7.9317	0.664	-6.73
PC_{76}	1323	2.169	0.156	-6.578
PC_{79}		4.081	0.300	-6.60
PC_{80}		6.475	0.476	-6.60
PC_{81}		8.187	0.614	-6.62
PC_{82}		10.477	0.826	-6.67
PC_{84}	1373	2.109	0.152	-6.58
PC_{85}		4.814	0.35	-6.589
PC_{87}		7.074	0.55	-6.656
PC_{89}		10.95	0.872	-6.68

TABLE-III.14 : Amount of sulphur dissolved in binary Pb-Cu alloy (N_{Pb}0.17, N_{Cu}0.83) at different p_{H_2S}/p_{H_2} ratios and temperatures.

Sample No.	Temp. °K	$\frac{p_{H_2S}}{p_{H_2}}\times 10^4$	at % S	$\ln(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{at\ \%S})$
PC_{90}	1273	1.6207	0.124	-6.64
PC_{91}		4.0456	0.308	-6.635
PC_{93}		5.566	0.425	-6.638
PC_{94}		7.431	0.568	-6.639
PC_{97}		10.33	0.788	-6.637
PC_{98}	1323	1.925	0.136	-6.56
PC_{99}		4.385	0.316	-6.58
PC_{100}		6.063	0.436	-6.578
PC_{102}		8.017	0.580	-6.584
PC_{104}		10.467	0.785	-6.62
PC_{106}	1373	1.656	0.108	-6.48
PC_{107}		3.900	0.262	-6.51
PC_{109}		7.015	0.468	-6.503
PC_{111}		9.08	0.633	-6.547
PC_{114}		12.046	0.868	-6.58

TABLE-III.15 : Amount of sulphur dissolved in binary Pb-Cu alloy (N_{Pb} 0.093, N_{Cu} 0.907) at different p_{H_2S}/p_{H_2} ratios and temperatures.

Sample No.	Temp. °K	$\frac{p_{H_2S}}{p_{H_2}} \times 10^4$	at % S	$\ln(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{\text{at \% S}})$
PC_{115}	1273	1.0134	0.076	-6.62
PC_{118}		2.7349	0.208	-6.634
PC_{120}		4.3393	0.332	-6.64
PC_{121}		6.2214	0.476	-6.64
PC_{124}		9.0817	0.716	-6.67
PC_{127}	1323	2.2989	0.156	-6.52
PC_{129}		4.8822	0.328	-6.51
PC_{130}		7.3794	0.516	-6.55
PC_{131}		9.686	0.676	-6.548
PC_{134}		12.0277	0.836	-6.544
PC_{135}	1373	1.8125	0.108	-6.39
PC_{137}		5.0162	0.308	-6.42
PC_{140}		8.3387	0.512	-6.42
PC_{141}		11.6218	0.728	-6.44
PC_{145}		14.3335	0.916	-6.46

TABLE-III.16 : Amount of sulphur dissolved in binary Cu/Ag alloy (N_{Cu}0.83,N_{Ag}0.17) at different p_{H_2S}/p_{H_2} ratios and temperatures.

Sample No.	Temp. °K	$\frac{p_{H_2S}}{p_{H_2}} \times 10^4$	at % S	$\ln(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{\text{at \% S}})$
CA_6	1273	0.7233	0.038	-6.264
CA_7		1.1715	0.0638	-6.30
CA_9		1.6159	0.088	-6.30
CA_{10}		2.0879	0.116	-6.32
CA_{12}		2.6222	0.147	-6.329
CA_{13}		3.2283	0.179	-6.318
CA_{14}	1323	0.4656	0.024	-6.245
CA_{16}		1.0539	0.054	-6.239
CA_{17}		1.5894	0.084	-6.27
CA_{19}		2.1963	0.1183	-6.289
CA_{21}		2.7085	0.1475	-6.30
CA_{23}	1373	0.4979	0.024	-6.178
CA_{24}		1.2105	0.058	-6.172
CA_{26}		1.7821	0.0872	-6.193
CA_{27}		2.5718	0.128	-6.21
CA_{30}		3.2471	0.160	-6.20

TABLE-III.17 : Amount of sulphur dissolved in binary Cu-Ag alloy (N_{Cu} 0.759, N_{Ag} 0.241) at different p_{H_2S}/p_{H_2} ratios and temperatures.

Sample No.	Temp. °K	$\frac{p_{H_2S}}{p_{H_2}} \times 10^4$	at %. S	$\ln(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{at\ \%S})$
CA_{31}	1273	0.6692	0.032	-6.17
CA_{32}		1.3357	0.064	-6.172
CA_{34}		2.0557	0.0985	-6.172
CA_{36}		2.7353	0.1295	-6.16
CA_{39}		3.3584	0.159	-6.16
CA_{41}	1323	0.5838	0.0272	-6.144
CA_{42}		1.2136	0.0585	-6.178
CA_{45}		1.9242	0.0935	-6.186
CA_{46}		2.5875	0.1275	-6.20
CA_{48}		3.2232	0.1635	-6.229
CA_{51}	1373	0.7177	0.032	-6.10
CA_{53}		1.5174	0.0682	-6.108
CA_{55}		2.2770	0.1078	-6.16
CA_{56}		3.1050	0.147	-6.16
CA_{59}		3.8077	0.1767	-6.14

TABLE-III.18 : Amount of sulphur dissolved in binary Cu-Ag alloy (N_{Cu}0.675, N_{Ag}0.325) at different p_{H_2S}/p_{H_2} ratios and temperatures.

Sample No.	Temp. °K	$\frac{p_{H_2S}}{p_{H_2}} \times 10^4$	at % S	$\ln(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{at\ \%S})$
CA_{62}	1273	1.0959	0.0362	-5.80
CA_{63}		1.8160	0.074	-6.01
CA_{65}		3.2697	0.108	-5.80
CA_{67}		3.5446	0.143	-6.00
CA_{70}		4.3314	0.1765	-6.01
CA_{72}	1323	0.8294	0.0338	-6.01
CA_{73}		1.7126	0.0722	-6.044
CA_{74}		2.4277	0.104	-6.06
CA_{76}		3.3031	0.1415	-6.06
CA_{77}		3.9803	0.175	-6.086
CA_{78}	1373	0.6878	0.028	-6.009
CA_{81}		1.4378	0.059	-6.017
CA_{82}		2.3432	0.098	-6.036
CA_{85}		3.3359	0.1373	-6.02
CA_{87}		4.2037	0.179	-6.054

TABLE-III.19 : Amount of sulphur dissolved in binary Cu-Ag alloy (N_{Cu}0.4775, N_{Ag}0.5225) at different p_{H_2S}/p_{H_2} ratios and temperatures.

Sample No.	Temp. °K	$\frac{p_{H_2S}}{p_{H_2}} \times 10^4$	at % S	$\ln(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{\text{at \% S}})$
CA_{88}	1273	1.0555	0.023	-5.384
CA_{90}		2.3173	0.049	-5.354
CA_{91}		3.5127	0.077	-5.39
CA_{93}		5.265	0.112	-5.36
CA_{96}		7.0786	0.1583	-5.41
CA_{99}	1323	1.2169	0.032	-5.572
CA_{100}		2.565	0.068	-5.58
CA_{101}		3.7903	0.1025	-5.60
CA_{102}		5.3186	0.1424	-5.59
CA_{105}		6.3702	0.174	-5.61
CA_{106}	1373	0.9368	0.028	-5.70
CA_{108}		2.1041	0.0639	-5.716
CA_{110}		3.3789	0.102	-5.71
CA_{112}		4.2885	0.1334	-5.74
CA_{113}		5.5361	0.1688	-5.72

TABLE-III.20 : Amount of sulphur dissolved in binary Cu-Ag alloy (N_{Cu} 0.3614, N_{Ag} 0.6386) at different p_{H_2S}/p_{H_2} ratios and temperatures.

Sample No.	Temp. °K	$\frac{p_{H_2S}}{p_{H_2}} \times 10^4$	at % S	$\ln(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{at\ \%S})$
CA$_{115}$	1273	2.0234	0.028	-4.93
CA$_{116}$		3.9457	0.057	-4.973
CA$_{120}$		6.9414	0.0978	-4.948
CA$_{122}$		9.3833	0.1338	-4.96
CA$_{124}$		11.7631	0.1674	-4.958
CA$_{127}$	1323	1.5222	0.0263	-5.152
CA$_{128}$		3.3704	0.058	-5.148
CA$_{130}$		5.0089	0.089	-5.18
CA$_{132}$		7.0268	0.1284	-5.208
CA$_{133}$		8.9757	0.165	-5.214
CA$_{136}$	1373	1.8779	0.038	-5.31
CA$_{138}$		3.8163	0.078	-5.32
CA$_{139}$		5.5190	0.1128	-5.32
CA$_{140}$		7.4858	0.147	-5.28
CA$_{141}$		8.9716	0.183	-5.318

TABLE-III.21 : Amount of sulphur dissolved in binary Cu-Ag alloy (N_{Cu} 0.095, N_{Ag} 0.905) at different p_{H_2S}/p_{H_2} ratios and temperatures.

Sample No.	Temp. °K	$\frac{p_{H_2S}}{p_{H_2}} \times 10^4$	at % S	$\ln(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{\text{at \% S}})$
CA_{145}	1273	4.384	0.023	-3.96
CA_{146}		11.247	0.059	-3.96
CA_{148}		16.032	0.0893	-4.02
CA_{149}		23.107	0.128	-4.01
CA_{150}		29.603	0.173	-4.068
CA_{151}	1323	4.011	0.023	-4.049
CA_{153}		10.045	0.059	-4.073
CA_{155}		16.231	0.096	-4.08
CA_{158}		20.705	0.1324	-4.158
CA_{161}		26.298	0.1685	-4.16
CA_{162}	1373	4.398	0.0279	-4.15
CA_{163}		9.208	0.059	-4.16
CA_{166}		17.247	0.1016	-4.076
CA_{169}		22.625	0.139	-4.118

TABLE-III.22 : Amount of sulphur dissolved in **ternary** Pb-Cu-Ag alloy (0.135 N_{Pb}, 0.7407 N_{Cu}, 0.1243 N_{Ag}) at different p_{H_2S}/p_{H_2} ratios and temperatures.

Sample No.	Temp. °K	$\frac{p_{H_2S}}{p_{H_2}} \times 10^4$	at % S	$\ln\left(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{\text{at \% S}}\right)$
TA_3	1273	1.453	0.088	-6.406
TA_5		2.1845	0.132	-6.404
TA_6		3.241	0.203	-6.44
TA_7		3.951	0.2475	-6.44
TA_9		4.780	0.2343	-6.52
TA_{10}	1323	1.47	0.0785	-6.28
TA_{12}		2.157	0.114	-6.27
TA_{14}		2.565	0.1383	-6.297
TA_{18}		3.097	0.167	-6.29
TA_{21}	1373	1.1282	0.057	-6.225
TA_{22}		1.5481	0.081	-6.26
TA_{24}		2.0641	0.108	-6.26
TA_{27}		2.88	0.148	-6.242
TA_{30}		3.375	0.178	-6.268

TABLE-III.23 : Amount of sulphur dissolved in ternary Pb-Cu-Ag alloy (N_{Pb} 0.27, N_{Cu} 0.6327, N_{Ag} 0.0937) at different p_{H_2S}/p_{H_2} ratios and temperatures.

Sample No.	Temp. °K	$\frac{p_{H_2S}}{p_{H_2}} \times 10^4$	at % S	$\ln\left(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{\text{at \% S}}\right)$
TA_{32}	1273	1.1494	0.066	-6.353
TA_{33}		1.972	0.112	-6.342
TA_{35}		2.808	0.164	-6.37
TA_{36}		3.376	0.198	-6.374
TA_{37}	1323	1.38	0.079	-6.35
TA_{39}		1.658	0.094	-6.34
TA_{42}		2.098	0.1182	-6.334
TA_{43}		2.431	0.1382	-6.343
TA_{45}		2.7378	0.158	-6.358
TA_{46}	1373	1.38	0.079	-6.35
TA_{48}		1.9635	0.117	-6.39
TA_{49}		2.493	0.149	-6.393
TA_{52}		2.791	0.168	-6.401

TABLE-III.24 : Amount of sulphur dissolved in ternary Pb-Cu-Ag alloy (N_{Pb} 0.445, N_{Cu} 0.481, N_{Ag} 0.074) at different p_{H_2S}/p_{H_2} ratios and temperatures.

Sample No.	Temp. °K	$\frac{p_{H_2S}}{p_{H_2}} \times 10^4$	at % S	$\ln(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{\text{at \%S}})$
TA_{53}	1273	1.656	0.092	-6.32
TA_{56}		2.411	0.136	-6.335
TA_{57}		2.9287	0.166	-6.34
TA_{58}		3.097	0.178	-6.354
TA_{59}	1323	1.2009	0.073	-6.41
TA_{61}		1.431	0.087	-6.41
TA_{63}		1.8865	0.117	-6.43
TA_{66}		2.2897	0.142	-6.43
TA_{67}		2.531	0.1586	-6.44
TA_{69}	1373	1.4851	0.0978	-6.49
TA_{70}		1.8675	0.128	-6.53
TA_{72}		2.2967	0.159	-6.54
TA_{73}		2.6441	0.186	-6.556

TABLE-III.25 : Amount of sulphur dissolved in ternary Pb-Cu-Ag alloy (N_{Pb} 0.135, N_{Cu} 0.634, N_{Ag} 0.231) at different p_{H_2S}/p_{H_2} ratios and temperatures.

Sample No.	Temp. °K	$\frac{p_{H_2S}}{p_{H_2}} \times 10^4$	at % S	$\ln(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{at\ \%S})$
TA_{74}	1273	1.6357	0.068	-6.03
TA_{76}		2.4286	0.103	-6.05
TA_{78}		3.328	0.144	-6.07
TA_{79}		3.601	0.159	-6.092
TA_{81}	1323	1.3716	0.058	-6.047
TA_{82}		2.1624	0.089	-6.02
TA_{85}		2.747	0.1165	-6.05
TA_{86}		3.601	0.1538	-6.057
TA_{88}	1373	1.564	0.067	-6.06
TA_{92}		2.0316	0.0895	-6.088
TA_{93}		2.539	0.109	-6.062
TA_{95}		2.886	0.1245	-6.067
TA_{96}		3.314	0.146	-6.088

TABLE-III.26 : Amount of sulphur dissolved in ternary Pb-Cu-Ag alloy (N_{Pb} 0.27, N_{Cu} 0.5353, N_{Ag} 0.1947) at different p_{H_2S}/p_{H_2} ratios and temperatures.

Sample No.	Temp. °K	$\frac{p_{H_2S}}{p_{H_2}} \times 10^4$	at % S	$\ln(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{\text{at \% S}})$
TA_{99}	1273	1.2825	0.052	-6.005
TA_{102}		2.041	0.084	-6.02
TA_{103}		3.1595	0.134	-6.05
TA_{104}		3.652	0.155	-6.051
TA_{105}	1323	1.212	0.0535	-6.09
TA_{106}		1.7968	0.079	-6.086
TA_{109}		2.537	0.112	-6.09
TA_{110}		3.573	0.1593	-6.10
TA_{111}	1373	1.325	0.062	-6.148
TA_{114}		1.7885	0.083	-6.14
TA_{115}		2.264	0.103	-6.12
TA_{117}		2.656	0.123	-6.138
TA_{118}		3.0416	0.144	-6.16

TABLE-III.27 : Amount of sulphur dissolved in ternary Pb-Cu-Ag alloy (N_{Pb} 0.445, N_{Cu} 0.407, N_{Ag} 0.148) at different p_{H_2S}/p_{H_2} ratios and temperatures.

Sample No.	Temp. °K	$\frac{p_{H_2S}}{p_{H_2}} \times 10^4$	at % S	$\ln(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{\text{at \%S}})$
TA_{119}	1273	1.8066	0.064	-5.87
TA_{123}		3.18	0.096	-5.71
TA_{124}		3.775	0.154	-6.011
TA_{125}		4.7387	0.1872	-5.979
TA_{126}	1323	1.6928	0.077	-6.12
TA_{129}		2.2957	0.1038	-6.114
TA_{130}		3.043	0.1394	-6.127
TA_{132}		3.543	0.1657	-6.148
TA_{135}	1373	1.5843	0.0776	-6.194
TA_{136}		2.0169	0.1018	-6.224
TA_{138}		2.6656	0.134	-6.22
TA_{141}		3.184	0.1638	-6.243

TABLE-III.28 : Amount of sulphur dissolved in ternary Pb-Cu-Ag alloy (N_{Pb} 0.135, N_{Cu} 0.481, N_{Ag} 0.384) at different p_{H_2S}/p_{H_2} ratios and temperatures.

Sample No.	Temp. °K	$\frac{p_{H_2S}}{p_{H_2}} \times 10^4$	at %S	$\ln\left(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{\text{at \% S}}\right)$
TA_{144}	1273	1.3046	0.034	-5.563
TA_{147}		2.5801	0.067	-5.559
TA_{148}		3.244	0.086	-5.58
TA_{149}		4.082	0.108	-5.578
TA_{150}		5.755	0.158	-5.615
TA_{151}	1323	1.324	0.0372	-5.638
TA_{153}		2.216	0.063	-5.65
TA_{154}		2.984	0.084	-5.64
TA_{155}		4.206	0.1184	-5.64
TA_{156}		5.657	0.1644	-5.672
TA_{159}	1373	1.519	0.046	-5.713
TA_{161}		2.066	0.063	-5.72
TA_{163}		2.546	0.0785	-5.731
TA_{164}		3.334	0.101	-5.71

TABLE-III.29 : Amount of sulphur dissolved in ternary Pb-Cu-Ag alloy (N_{Pb} 0.27, N_{Cu} 0.4056, N_{Ag} 0.3244) at different p_{H_2S}/p_{H_2} ratios and temperatures.

Sample No.	Temp. °K	$\frac{p_{H_2S}}{p_{H_2}} \times 10^4$	at % S	$\ln(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{\text{at }\%S})$
TA_{165}	1273	1.232	0.031	-5.528
TA_{166}		2.323	0.058	-5.52
TA_{168}		3.65	0.0923	-5.533
TA_{171}		5.703	0.147	-5.552
TA_{172}	1323	1.929	0.0554	-5.66
TA_{174}		2.823	0.0818	-5.669
TA_{175}		3.886	0.115	-5.69
TA_{178}		4.895	0.144	-5.684
TA_{180}	1373	1.5801	0.0495	-5.753
TA_{181}		2.295	0.0716	-5.743
TA_{183}		3.103	0.0985	-5.76
TA_{184}		3.7498	0.119	-5.76

TABLE-III.30 : Amount of sulphur dissolved in ternary Pb-Cu-Ag alloy (N_{Pb} 0.445, N_{Cu} 0.308, N_{Ag} 0.247) at different p_{H_2S}/p_{H_2} ratios and temperatures.

Sample No.	Temp. °K	$\frac{p_{H_2S}}{p_{H_2}} \times 10^4$	at % S	$\ln(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{\text{at \% S}})$
TA_{185}	1273	1.164	0.028	-5.483
TA_{186}		2.225	0.055	-5.51
TA_{188}		3.652	0.089	-5.496
TA_{192}		4.867	0.122	-5.524
TA_{194}		7.17	0.179	-5.520
TA_{196}	1323	1.779	0.0515	-5.668
TA_{198}		2.409	0.072	-5.70
TA_{199}		2.89	0.087	-5.707
TA_{201}		4.054	0.123	-5.715
TA_{206}	1373	1.33	0.0426	-5.769
TA_{207}		1.808	0.059	-5.788
TA_{209}		2.706	0.0886	-5.791
TA_{210}		3.542	0.117	-5.801

TABLE-III.31 : Amount of sulphur dissolved in ternary Pb-Cu-Ag alloy (N_{Pb} 0.135, N_{Cu} 0.247, N_{Ag} 0.618) at different p_{H_2S}/p_{H_2} ratios and temperatures.

Sample No.	Temp. °K	$\frac{p_{H_2S}}{p_{H_2}} x10^4$	at % S	$\ln(\frac{p_{H_2S}}{p_{H_2}} x \frac{1}{at \%S})$
TA_{213}	1273	2.656	0.028	-4.654
TA_{215}		4.825	0.052	-4.678
TA_{216}		7.5708	0.082	-4.685
TA_{217}		10.45	0.116	-4.709
TA_{218}	1323	1.484	0.0184	-4.82
TA_{221}		2.384	0.0292	-4.808
TA_{222}		3.337	0.042	-4.835
TA_{225}		5.122	0.0635	-4.82
TA_{226}	1373	1.232	0.018	-4.984
TA_{228}		2.368	0.033	-4.937
TA_{229}		3.527	0.0493	-4.94
TA_{231}		4.525	0.062	-4.92
TA_{232}		6.15	0.083	-4.905

TABLE-III.32 : Amount of sulphur dissolved in ternary Pb-Cu-Ag alloy (N_{Pb} 0.27, N_{Cu} 0.2086, N_{Ag} 0.5214) at different p_{H_2S}/p_{H_2} ratios and temperatures.

Sample No.	Temp. °K	$\frac{p_{H_2S}}{p_{H_2}} \times 10^4$	at % S	$\ln(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{at\ \%\ S})$
TA_{234}	1273	1.16	0.012	-4.64
TA_{235}		2.308	0.024	-4.644
TA_{239}		3.792	0.0397	-4.651
TA_{240}		6.551	0.069	-4.657
TA_{241}		9.37	0.1023	-4.693
TA_{242}	1323	2.622	0.0335	-4.85
TA_{244}		3.726	0.0475	-4.848
TA_{246}		5.353	0.069	-4.859
TA_{247}		6.69	0.087	-4.868
TA_{248}	1373	1.604	0.024	-5.008
TA_{250}		2.938	0.0427	-4.979
TA_{253}		4.177	0.062	-5.001
TA_{254}		6.177	0.0895	-4.976
TA_{257}		7.563	0.1098	-4.978

TABLE-III.33 : Amount of sulphur dissolved in ternary Pb-Cu-Ag alloy (N_{Pb} 0.445, N_{Cu} 0.1586, N_{Ag} 0.3964) at different p_{H_2S}/p_{H_2} ratios and temperatures.

Sample No.	Temp. °K	$\frac{p_{H_2S}}{p_{H_2}} x10^4$	at % S	$\ln(\frac{p_{H_2S}}{p_{H_2}} x \frac{1}{at\% S})$
TA_{261}	1273	1.7807	0.0182	-4.627
TA_{262}		2.759	0.028	-4.62
TA_{263}		5.11	0.052	-4.623
TA_{264}		7.845	0.0818	-4.647
TA_{268}		10.45	0.1081	-4.639
TA_{269}	1323	1.6276	0.021	-4.86
TA_{270}		2.751	0.0355	-4.86
TA_{271}		4.78	0.0645	-4.905
TA_{273}		6.537	0.0892	-4.916
TA_{276}	1373	1.9101	0.029	-5.022
TA_{277}		3.242	0.049	-5.018
TA_{278}		4.893	0.074	-5.0187
TA_{281}		6.495	0.098	-5.0165

III.2 Calculations and Discussion of Results

Equilibration of sulphur between a gaseous phase containing a mixture of hydrogen and hydrogen sulphide, and any solvent, X, which may either be a pure metal or an alloy, can be expressed by the following chemical equation:

$$\underline{S}(X) + H_2 = H_2S \qquad \ldots \text{(III.1)}$$

where, the symbol $\underline{S}(X)$ refers to the sulphur dissolved in the solvent X. Since the solubility of sulphur in metals and alloys is observed to be low, one can consider the resulting solutions, on dissolution of sulphur in respective solvents, as dilute solutions of sulphur . One can, therefore, work with Henrian activities with any standard state, because of ease of its conversion to 'infinite dilution' and '1 wt %' standard states.

III.2.1 Sulphur in pure Molten Metals

Assuming 1 at % S as standard state, one can write the following expression for equilibrium constant, $K_{HS}(X)$, for eq. (III.1),

$$K_{HS}(X) = \frac{p_{H_2S}}{p_{H_2} \cdot h_{S(X)}} \qquad \ldots \text{(III.2)}$$

$$= \frac{p_{H_2S}}{p_{H_2} \cdot f_{S(X)} \cdot (\text{at } \% \text{ S})} \qquad \ldots \text{(III.3)}$$

where, p_{H_2S} and p_{H_2} are respectively the partial pressures of hydrogen sulphide and hydrogen in the gaseous phase and $h_{S(X)}$, $f_{S(X)}$, and at % S are respectively the Henrian activity, Henrian activity coefficient and percent sulphur dissolved in the pure molten metal. In the above expressions, fugacities of different gases have been substituted by their partial pressures.

In logrithmic form, the above expression may be written as,

$$\Delta G^o_{HS(X)}/_{RT} = -\ln\left[\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{(\text{at }\%S)}\right] + \ln f_{S(X)}$$

$$= -\ln\left[\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{(\text{at }\%S)}\right] + \varepsilon^S_S.(\text{at }\%S) \qquad \ldots \text{(III.4)}$$

where, $\Delta G^o_{HS(X)}$ is the free energy of equilibration of sulphur in solvent ie, in the pure metallic solvent referred to 1 at %S as standard state and ε^S_S, the self interaction parameter of sulphur in solvent X, defined by the following expression,

$$\varepsilon^S_S = \left[\frac{\partial \ln f_{S(X)}}{\partial\,(\text{at }\%S)}\right]_{\text{at }\%S \rightarrow 0} \qquad \ldots \text{(III.5)}$$

As seen from eq. (III.4), if ε^S_S is independent of the sulphur content of solution, the plot of function $[-\ln(\frac{p_{H_2S}}{p_{H_2}} x \frac{1}{\text{at }\%S})]$ Vs. (at %S) should be a straight line. One can therefore calculate the values of $\Delta G^o_{HS(X)}$ and ε^S_S from such linear plots. In the following analysis, such plots shall be drawn from the experimental data, already reported for the different pure metallic solvents.

III. 2.1.1 Sulphur in Pure Lead Solvent

In Fig. III.1, function $[-\ln(p_{H_2S}/p_{H_2} \cdot 1/\text{at.}\%S)]$, calculated from the experimental data reported in Table-III.1, is plotted against at.%S at different temperatures viz., 723, 773, 823, 873 and 923°K of study of equilibration in the solvent lead. Further, linear regression analysis of the data plotted at different temperatures yields, the following expressions ,

i) At 723°K

$$\ln\left(\frac{p_{H_2S}}{p_{H_2}} \cdot \frac{1}{\text{at }\%S}\right) = -\ 7.84 - 0.08\ x(\text{at }\%S) \qquad \dots\ (III.6)$$

ii) At 773°K

$$\ln\left(\frac{p_{H_2S}}{p_{H_2}} \cdot \frac{1}{\text{at }\%S}\right) = -\ 7.43 - 0.05\ x(\text{at }\%S) \qquad \dots\ (III.7)$$

iii) At 823°K

$$\ln\left(\frac{p_{H_2S}}{p_{H_2}} \cdot \frac{1}{\text{at }\%S}\right) = -\ 7.07 + 0.05\ x(\text{at }\%S) \qquad \dots\ (III.8)$$

iv) At 873°K

$$\ln\left(\frac{p_{H_2S}}{p_{H_2}} \cdot \frac{1}{\text{at }\%S}\right) = -\ 6.78 + 0.18\ x(\text{at }\%S) \qquad \dots\ (III.9)$$

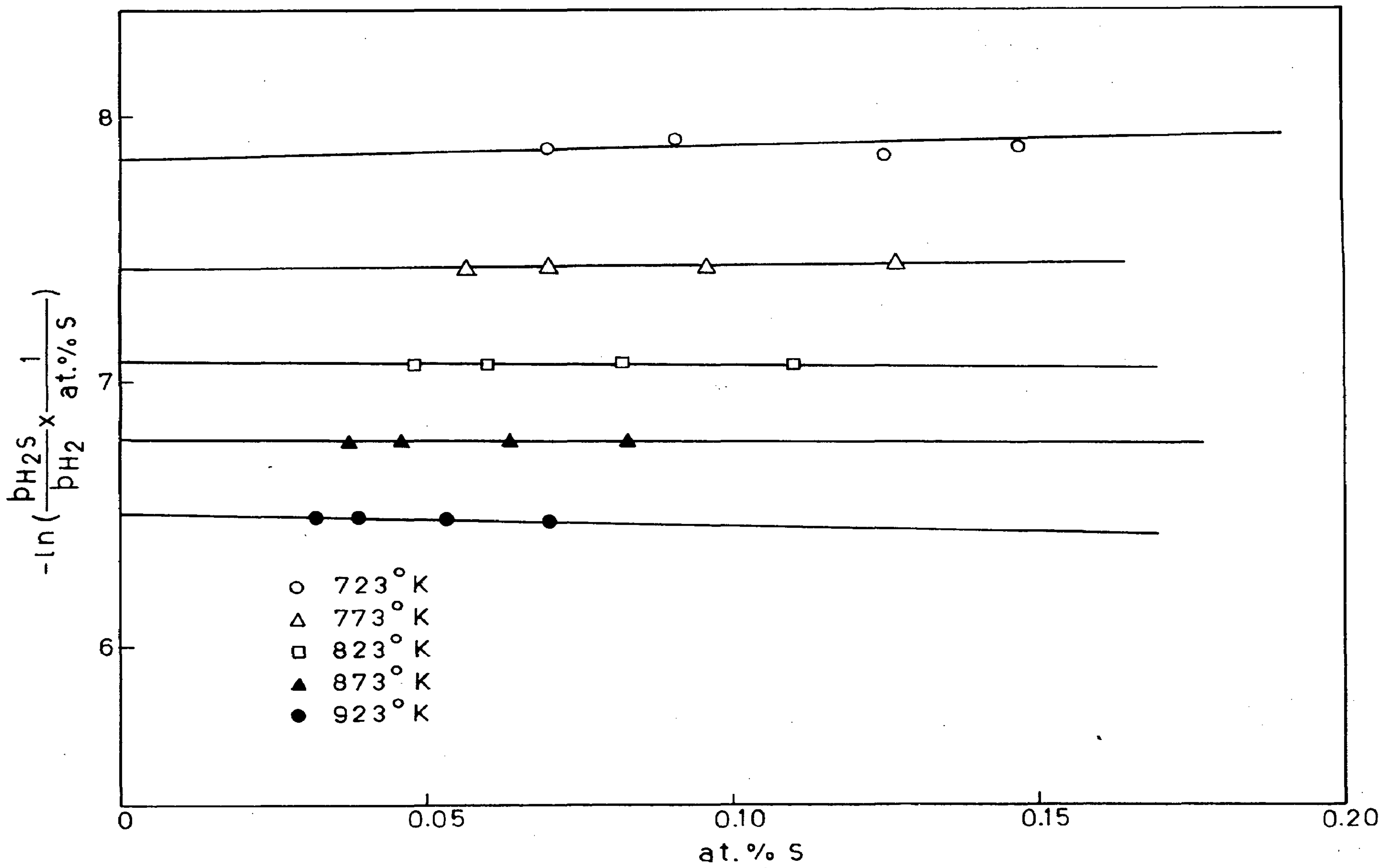

FIG. III.1 PLOT OF FUNCTION $\left[-\ln\left(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{\text{at.\% S}}\right)\right]$ Vs. at.% S FOR DISSOLUTION OF SULPHUR IN PURE LEAD AT DIFFERENT TEMPERATURES.

and, v) at 923°K,

$$\ln\left(\frac{p_{H_2S}}{p_{H_2}} \cdot \frac{1}{\text{at } \% S}\right) = -6.50+0.37 \times (\text{at } \% S) \qquad \ldots (III.10)$$

A comparison of above expressions with eq. (III.4) yields respectively 11248, 11416, 11584, 11751 and 11919 cals values of $\Delta G^{o}_{HS(Pb)}$ for the equilibration reaction (III.1) and -0.08, -0.05, 0.05, 0.18 and 0.37 as the respective values for self interaction parameter, ε_S^S, at the different temperatures of study viz., 723, 773, 823, 873 and 923°K.

The free energy of reaction,

$$H_2(g) + 1/2\ S_2(g) = H_2S(g) \qquad \ldots (III.11)$$

is known to be given by the following expression

$$\Delta G^{o} = -21580 + 11.8T \qquad \ldots (III.12)$$

Combination of the calculated values of ΔG^{o} for the reaction (III.11) at different temperatures of study with the values of $\Delta G^{o}_{HS(Pb)}$ for eq. (III.1) in pure lead solvent yields the values -16.8, -15.44, -14.25, -13.2 and -12.25 respectively for ln $K_{S(Pb)}$ at 723, 773, 823, 873 and 923°K temperatures, for the equilibrium reaction,

$$\underline{S}(Pb) = 1/2\ S_2(g) \qquad \ldots (III.13)$$

In Fig. III.2, the function ln $K_{S(Pb)}$ is plotted against $(\frac{1}{T})$. Regression analysis of the data plotted in this figure leads to the following expression,

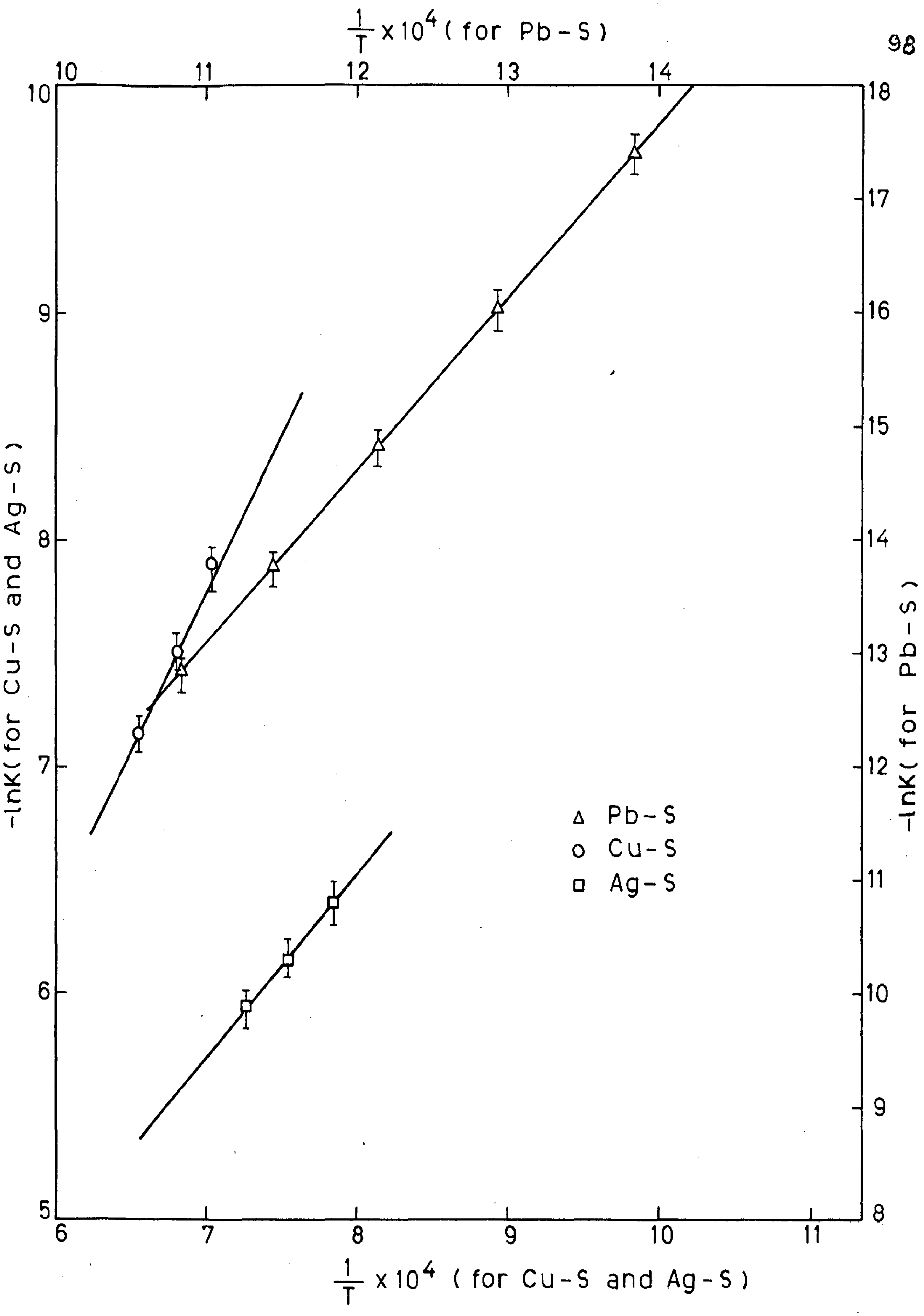

FIG. III.2 PLOT OF FUNCTION (-lnK) Vs. $1/T$ FOR EQUILIBRIA OF SULPHUR IN PURE LEAD, COPPER AND SILVER SOLVENTS.

$$\ln K_{S(Pb)} = 4.25 - \frac{15300}{T} \qquad \ldots \text{(III.14)}$$

Thus the enthalpy and entropy of the dissolution of sulphur in pure lead solvent, represented by eq. (III.13) are found to be 30400 cals and 8.44 e.u. respectively.

Free energy of the above reaction has also been determined by Hagiwara [54] and Alcock and Cheng [53] in the temperature ranges 1073 - 1223°K ana 773° - 953°K respectively. As will be noted the data obtained in the present investigations corresponds well with that reported by Hagiwara.

III. 2.1.2 Sulphur in Pure Liquid Copper Solvent

The experimental data on dissolution of sulphur in pure liquid copper as solvent is presented in Table III.2 and has been used to calculate the function $[\ln(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{at.\% S})]$, values of which are also given in the above table. Further, function $[-\ln(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{at.\%S})]$ has been plotted against at.%S in Fig. III.3 at different temperatures of study viz., 1423, 1473 and 1523°K and linear regression analysis of the data so plotted yields the following expressions,

i) At 1423°K

$$\ln(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{at.\%S}) = -6.22-0.192 \times (at.\%S) \ldots \text{(III.15)}$$

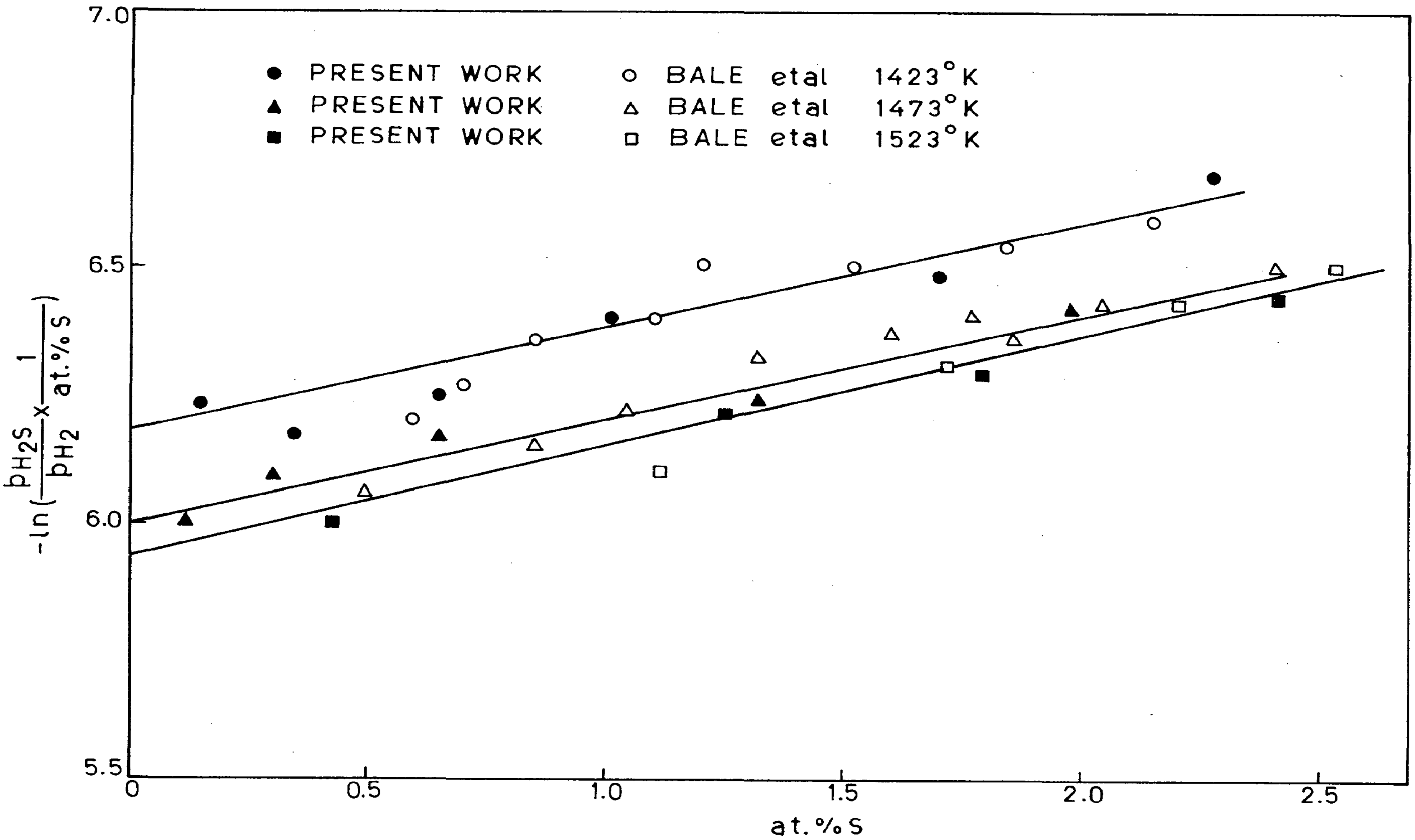

FIG.III.3 PLOT OF FUNCTION $\left[-\ln\left(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{at.\%S}\right)\right]$ Vs. at.%S FOR DISSOLUTION OF SULPHUR IN PURE COPPER AT DIFFERENT TEMPERATURES.

ii) At 1473°K

$$\ln\left(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{\text{at.\% S}}\right) = -6.00-0.203 \times (\text{at.\%S}) \quad \text{...(III.16)}$$

and

iii) At 1523°K

$$\ln\left(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{\text{at.\%S}}\right) =- 5.94-0.199 \times (\text{at.\%S}) \quad \text{...(III.17)}$$

On comparing the above expressions with eq. (III.4), one obtains the values of $\Delta G^o_{HS(Cu)}$ as 17510, 17780 and 18050 cals and those of self interaction parameter, ε^S_S as -0.192, -0.203 and -0.199 at temperatures 1423, 1473 and 1523°K respectively.

As done in case of lead solvent, a combination of above values of free energy, $\Delta G^o_{HS(Cu)}$ with the free energy, ΔG^o, for the reaction (III.11) yields the values of equilibrium constant, $K_{S(Cu)}$, as -7.80, -7.54 and -7.26 at 1423, 1473 and 1523°K temperatures, for the reaction,

$$\underline{S}(Cu) = 1/2\ S_2(g) \qquad \text{...(III.18)}$$

where $\underline{S}(Cu)$ is the sulphur in solution with pure molten copper.

In Fig. III.2, function [$\ln K_{S(Cu)}$] is plotted against $(\frac{1}{T})$. Further, regression analysis of the data plotted in this figure leads to the following expression

$$\ln K_{S(Cu)} = 3.211 - \frac{15803}{T} \qquad \text{...(III.19)}$$

From eq. (III.19), values of enthalpy and entropy for the reaction expressed by eq. (III.18) are computed and found to be 31400 cals and 6.39 e.u. respectively.

Values of free energy for the above reaction (III.18) have also been determined by Bale et al. [25]. As will be noted, the results obtained in the present work are in good agreement with the work of these investigators.

III. 2.1.3 Sulphur in Pure Liquid Silver Solvent

Experimental data on dissolution of sulphur in pure liquid silver are presented in Table III.3 and have been used to calculate the function $[\ln(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{at.\%S})]$, also given in the above table. Further, the function $[-\ln(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{at.\%S})]$ has been plotted against at.%S in Fig. III.4 at temperatures 1273, 1323 and 1373°K. By doing linear regression analysis of the data so plotted, following expressions have been obtained

i) At 1273°K

$$\ln(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{at.\%S}) = -3.353-1.354x(at.\%S) \quad \ldots \text{(III.20)}$$

ii) At 1323°K

$$\ln(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{at.\%S}) = -3.437-1.21\ x(at.\%S) \quad \ldots \text{(III.21)}$$

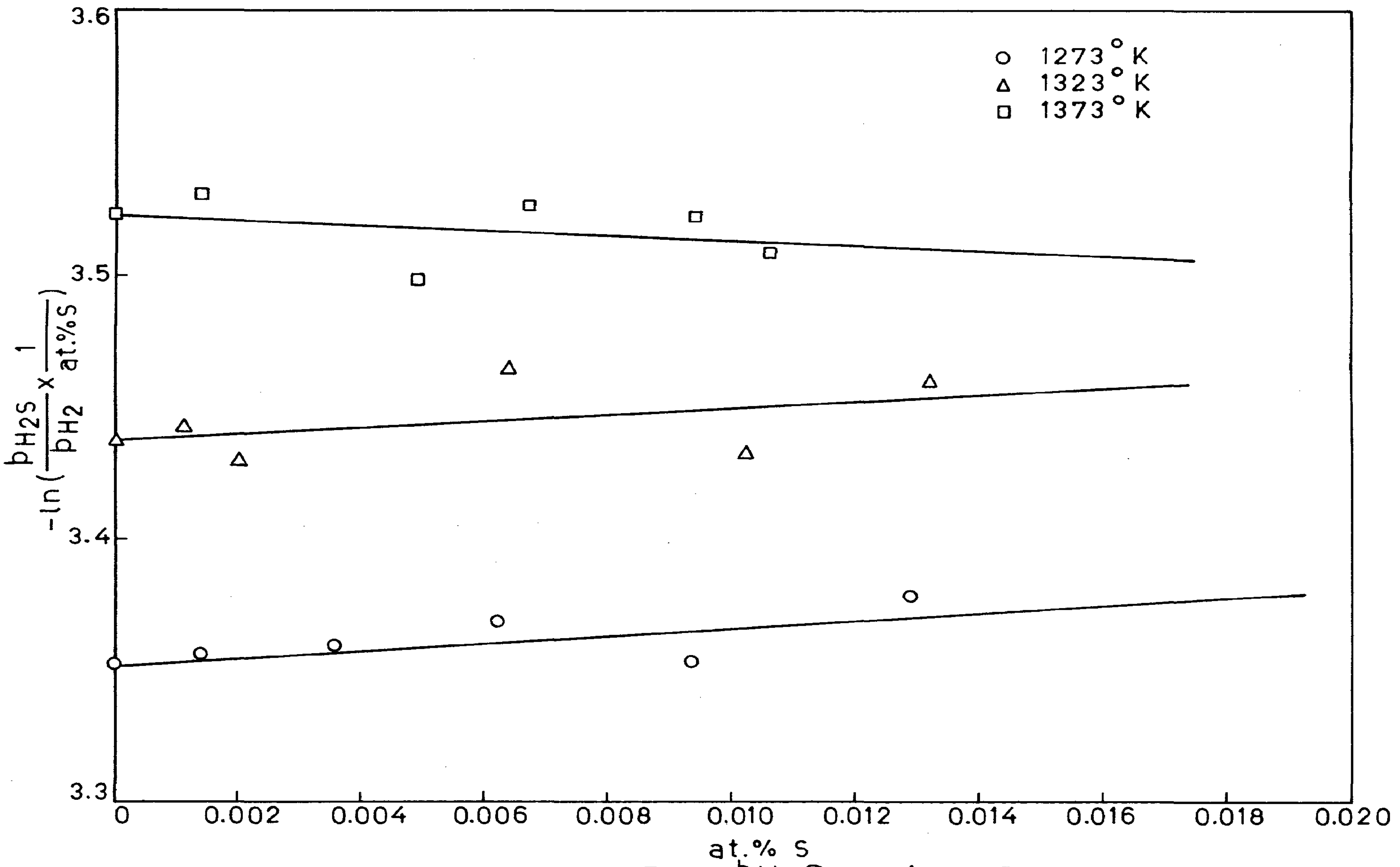

FIG. III.4 PLOT OF FUNCTION $\left[-\ln\left(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{\text{at.\% S}}\right)\right]$ Vs. at. % S FOR DISSOLUTION OF SULPHUR IN PURE SILVER AT DIFFERENT TEMPERATURES.

and, iii) At 1373°K

$$\ln\left(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{\text{at.\% S}}\right) = -3.523+0.958\times(\text{at.\%S}) \qquad \text{... (III.22)}$$

By comparing the above expressions with eq.(III.4), values of free energy $\Delta G^{o}_{HS(Ag)}$ for the reaction (III.1), and self interaction parameter, ε^{S}_{S}, are computed and found to be respectively equal to 9550, 9120 and 9667 cals and -1.354, -1.21 and 0.958 at temperatures 1273, 1323 and 1373°K respectively.

Again for the equilibrium between the sulphur in gaseous phase and sulphur dissolved in pure silver, represented by the following expression,

$$\underline{S}(Ag) = 1/2\ S_2(g) \qquad \text{... (III.23)}$$

values of free energy, $\Delta G^{o}_{S(Ag)}$, can be computed from the values of $\Delta G^{o}_{HS(Ag)}$ and eq. (III.12) at 1273, 1323 and 1373°K respectively and are found to be 15100, 15076, and 15040 cals. From these free energy values, ln $K_{S(Ag)}$ is computed and plotted against (1/T) in Fig. III.2. The regression analysis of this data leads to the following expression,

$$\ln K_{S(Ag)} = 0.467 - \frac{8198}{T} \qquad \text{... (III.24)}$$

The values of free energy of reaction, represented by eq. (III.23), obtained in the present work compare well with those obtained by Rosenqvist [18].

III. 2.2 Sulphur in Binary Molten Metallic Solvents

Let us consider a binary metallic solvent containing components A and B (where A and B represent any two of the pure metals lead, silver or copper used in the present study), in equilibrium with a gaseous phase, having p_{H_2S} and p_{H_2} as the partial pressures of the components H_2S and H_2 respectively. According to eq. (III.1), for equilibrium between sulphur dissolved in binary solvent and the gaseous mixture containing H_2S and H_2, one can write the following expression for the equilibrium constant, $K_{HS(A-B)}$,

$$\ln K_{HS(A-B)} = \ln\left(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{\text{at.\% S}}\right) - \ln f^{S}_{S(A-B)}$$

$$= \ln\left(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{\text{at.\% S}}\right) - \varepsilon^{S}_{S(A-B)} \times (\text{at.\% S}) \quad \ldots \text{(III.25)}$$

where, $f^{S}_{S(A-B)}$ and ε^{S}_{S} are respectively the interaction coefficient and self interaction parameter of sulphur in the binary solvent (A-B). The above expression also shows that, if ε^{S}_{S} is independent of the amount of sulphur present in the binary solvent, the intercept (at at.% S equal to zero) of the linear plot of function $[\ln(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{\text{at.\% S}})]$ against at.% S for a binary solvent of constant composition, will lead to the value of $\ln K_{HS(A-B)}$, whereas the slope will yield the value of self interaction parameter, ε^{S}_{S}, of sulphur in that solvent.

Further, one can also arrive at the values of interaction parameters, for the effect of B and A on sulphur in the solvents A and B respectively. To arrive at a suitable relationship for the calculation of these interaction parameters, one considers a solvent which is a dilute solution of component B in A. As ln $K_{HS(A-B)}$ is a continuous function of the composition, one can write the following Taylor's expansion for the above mentioned solvent

$$\ln K_{HS(A-B)} = \ln k_{HS(A)} + \left[\frac{\partial \ln k_{HS(A-B)}}{\partial (\text{at \% B})}\right]_{(\text{at \% B}) \to 0} . (\text{at \%B})$$

$$+ \left[\frac{\partial^2 \ln K_{HS(A-B)}}{\partial (\text{at \% B})^2}\right]_{(\text{at \% B}) \to 0} . \frac{(\text{at \% B})^2}{2} + \ldots\ldots$$

$$\ln K_{HS(A)} + \left[\frac{\partial \ln K_{HS(A-B)}}{\partial (\text{at \% B})}\right]_{(\text{at \% B}) \to 0} . (\text{at \% B}) \qquad \ldots (\text{III.26})$$

Further, one can also write the following expression for the ratio of at.% S dissolved, under the same H_2S - H_2 mixture (i.e., for the same sulphur chemical potential), in pure liquid solvent A and a binary solvent consisting of a dilute solution of component B in component A,

$$\ln \frac{(\text{at.\%S})_A}{(\text{at.\%S})_{(A-B)}} = \ln K_{HS(A-B)} - \ln K_{HS(A)} \qquad \ldots (\text{III.27})$$

For the above mentioned conditions, one can, therefore, write the following expression,

$$\ln \frac{(\text{at.\% S})_A}{(\text{at.\% S})_{(A-B)}} = -\ln f_S^B = -\varepsilon_S^B \cdot (\text{at.\% B}) \ldots \text{(III.28)}$$

where, f_S^B and ε_S^B are respectively the interaction coefficient and interaction parameter. Thus, from eqs. (III.26) and (III.28), one can infer,

$$\varepsilon_S^B = -\left[\frac{o \ln k_{HS(A-B)}}{o\ (\text{at.\% B})}\right]_{(\text{at.\% B}) \text{ --- } o} \qquad \ldots \text{(III.29)}$$

i.e., the value of slope at at.% B ---o on the ln $K_{S(A-B)}$ Vs. at.% B curve is equal to the negative of interaction parameter, ε_S^B. Thus one can also derive values of interaction parameters from present investigations. The above expressions shall now be applied to the binary systems studied in the present investigations to make calculations.

III.2.2.1 Sulphur in Binary Lead-Silver Solvents

From the data reported in Sec. (III.1) in Tables III.4 - III.9, the function $[-\ln(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{\text{at.\% S}})]$ is plotted in Figs.III.5, III.6 and III.7 against at.%S respectively at temperatutes 1273, 1323 and 1373°K for the binary lead-silver solvent of different compositions. These figures show a linear relationship between the two functions. Values of functions ln $K_{HS(Pb-Ag)}$ and the self-interaction parameters of sulphur, ε_S^S, have been computed by linear regression analysis of the above plotted data. From a knowledge of the values of function RT ln $K_{HS(Pb-Ag)}$ and free energy, ΔG^o, of the reaction expressed by eq.(III.11),

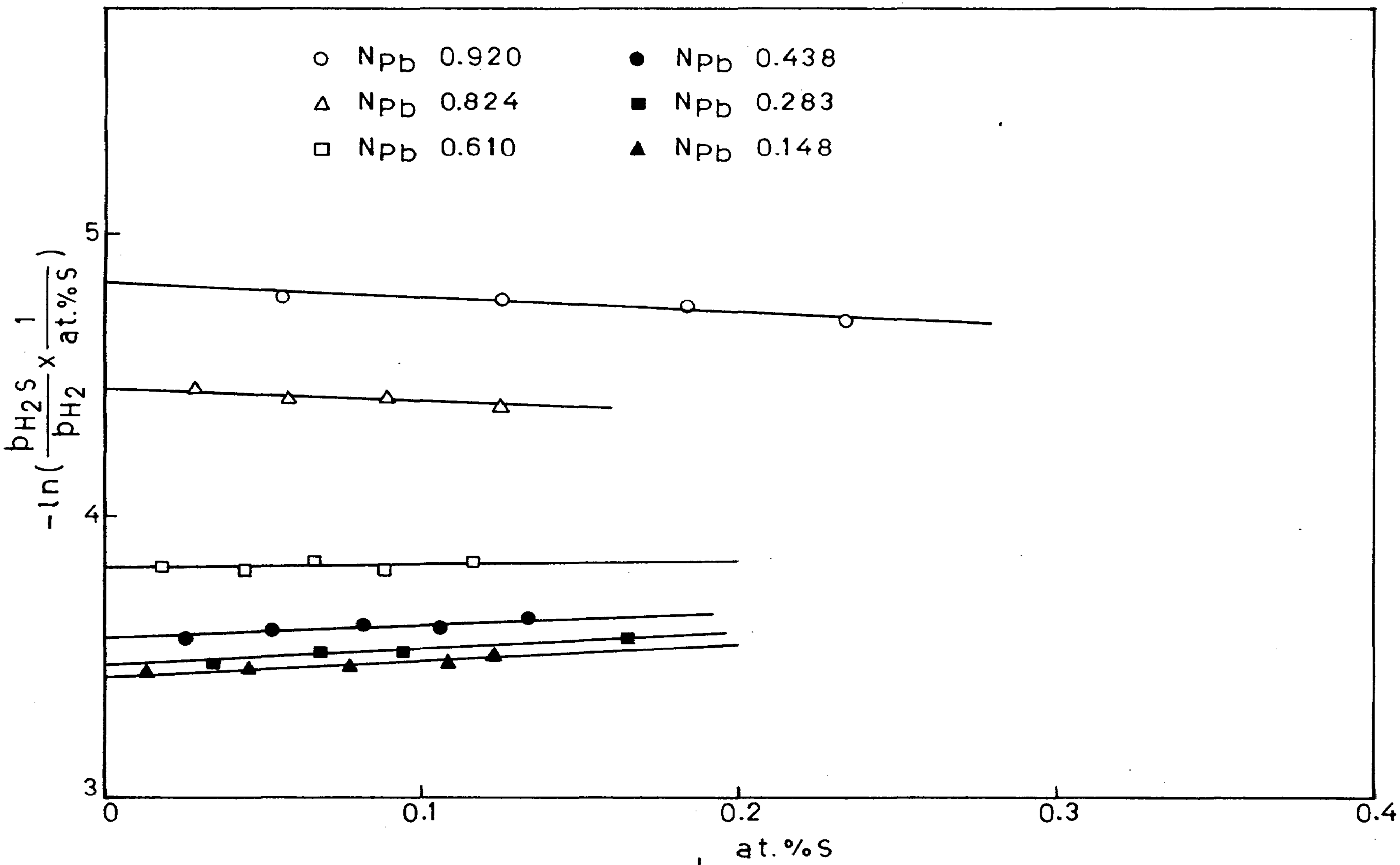

FIG. III.5 PLOT OF FUNCTION $\left[-\ln\left(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{\text{at.\%S}}\right)\right]$ Vs. at.%S FOR DISSOLUTION OF SULPHUR IN BINARY LEAD-SILVER ALLOYS AT 1273 °K.

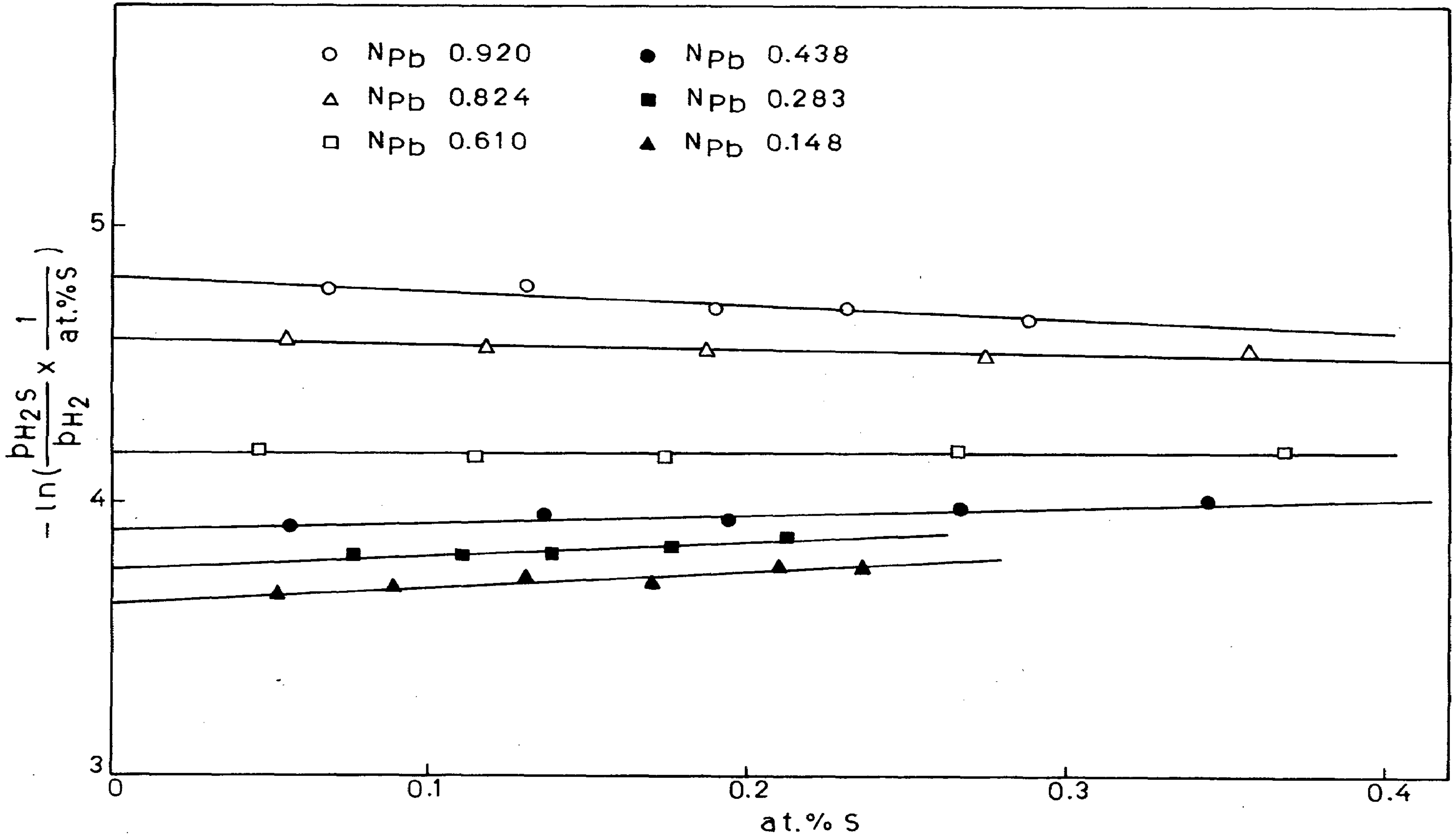

FIG. III.6 PLOT OF FUNCTION $\left[-\ln\left(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{at.\% S}\right)\right]$ Vs. at.% S FOR DISSOLUTION OF SULPHUR IN BINARY LEAD-SILVER ALLOYS AT 1323 °K.

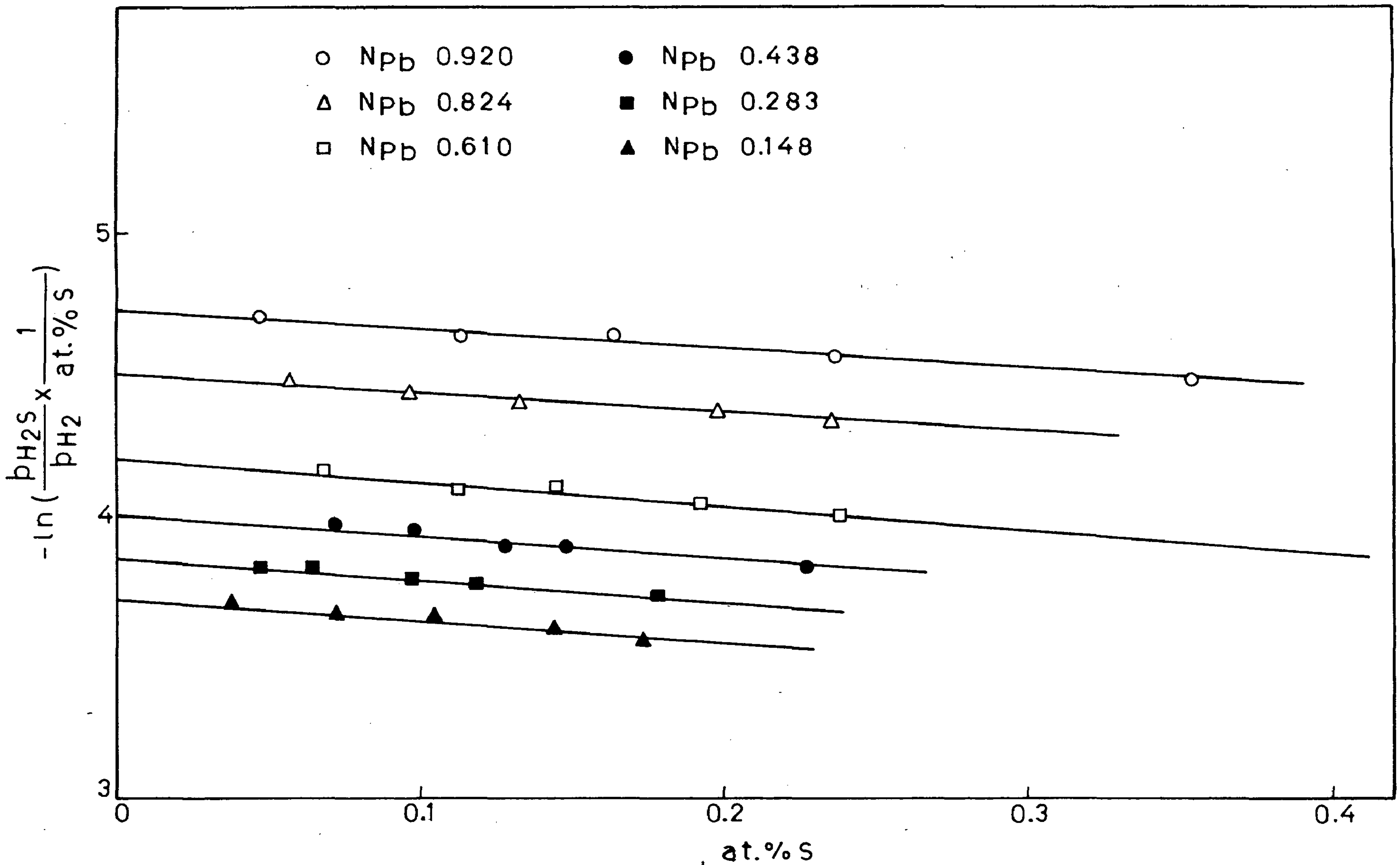

FIG. III.7 PLOT OF FUNCTION $\left[-\ln\left(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{at.\% S}\right)\right]$ Vs. at.% S FOR DISSOLUTION OF SULPHUR IN BINARY LEAD-SILVER ALLOYS AT 1373 °K.

the free energy, $\Delta G^{o}_{S(Pb-Ag)}$, of the reaction

$$\underline{S}(\text{in Pb-Ag alloy}) = 1/2\ S_2(g) \qquad \ldots\ (III.30)$$

for different binary alloy solvents has been calculated and plotted against composition for different temperatures in Fig. III.8. Regression analysis of the data plotted in this figure shows the values computed within an average accuracy of ± 550, ±550 and ±530 cals at temperatures 1273, 1323 and 1373°K respectively. Further, from $(\frac{\Delta G^{o}_{S(Pb-Ag)}}{T})$ Vs. (1/T) plots, the entropy, $\Delta {}^{o}_{S(Pb-Ag)}$, and enthalpy, $\Delta H^{o}_{S(Pb-Ag)}$ of the reaction expressed by eq. (III.30) for different binary Pb-Ag alloy solvents are evaluated. These thermodynamic properties are also plotted in Fig. III.8 together with the values of $\Delta G^{o}_{S(Pb-Ag)}$ for the same reaction as reported by Mohapatra and Frohberg [85]. It will be noted that values of free energy obtained in the present investigations differ slightly from those obtained by these investigators at 1100°K. This difference is attributed to, (i), the different experimental techniques employed, and, (ii) the basic assumptions made for calculations. In their work, Mohapatra et al. [85] have assumed that the behaviour of sulphur in the solvent, a mixture of chlorides, follows Henry's law. However, this assumption is not substantiated by the experimental work, and is considered to be mainly responsible for the difference pointed out above.

The method employed in the present investigations is a direct one and yields reproducible and reliable data on

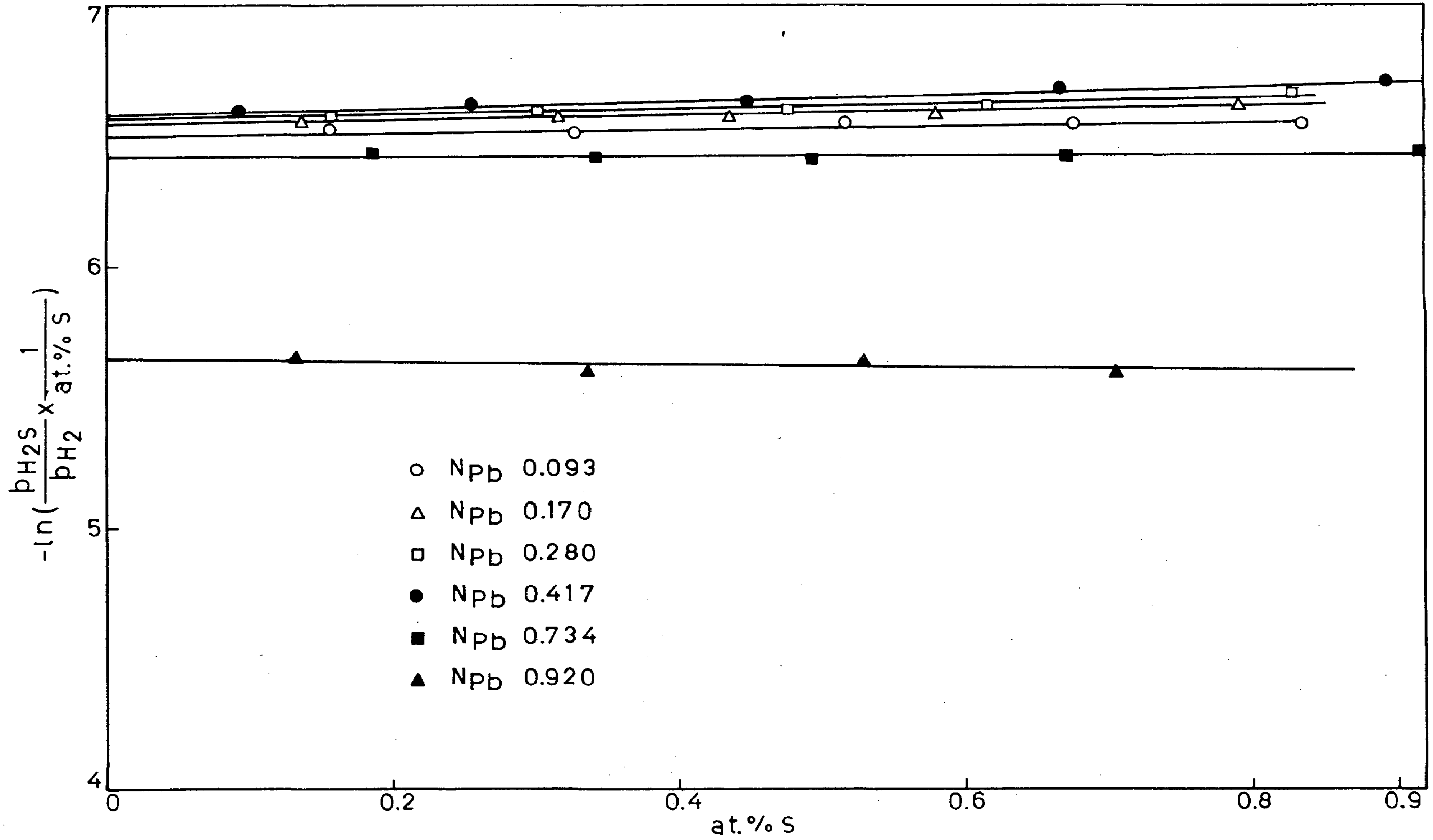

FIG. III.10 PLOT OF FUNCTION $\left[-\ln\left(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{at.\% S}\right)\right]$ Vs. at.% S FOR DISSOLUTION OF SULPHUR IN BINARY LEAD-COPPER ALLOYS AT 1323°K.

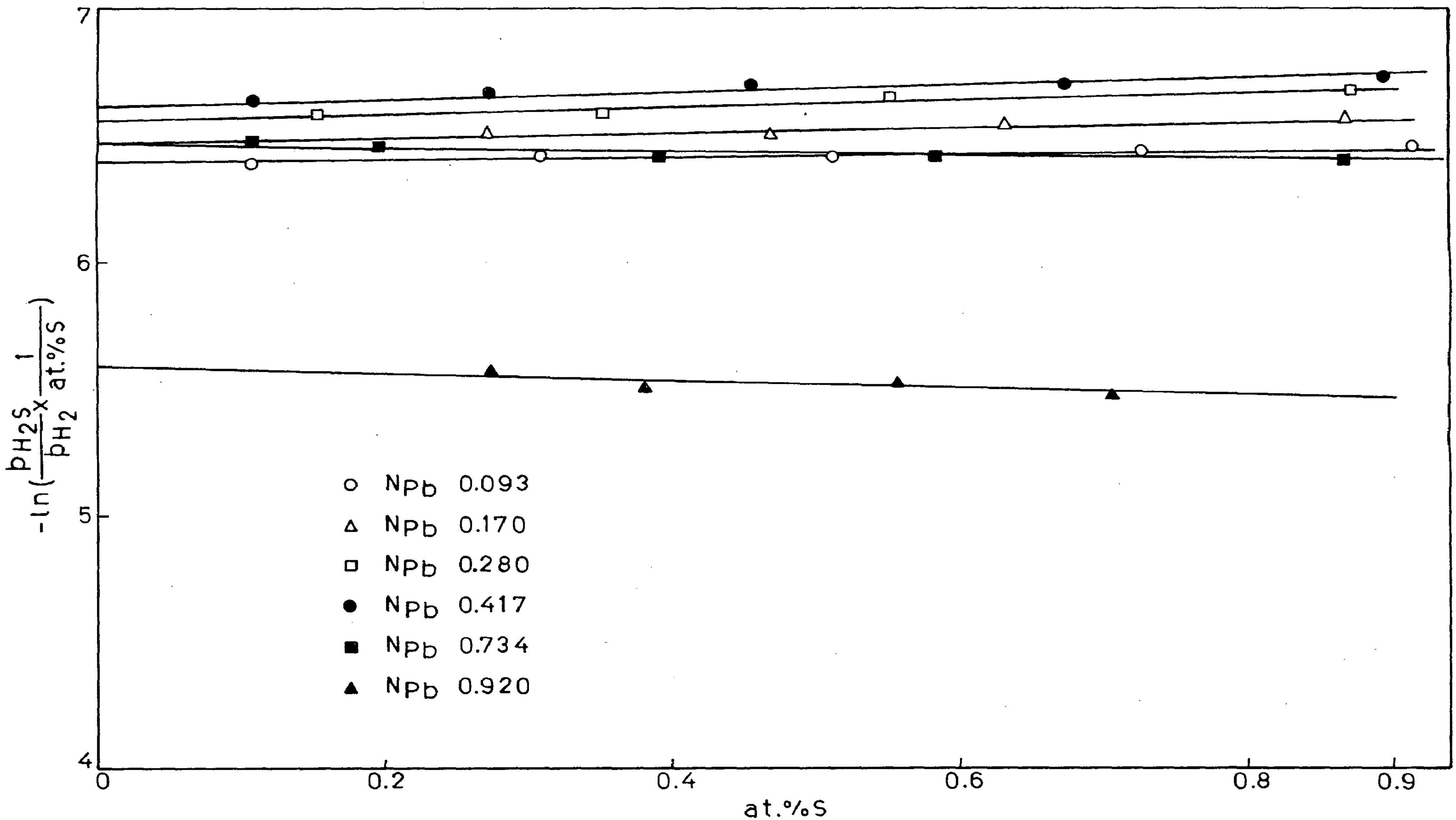

FIG. III.11 PLOT OF FUNCTION $\left[-\ln\left(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{at.\%S}\right)\right]$ Vs. at.% S FOR DISSOLUTION OF SULPHUR IN BINARY LEAD-COPPER ALLOYS AT 1373°K.

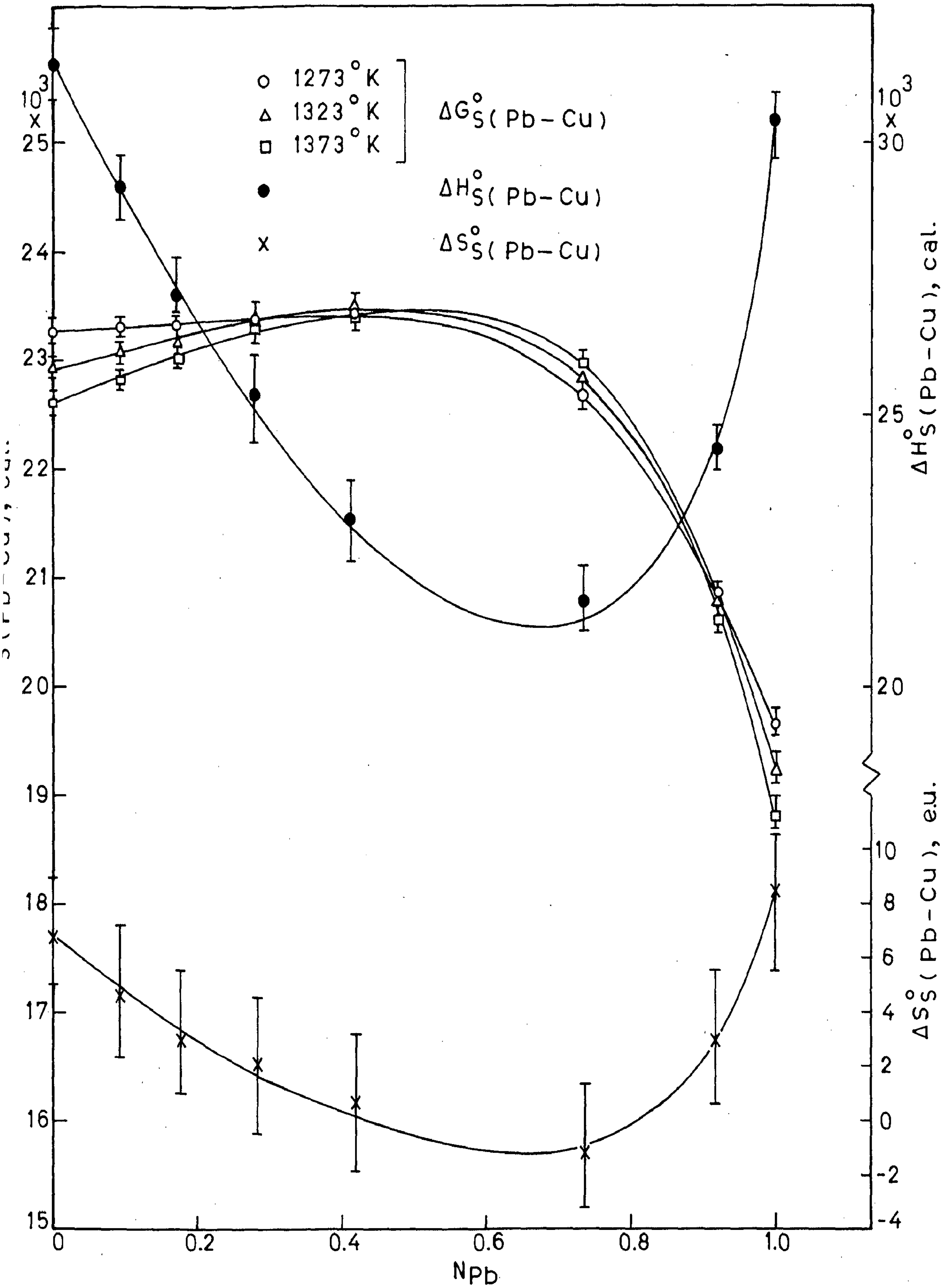

FIG. III.12 FREE ENERGY, ENTHALPY AND ENTROPY OF SULPHUR EQUILIBRIA IN BINARY LEAD-COPPER ALLOYS.

These plots also show a linear relationship between these two functions and hence values of ln $K_{HS(Pb-Cu)}$ and the self-interaction parameters, ε_S^S , are evaluated by linear regression analysis of the above plotted data at different temperatures and alloy composition. From a knowledge of the values of the function RT ln $K_{HS(Pb-Cu)}$ and values of ΔG^o for the reaction expressed by eq. (III.11), the values for free energy, $\Delta G^o_{S(Pb-Cu)}$, for the reaction.

$$\underline{S}(\text{Pb-Cu alloy}) = 1/2\ S_2(g) \qquad \ldots \text{(III.31)}$$

are determined for different binary Pb-Cu alloys at the above mentioned temperatures. These values of free energy, $\Delta G^o_{S(Pb-Cu)}$, have been plotted for different alloys against composition in Fig. III.12. Regression analysis of the free energy data plotted in this curve shows that the free energy values obtained have an average accuracy of ±540, ±560 and ±580 cals respectively at temperatures 1273, 1323 and 1373°K.

Enthalpy and entropy for the reaction (III.1) for these alloys have also been determined from the plots $\left(\frac{\Delta G^o_{S(Pb-Cu)}}{T}\right)$ and (1/T). These are also plotted in Fig. III.12 against the composition. From the $\Delta G^o_{S(Pb-Cu)}$ Vs. composition plots, values of interaction parameter , $\varepsilon^{Cu}_{S\,(Pb)}$, and $\varepsilon^{Pb}_{S(Cu)}$ have been calculated and are found to be -5.972, -7.817 and -8.705 and -0.05 , -0.245 and -0.512 respectively at temperatures 1273, 1323 and 1373°K. The values computed for different functions are given in Table III.35 .

TABLE-III.35 : Different thermodynamic parameters calculated from experimental data for binary lead-copper alloy solvents

Composition N_{Pb}	Temp ^{o}K	ln K_{HS}	$\varepsilon^{S}_{S(Pb-Cu)}$	$\Delta G^{o}_{S(Pb-Cu)}$ (cals)	$\varepsilon^{Pb}_{S(Cu)}$	$\varepsilon^{Cu}_{S(Pb)}$
0.093	1273	-6.62 (±0.21)	-0.148 (±0.07)	23310 (±500)	-0.05	-5.972
0.17	"	-6.62 (±0.23)	-0.138 (±0.06)	23330 (±520)		
0.28	"	-6.66 (±0.27)	-0.137 (±0.12)	23400 (±560)		
0.417	"	-6.67 (±0.24)	-0.247 (±0.07)	23440 (±540)		
0.734	"	-6.37 (±0.22)	0.107 (±0.05)	22680 (±520)		
0.92	"	-5.66 (±0.29)	0.178 (±0.04)	20870 (±580)		
0.093	1323	-6.50 (±0.23)	-0.147 (±0.05)	23070 (±520)	-0.245	-7.817
0.17	"	-6.54 (±0.24)	-0.159 (±0.04)	23170 (±550)		
0.28	"	-6.62 (±0.27)	-0.093 (±0.03)	23380 (±580)		

Table-III.35 : Contd.

Composition N_{Pb}	Temp ^{o}K	ln K_{HS}	$\varepsilon^{S}_{S(Pb-Cu)}$	$\Delta G^{o}_{S(Pb-Cu)}$ (cals)	$\varepsilon^{Pb}_{S(Cu)}$	$\varepsilon^{Cu}_{S(Pb)}$
0.417	1323	-6.66 (±0.21)	-0.116 (±0.04)	23480 (±500)		
0.734	"	-6.42 (±0.23)	0.086 (±0.02)	22850 (±520)		
0.92	"	-5.65 (±0.22)	0.165 (±0.07)	20830 (±520)		
0.093	1373	-6.40 (±0.25)	-0.164 (±0.05)	22830 (±570)	-0.512	-8.705
0.17	"	-6.47 (±0.27)	-0.163 (±0.03)	23025 (±580)		
0.28	"	-6.56 (±0.29)	-0.115 (±0.03)	23280 (±600)		
0.417	"	-6.60 (±0.21)	-0.096 (±0.05)	23400 (±520)		
0.730	"	-6.46 (±0.23)	0.075 (±0.04)	22990 (±530)		
0.92	"	-5.60 (±0.23)	0.125 (±0.03)	20640 (±530)		

Twidwell and Larson [58] have also carried out investigations on lead-copper alloys containing 0.43, 1.87 and 2.54 at.% Cu at 873°K and have reported the value of interaction parameter of copper on sulphur, ε_S^{Cu}, in lead as - 55.0.

III.2.2.3 Sulphur in Binary Copper-Silver Solvents

Experimental data on equilibrium between copper-silver binary alloys and H_2-H_2S gaseous mixture are reported in Tables III.16 - III.21 and has been used to calculate the function $[\ln(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{at.\%\ S})]$ for different compositions of the solvent at different temperatures. Function $[-\ln(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{at.\%\ S})]$ is plotted in Figs. III.13 - III.15 against at.% S at temperatures 1273, 1323 and 1373°K for the different studies made. These plots also show a linear relationship between these two functions and hence linear regression analysis of the above data is used to calculate the values of $\ln K_{HS(Cu-Ag)}$ and the self interaction parameters, ε_S^S, of sulphur at these temperatures and for alloys of different compositions. By making use of the free energy of the reaction expressed by eq. (III.11) and the computed values of the function $RT \ln K_{HS(Cu-Ag)}$, values of the free-energy, $\Delta G^o_{S(Cu-Ag)}$, for the reaction.

$$\underline{S}(\text{Cu-Ag alloy}) = 1/2\ S_2 \qquad \ldots\ (\text{III.32})$$

for different alloys at temperatures 1273, 1323 and 1373°K

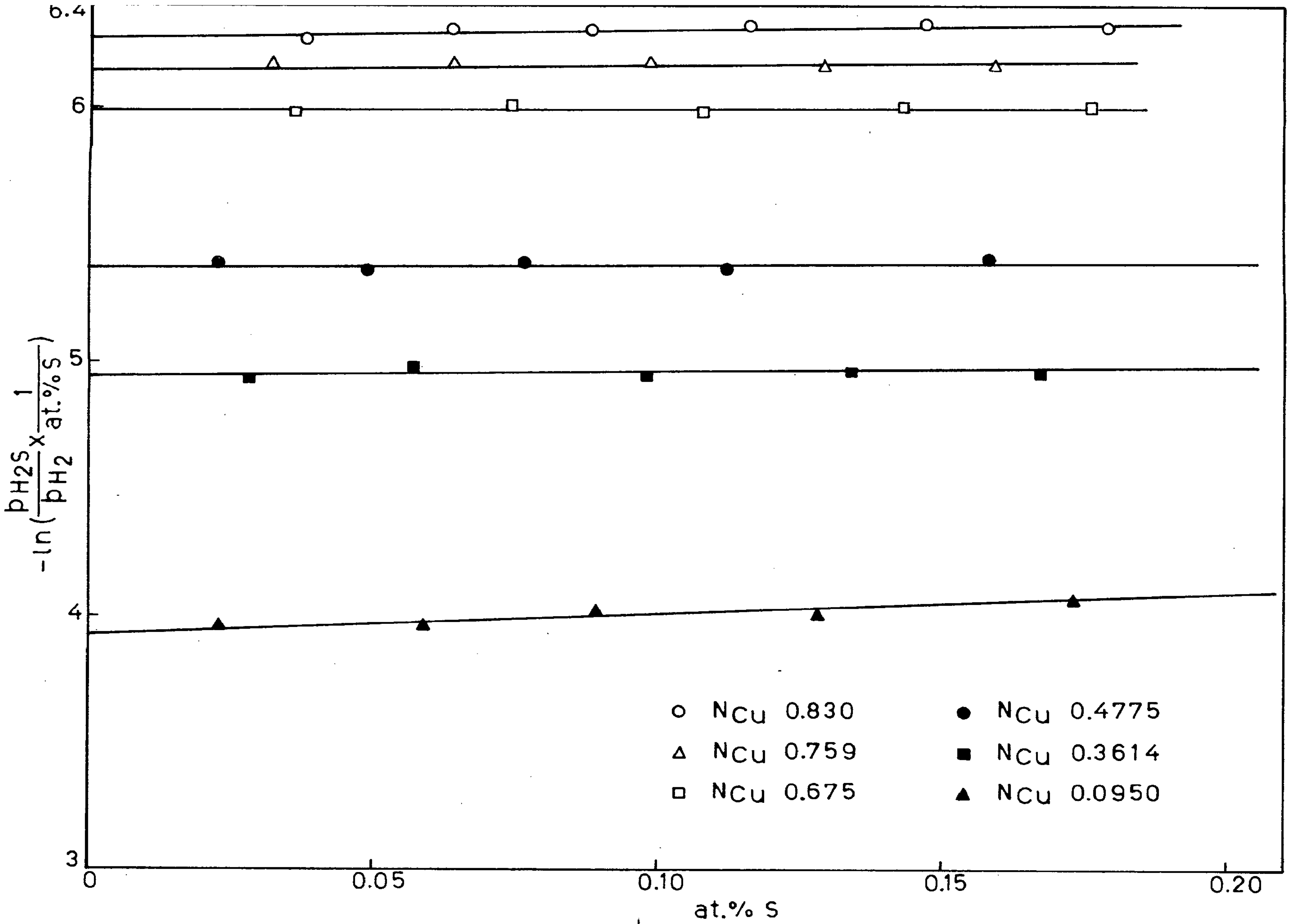

FIG. III.13 PLOT OF FUNCTION $\left[-\ln\left(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{\text{at.\% S}}\right)\right]$ Vs. at.% S FOR DISSOLUTION OF SULPHUR IN BINARY COPPER-SILVER ALLOYS AT 1273 °K

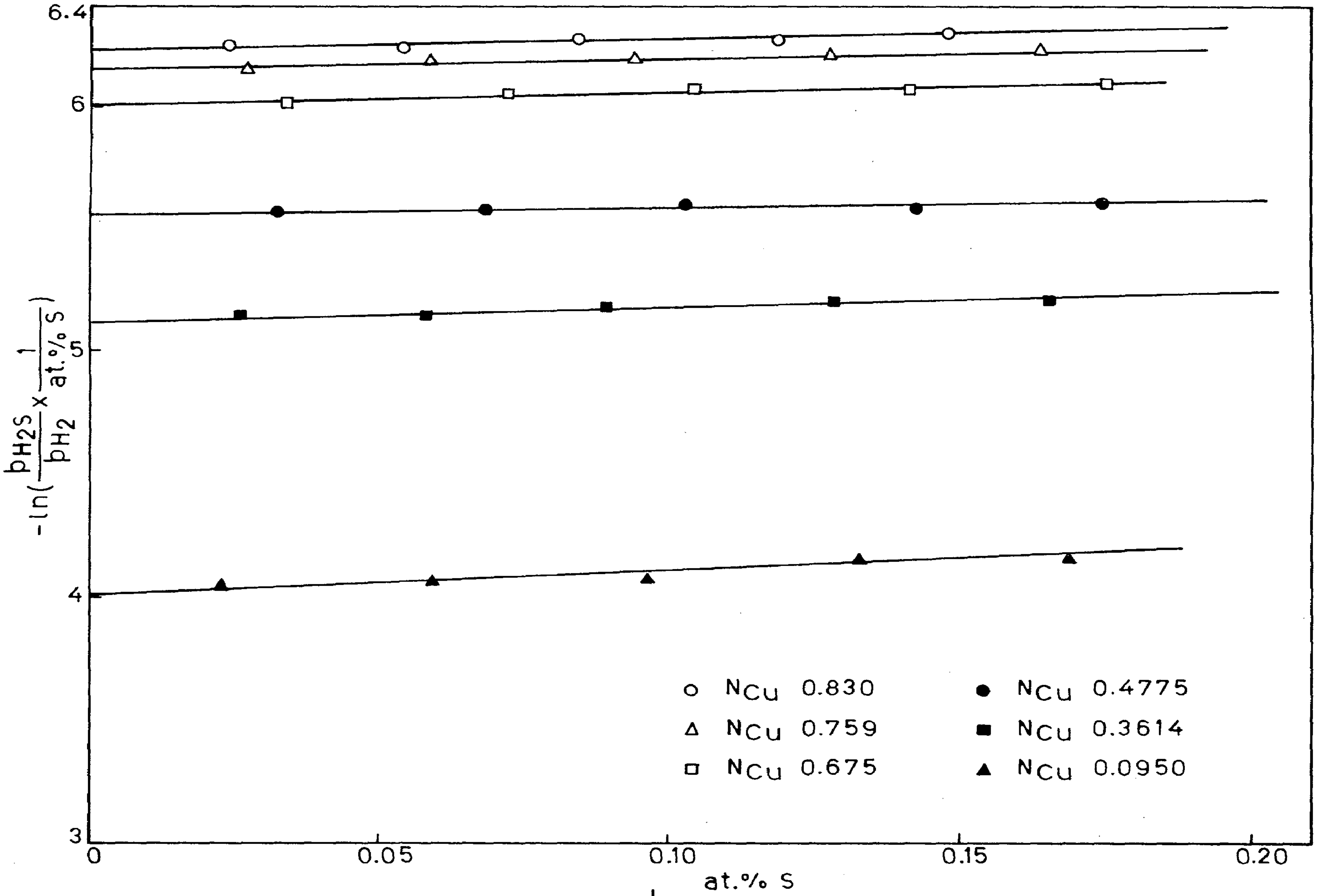

FIG. III.14 PLOT OF FUNCTION $\left[-\ln\left(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{at.\% S}\right)\right]$ Vs. at.% S FOR DISSOLUTION OF SULPHUR IN BINARY COPPER-SILVER ALLOYS AT 1323°K.

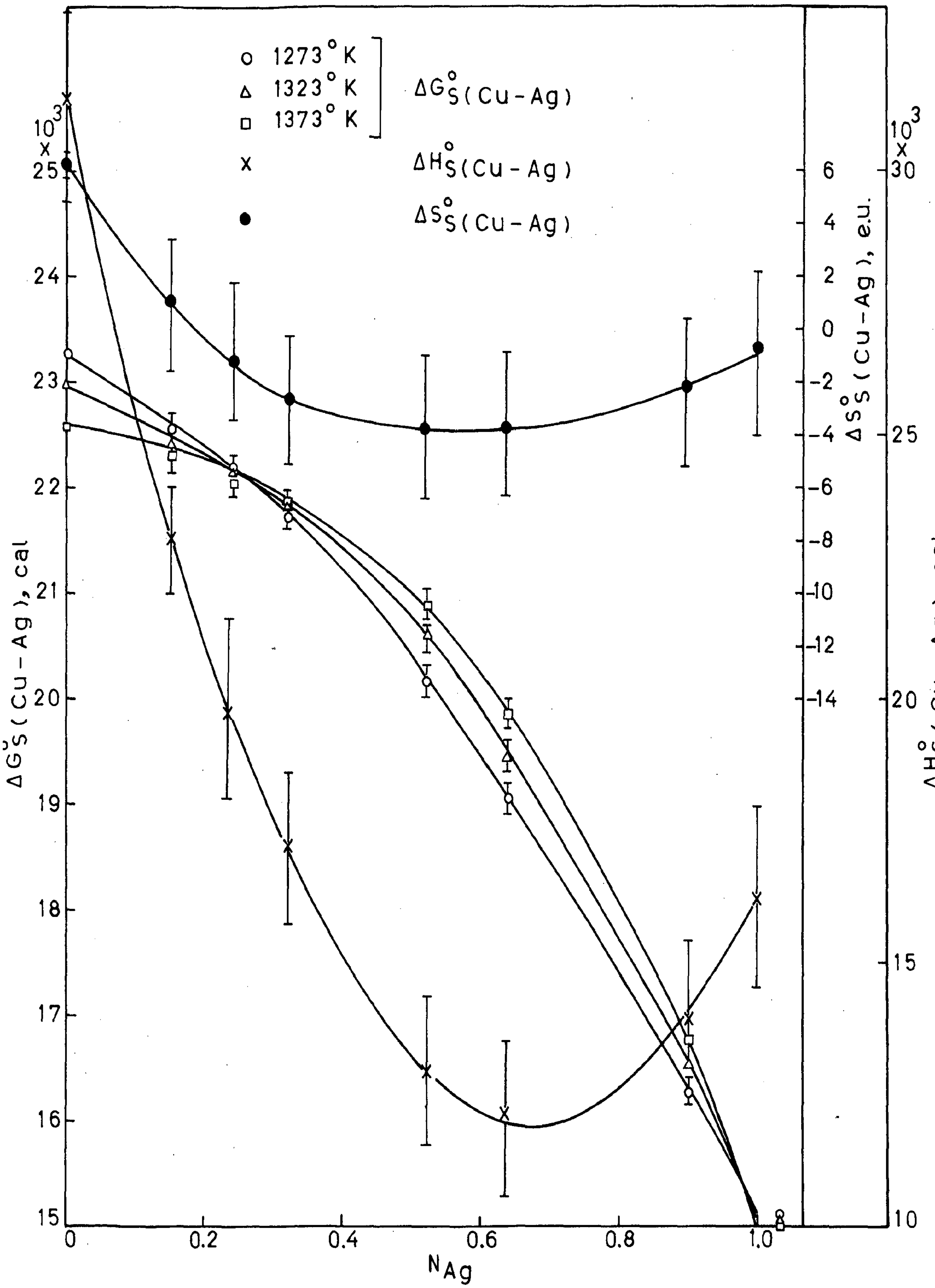

FIG. III.16 FREE ENERGY, ENTHALPY AND ENTROPY OF SULPHUR EQUILIBRIA IN BINARY COPPER-SILVER ALLOYS.

TABLE-III.36 : Different thermodynamic parameters calculated from experimental data for binary copper-silver alloy solvents

Composition N_{Cu}	Temp ^{o}K	ln K_{HS}	$\varepsilon^{S}_{S(Cu-Ag)}$	$\Delta G^{o}_{S(Cu-Ag)}$ (cals)	$\varepsilon^{Cu}_{S(Ag)}$	$\varepsilon^{Ag}_{S(Cu)}$
0.83	1273	-6.26 (±0.22)	-0.18 (±0.03)	22520 (±550)	-4.665	1.5
0.759	"	-6.15 (±0.29)	-0.34 (±0.05)	22100 (±540)		
0.675	"	-5.99 (±0.25)	-0.29 (±0.06)	21760 (±500)		
0.4775	"	-5.38 (±0.31)	-0.56 (±0.11)	20160 (±550)		
0.3614	"	(-4.94 (±0.23)	-0.32 (±0.12)	19060 (±500)		
0.095	"	-3.93 (±0.30)	-1.16 (±0.23)	16290 (±530)		
0.83	1323	-6.33 (±0.25)	-0.23 (±0.04)	22430 (±510)	-5.33	1.033
0.759	"	-6.15 (±0.28)	-0.27 (±0.05)	22140 (±540)		
0.675	"	-6.03 (±0.21)	-0.23 (+0.04)	21810 (±490)		

Table-III.36 : Contd.

Composition N_{Cu}	Temp ^oK	ln K_{HS}	$\varepsilon_{S(Cu-Ag)}^{S}$	$\Delta G^o_{S(Cu-Ag)}$ (cals)	$\varepsilon_{S(Ag)}^{Cu}$	$\varepsilon_{S(Cu)}^{Ag}$
0.4775	1323	-5.56 (±0.25)	-0.43 (±0.07)	20600 (±520)		
0.3614	"	-5.12 (±0.30)	0.27 (±0.08)	19430 (±550)		
0.095	"	-4.01 (±0.30)	-0.97 (±0.27)	16520 (±560)		
0.83	1373	-6.16 (±0.30)	-0.21 (±0.02)	22330 (±530)	-6.11	0.437
0.759	"	-6.12 (±0.33)	0.23 (±0.05)	22060 (±580)		
0.675	"	-6.03 (±0.32)	-0.19 (±0.07)	21830 (±570)		
0.4775	"	-5.68 (±0.25)	-0.31 (±0.06)	20880 (±550)		
0.3614	"	-5.30 (±0.27)	0.23 (±0.07)	19850 (±560)		
0.095	"	-4.18 (±0.25)	0.79 (±0.12)	16780 (±550)		

have been calculated. Further, values of $\Delta G^{o}_{S(Cu-Ag)}$, so obtained, have been plotted for different temperatures against the composition of binary alloy solvents in Fig. III.16. The average accuracy in the computed values of free energy, as evaluated by the linear regression analysis of the data, has been found to be respectively ±520, ±530, ±560 cals. at the three temperatures of investigation -1273, 1323 and 1373°K. From these plots values of interaction parameters $\varepsilon^{Ag}_{S(Cu)}$ and $\varepsilon^{Cu}_{S(Ag)}$ have been calculated and are found respectively 1.5, 1.033 and 0.437 and -4.66, -5.33 and -6.11 at temperatures 1273, 1323 and 1373°K.

Values of the entropy and enthalpy change for the reaction expressed by eq. (III.32) in different Cu-Ag alloy solvents have been computed from the plots of the functions $(\frac{\Delta G^{o}_{S(Cu-Ag)}}{T})$ Vs. $(\frac{1}{T})$ and shown in Fig.III.16. The values of different functions computed above are given in Table III.36. In literature no work has been reported on solubility of sulphur in these alloys in the dilute solution range.

III.2.3 Sulphur in Ternary Molten Metallic Solvent

In case of ternary solvents, consisting of components A, B and C (where A, B and C represent lead, copper and silver in the present investigations), in equilibrium with gaseous phase of known $\frac{p_{H_2S}}{p_{H_2}}$ ratio (corresponding to a

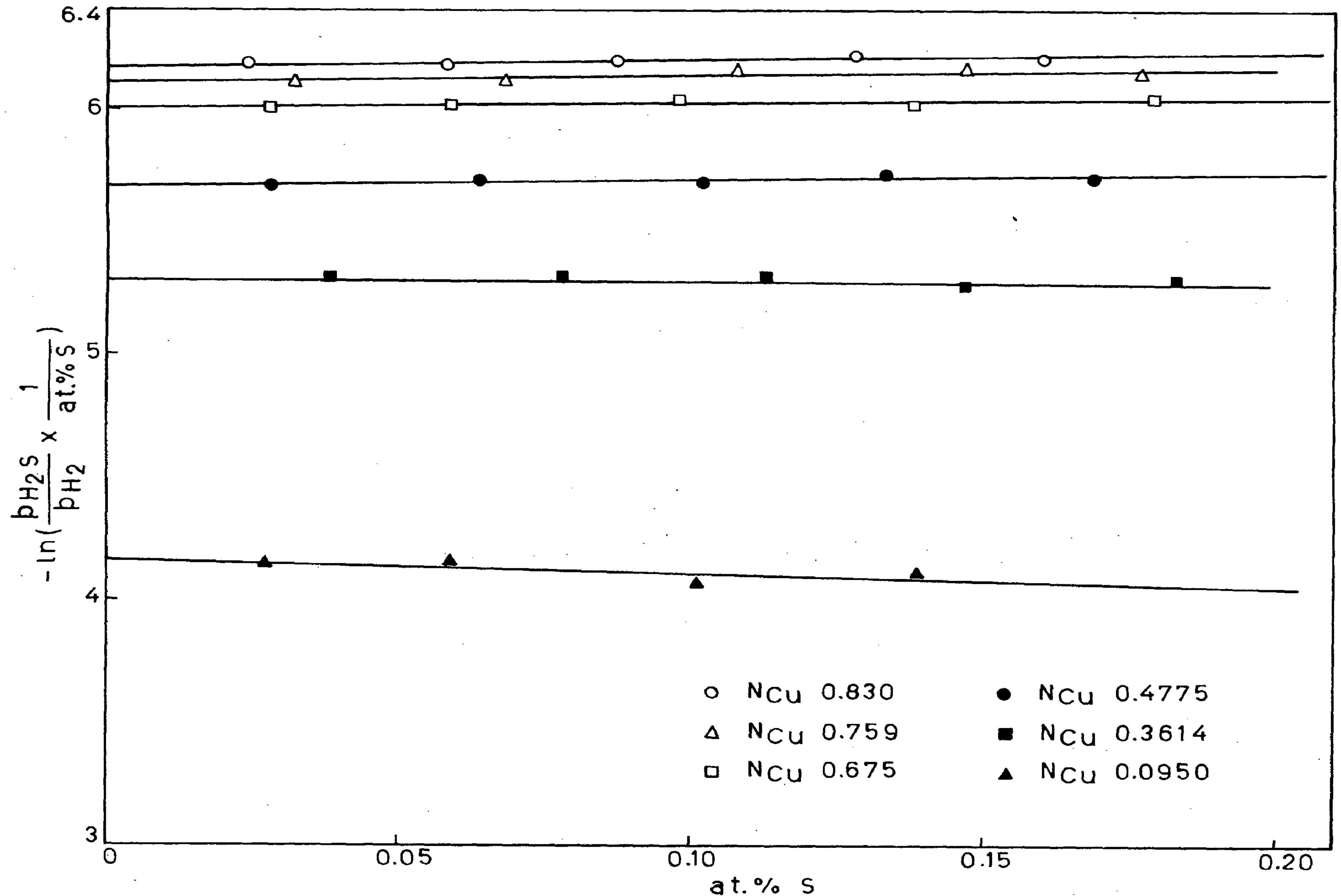

FIG. III.15 PLOT OF FUNCTION $\left[-\ln\left(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{at.\% S}\right)\right]$ Vs. at.% S FOR DISSOLUTION OF SULPHUR IN BINARY COPPER-SILVER ALLOYS AT 1373°K.

definite chemical potential of sulphur), one can write the following expression for the equilibrium constant, $K_{HS(A-B-C)}$, for the equilibrium reaction represented by eq. (III.1).

$$\ln K_{HS(A-B-C)} = \ln(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{at.\%S}) - \ln f_S^S$$

$$= \ln(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{at.\%S}) = \varepsilon^S_{S(A-B-C)} \times (at. \%S) \qquad \text{... (III.33)}$$

where f_S^S and $\varepsilon^S_{S(A-B-C)}$ respectively represent the self-interaction coefficient and self interaction parameter of sulphur in ternary molten metallic solvent.

Plot between the functions $[\ln(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{at.\%S})]$ and at.% S will yield the values of the equilibrium constant, $K_{HS(A-B-C)}$ and self interaction parameter, ε^S_S, in the ternary solvent. Different interaction parameters quantifying the effect of other solute components on the behaviour of sulphur in ternary solvent can similarly be defined, as described in Section III.2.2 for binary metallic solvents.

III.2.3.1 Sulphur in Ternary Lead-Copper-Silver Solvents

Experimental data on dissolution of sulphur in ternary Pb-Cu-Ag alloy solvents of different compositions in equilibrium with gaseous mixtures of known $\frac{p_{H_2S}}{p_{H_2}}$ ratios have been reported in Tables III.22 - III.33. From these data, values of the function $[\ln(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{at.\%S})]$ have been calculated for each composition of the alloy at different $\frac{p_{H_2S}}{p_{H_2}}$ ratios and at different temperatures used for study viz., 1273, 1323 and 1373°K respectively. The function $[-\ln(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{at.\%S})]$ is then plotted against at.%S in Figs. III.17 - III.19 at temperatures 1273, 1323 and 1373°K respectively which clearly indicates linear relationship between these two functions. Linear regression analysis of the data, therefore, yields the values of ln $K_{HS(Pb-Cu-Ag)}$ and self interaction parameter of sulphur, ε_S^S, at above temperatures for different ternary alloys.

The RT ln $K_{HS(Pb-Cu-Ag)}$ values computed above, when combined with the free energy, ΔG^o, for the reaction expressed by eq. (III.11), yield the value of free energy, $\Delta G^o_{S(Pb-Cu-Ag)}$ for the following equilibrium reaction.

$$\underline{S}(\text{Pb-Cu-Ag alloy}) = 1/2\ S_2 \qquad \ldots \text{(III.34)}$$

for different ternary alloys. These values are plotted in Fig. III.20 against composition (varying with respect to one of the constituents) of the ternary alloys at temperatures 1273, 1323 and 1373°K. Further, linear regression analysis of the data on free energy for different alloy solvents at these temperatures yields values of an average accuracy of ±600, ±580, ±550 cals at temperatures 1273, 1323 and 1373°K respectively. Also from the

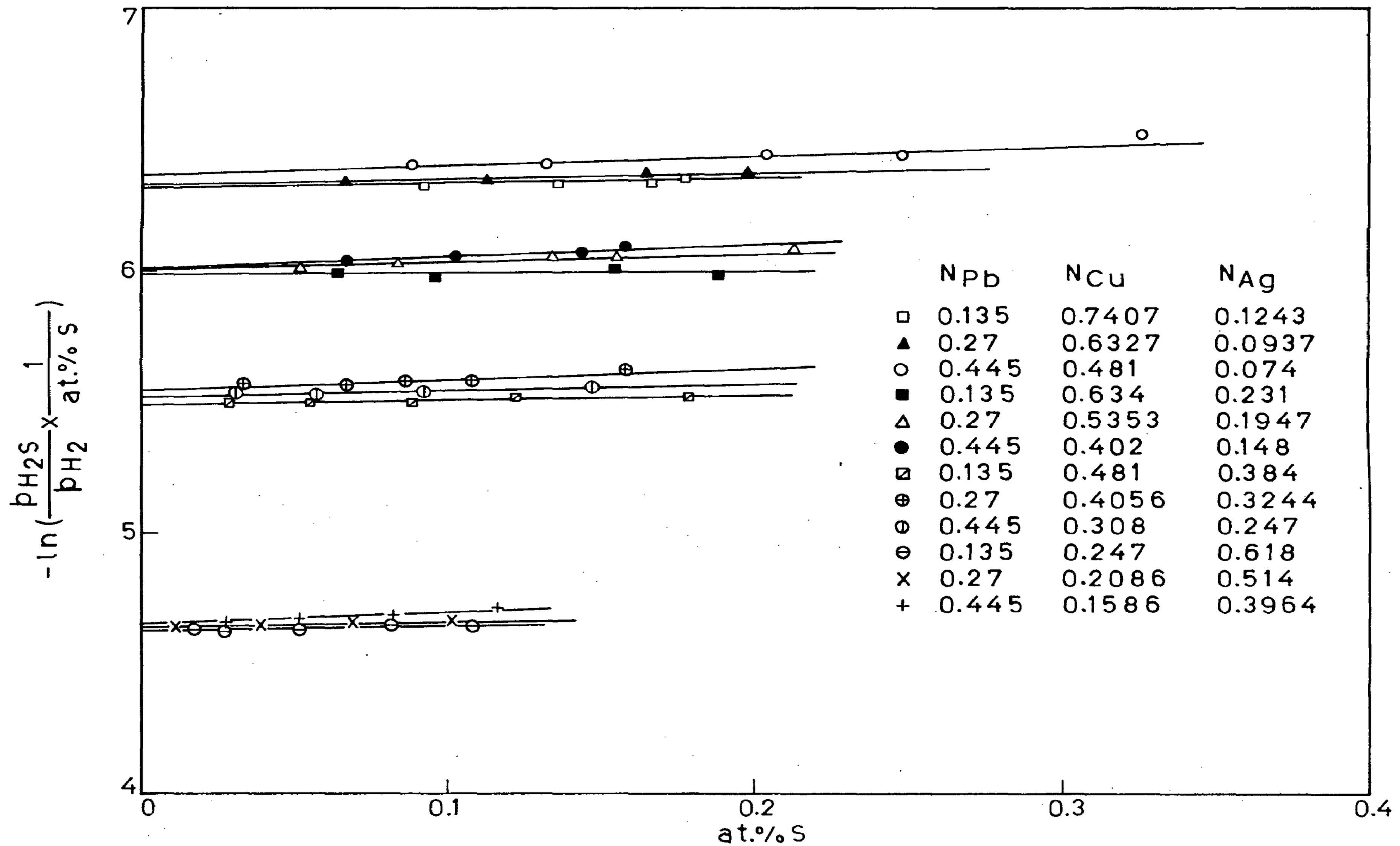

FIG.III.17 PLOT OF FUNCTION $\left[-\ln\left(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{at.\% S}\right)\right]$ Vs. at.% S FOR DISSOLUTION OF SULPHUR IN LEAD-COPPER-SILVER TERNARY ALLOYS AT 1273°K.

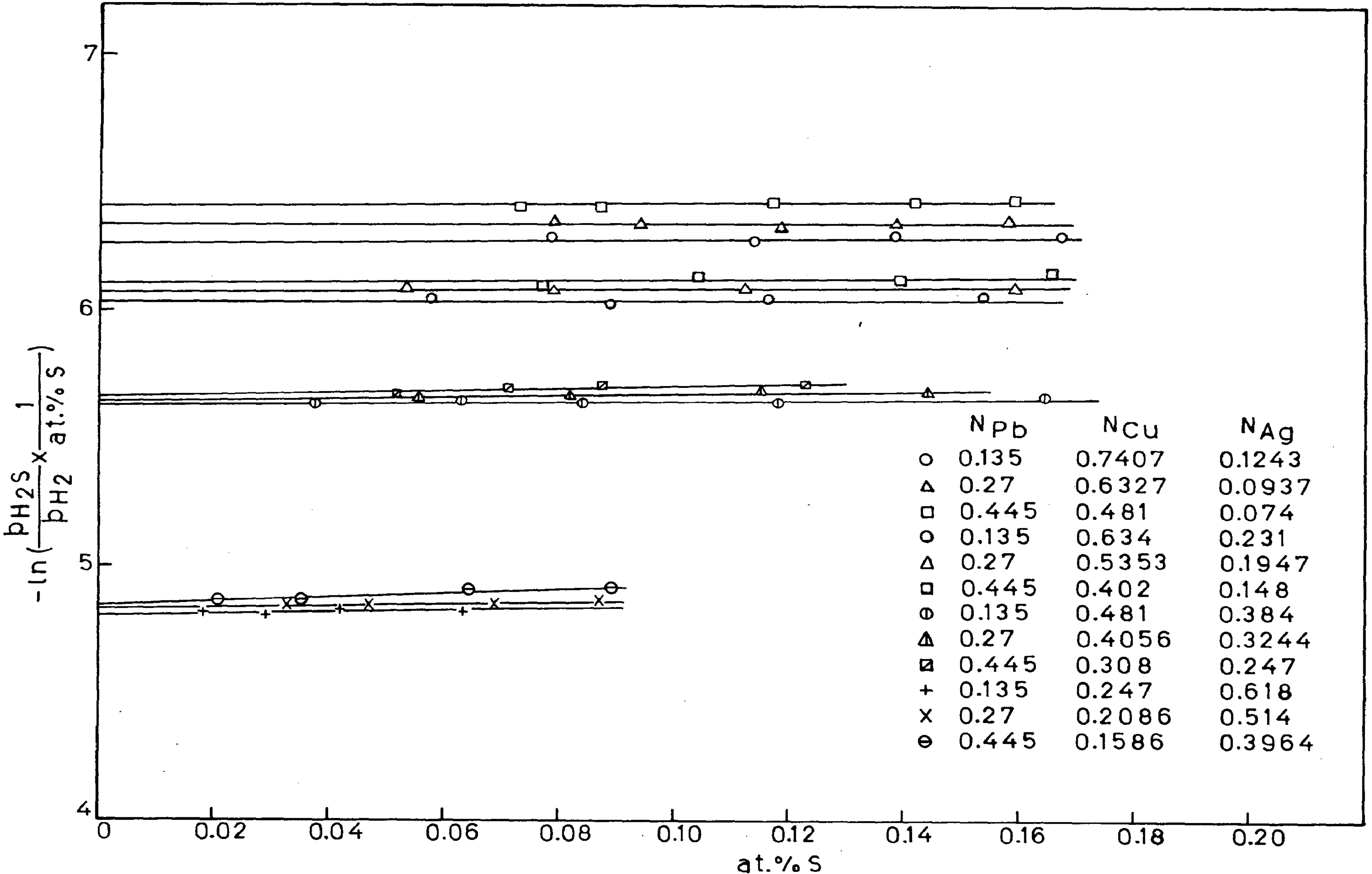

FIG. III.18 PLOT OF FUNCTION $\left[-\ln\left(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{at.\% S}\right)\right]$ Vs. at.% S FOR DISSOLUTION OF SULPHUR IN LEAD-COPPER-SILVER TERNARY ALLOYS AT 1323°K.

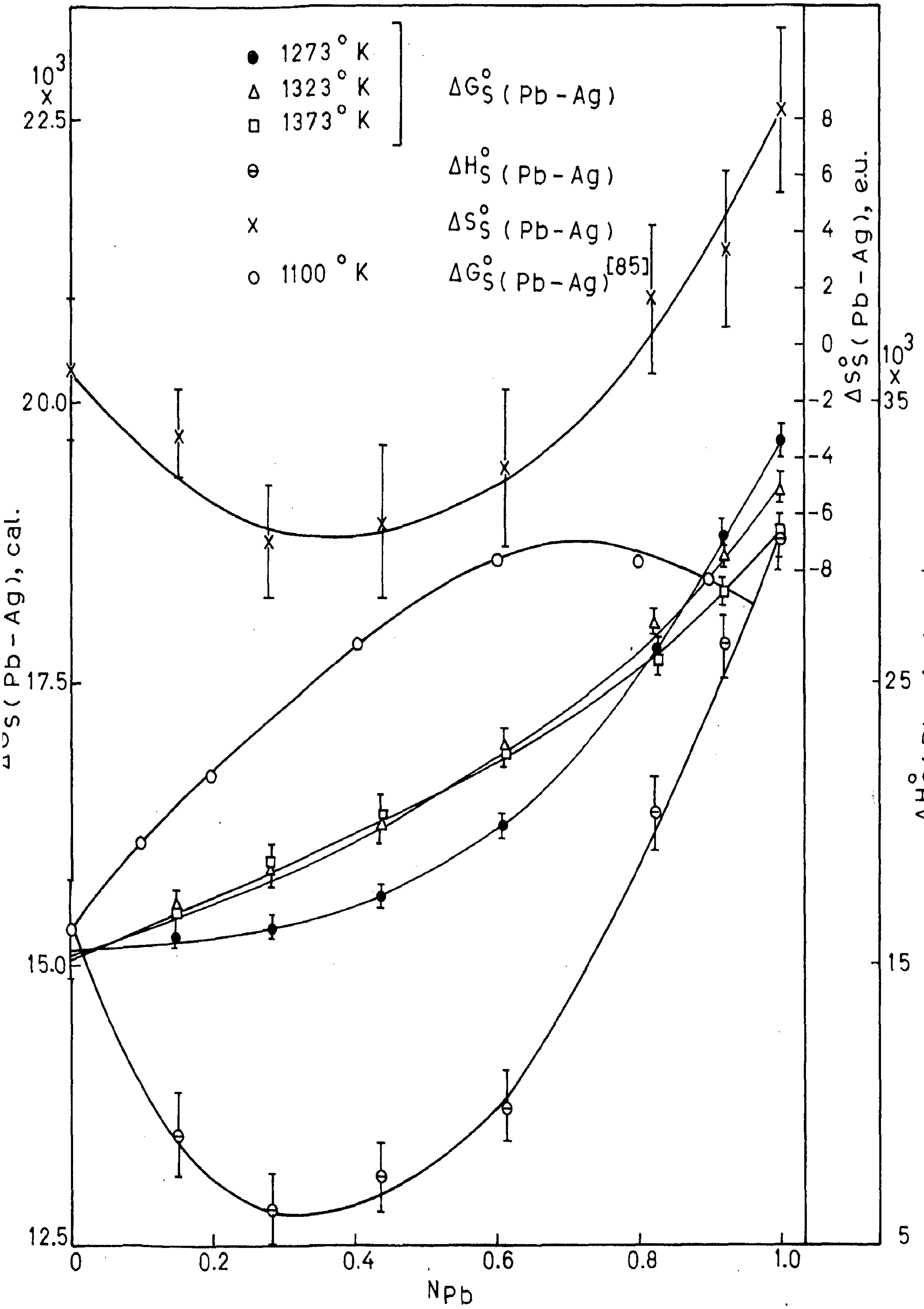

FIG.III.8 FREE ENERGY ENTHALPY AND ENTROPY OF SULPHUR EQUILIBRIA IN BINARY LEAD-SILVER ALLOYS.

TABLE-III.34 : Different thermodynamic parameters calculated from experimental data for binary lead-silver alloy solvents

Composition N_{Pb}	Temp °K	ln K_{HS}	$\varepsilon^{S}_{S(Pb-Ag)}$	$\Delta G^{o}_{S(Pb-Ag)}$ (cals)	$\varepsilon^{Pb}_{S(Ag)}$	$\varepsilon^{Ag}_{S(Pb)}$
0.92	1273	-4.85 (±0.29)	1.16 (±0.12)	18810 (±600)	-0.33	5.68
0.824	"	-4.45 (±0.23)	0.89 (±0.13)	17810 (±540)		
0.61	"	-3.82 (±0.24)	0.91 (±0.07)	16220 (±550)		
0.438	"	-3.58 (±0.21)	1.02 (±0.02)	15610 (±520)		
0.283	"	-3.47 (±0.23)	1.31 (±0.08)	15340 (±550)		
0.148	"	-3.44 (±0.21)	0.85 (±0.07)	15250 (±500)		
0.92	1323	-4.79 (±0.29)	0.81 (±0.09)	18620 (±540)	-0.47	4.39
0.824	"	-4.59 (±0.25)	0.54 (±0.11)	18030 (±500)		
0.61	"	-4.17 (±0.27)	0.78 (±0.05)	18940 (±530)		

Table-III.34 : Contd.

Composition N_{Pb}	Temp ^oK	ln K_{HS}	$\varepsilon^{S}_{S(Pb-Ag)}$	$\Delta G^{o}_{S(Pb-Ag)}$ (cals)	$\varepsilon^{Pb}_{S(Ag)}$	$\varepsilon^{Ag}_{S(Pb)}$
0.438	1323	-3.90 (±0.23)	0.73 (±0.03)	16220 (±500)		
0.283	"	-3.76 (±0.25)	0.84 (±0.05)	15850 (±520)		
0.148	"	-3.63 (±0.30)	0.67 (±0.11)	15520 (±600)		
0.92	1373	-4.74 (±0.23)	0.65 (±0.03)	18310 (±510)	-0.63	3.08
0.824	"	-4.52 (±0.21)	0.47 (±0.04)	17700 (±480)		
0.61	"	-4.21 (±0.27)	0.63 (±0.03)	16860 (±550)		
0.438	"	-4.017 (±0.29)	0.81 (±0.05)	16340 (±570)		
0.283	"	-3.85 (±0.27)	0.96 (±0.04)	15910 (±540)		
0.148	"	-3.701 (±0.25)	0.48 (±0.04)	15480 (±530)		

pure metallic solvents (as already discussed in Secs. (III.2.1.1 - III.2.1.3) above). Therefore, the data obtained in the present study on binary lead-silver alloy solvents are considered to be more reliable than those reported by Mohapatra et al. Twidwell and Larson [58] have also studied the behaviour of sulphur in dilute solution range at temperature 873°K for lead-silver alloys containing 4.5, 9.2, 16.6 and 32.2 at.% Silver and reported activity coefficient values of sulphur as 1.151, 1.355, 1.725 and 2.43 respectively.

From plots of $\Delta G^{o}_{S(Pb-Ag)}$ Vs. composition interaction parameters $\varepsilon^{Ag}_{S(Pb)}$ and $\varepsilon^{Pb}_{S\,(Ag)}$ have also been calculated. Values of these parameters are found to be 5.68, 4.39 and 3.08 and-0.330,-0.47 and-0.63 respectively at temperatures 1273, 1323 and 1373°K. Twidwell et al. [58] have reported the value of interaction parameter ε^{Ag}_{S} as 3.3 at 873°K. The values of different function calculated above are given in Table III.34.

III.2.2.2 Sulphur in Binary Lead-Copper Solvents

The experimental data on equilibria-runs for different lead-copper alloys is presented in Tables III.10 - III.15 and from these,the function $[\ln(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{at.\%S})]$ has been calculated for different binary Pb-Cu alloy solvents at the three temperatures of investigation i.e., 1273, 1323 and 1373°K and plotted against at.% S in Figs. III.9-III.11.

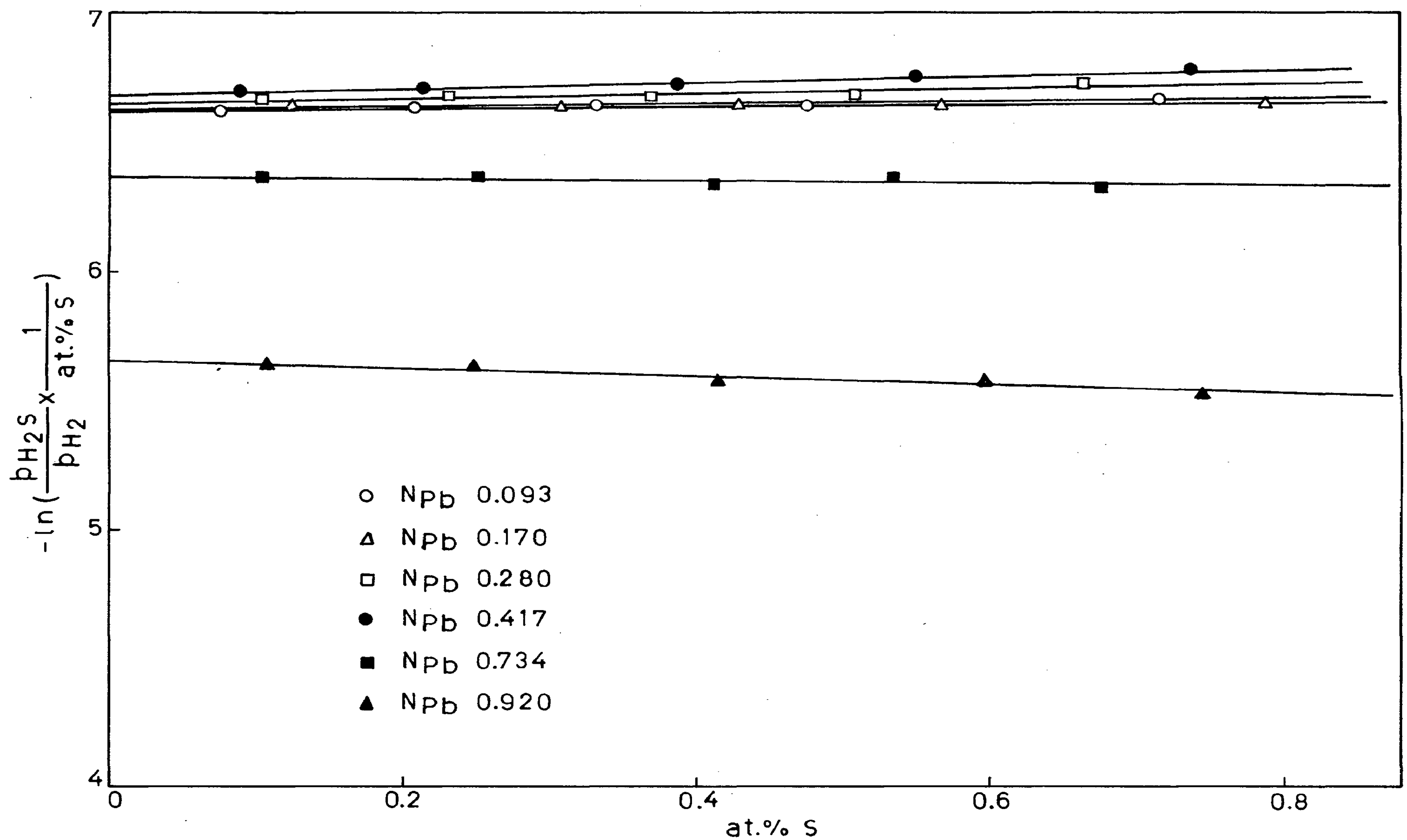

FIG.III.9 PLOT OF FUNCTION $\left[-\ln\left(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{\text{at.\% S}}\right)\right]$ Vs. at.% S FOR DISSOLUTION OF SULPHUR IN BINARY LEAD-COPPER ALLOYS AT 1273 °K.

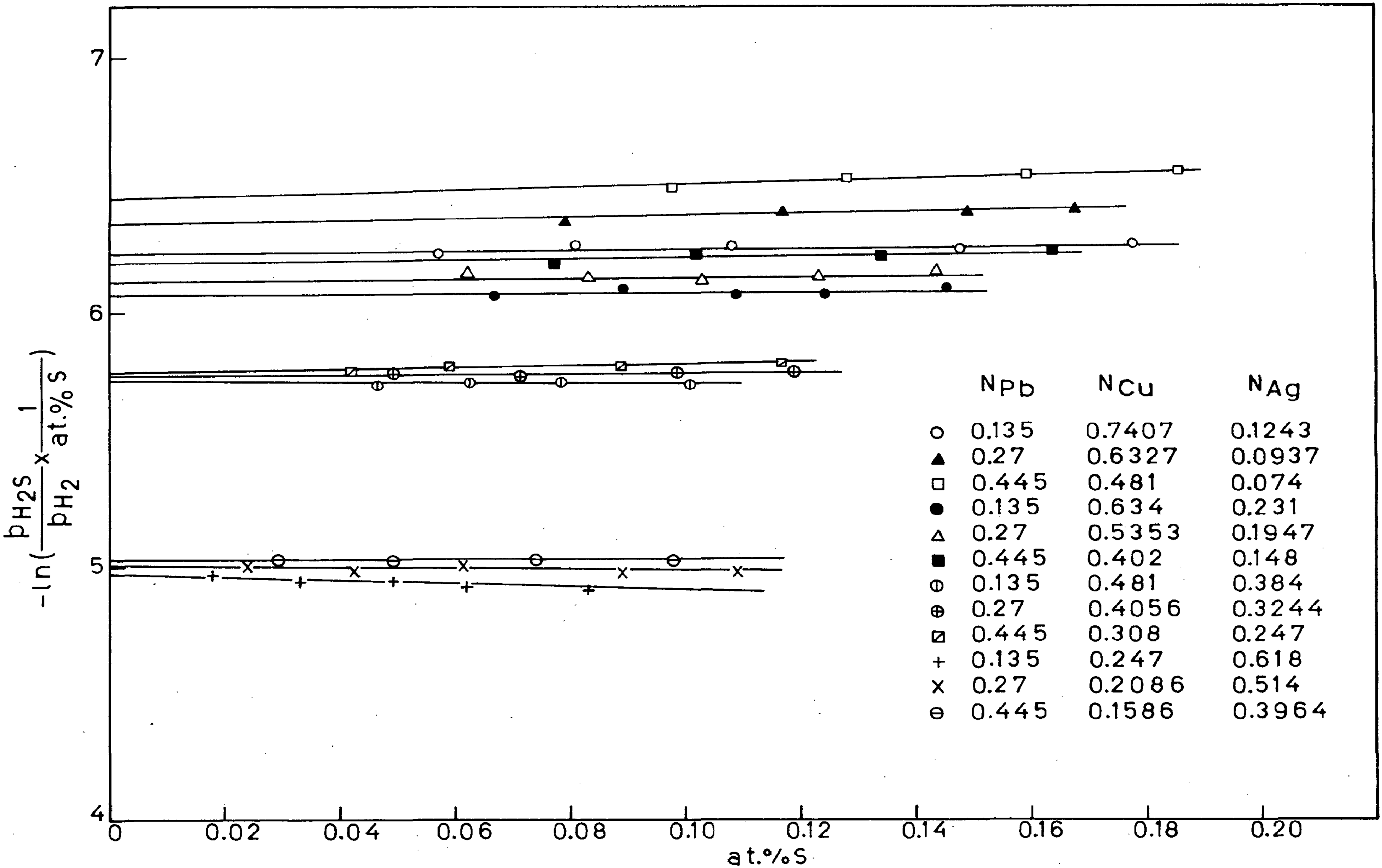

FIG. III.19 PLOT OF FUNCTION $\left[-\ln\left(\frac{p_{H_2S}}{p_{H_2}} \times \frac{1}{at.\%\ S}\right)\right]$ Vs. at.%S FOR DISSOLUTION OF SULPHUR IN LEAD-COPPER-SILVER TERNARY ALLOYS AT 1373°K.

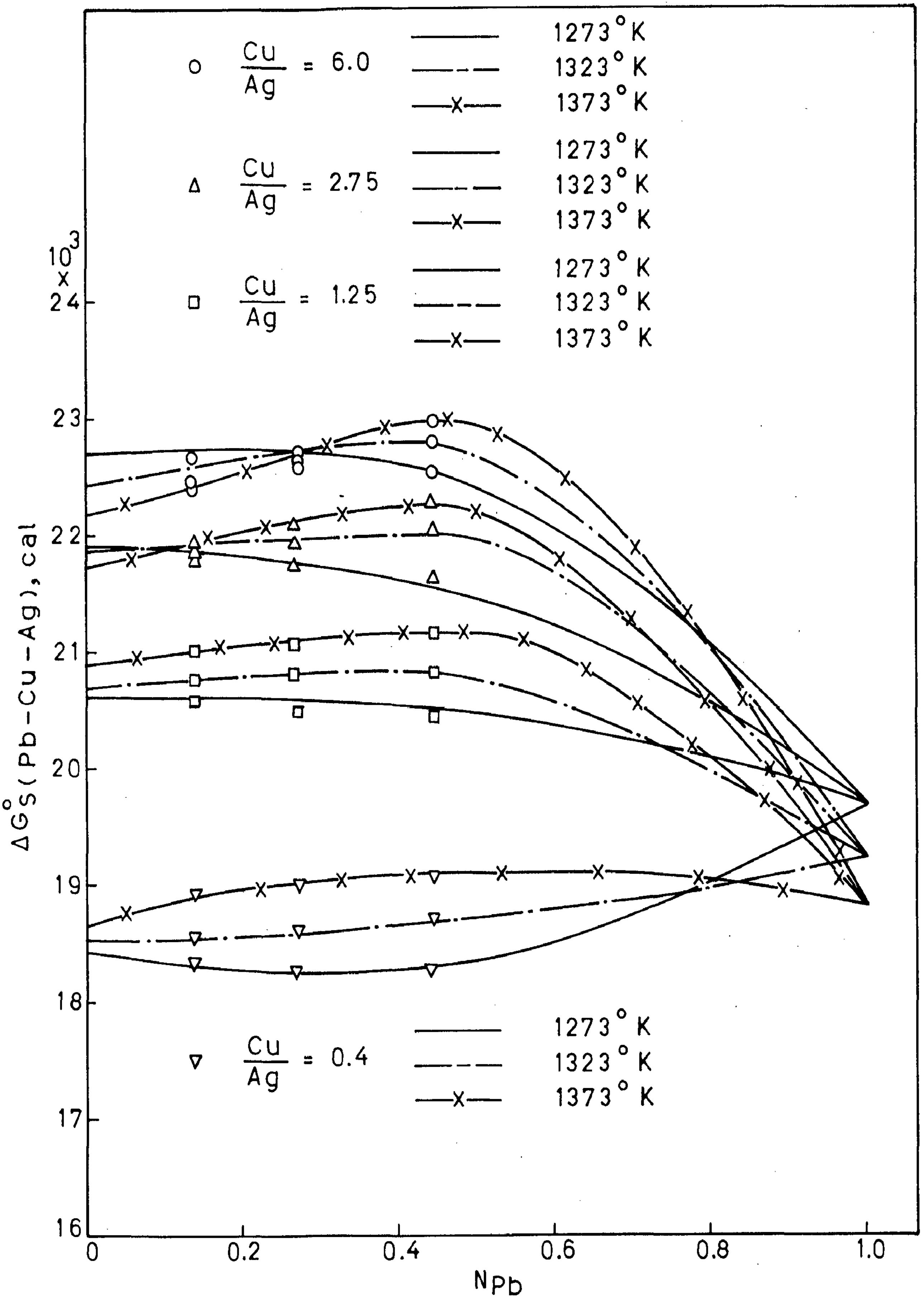

FIG.III.20 PLOT SHOWING VARIATION IN FREE ENERGY OF EQUILIBRIA OF SULPHUR WITH N_{Pb} IN TERNARY ALLOYS OF DIFFERENT Cu : Ag RATIOS.

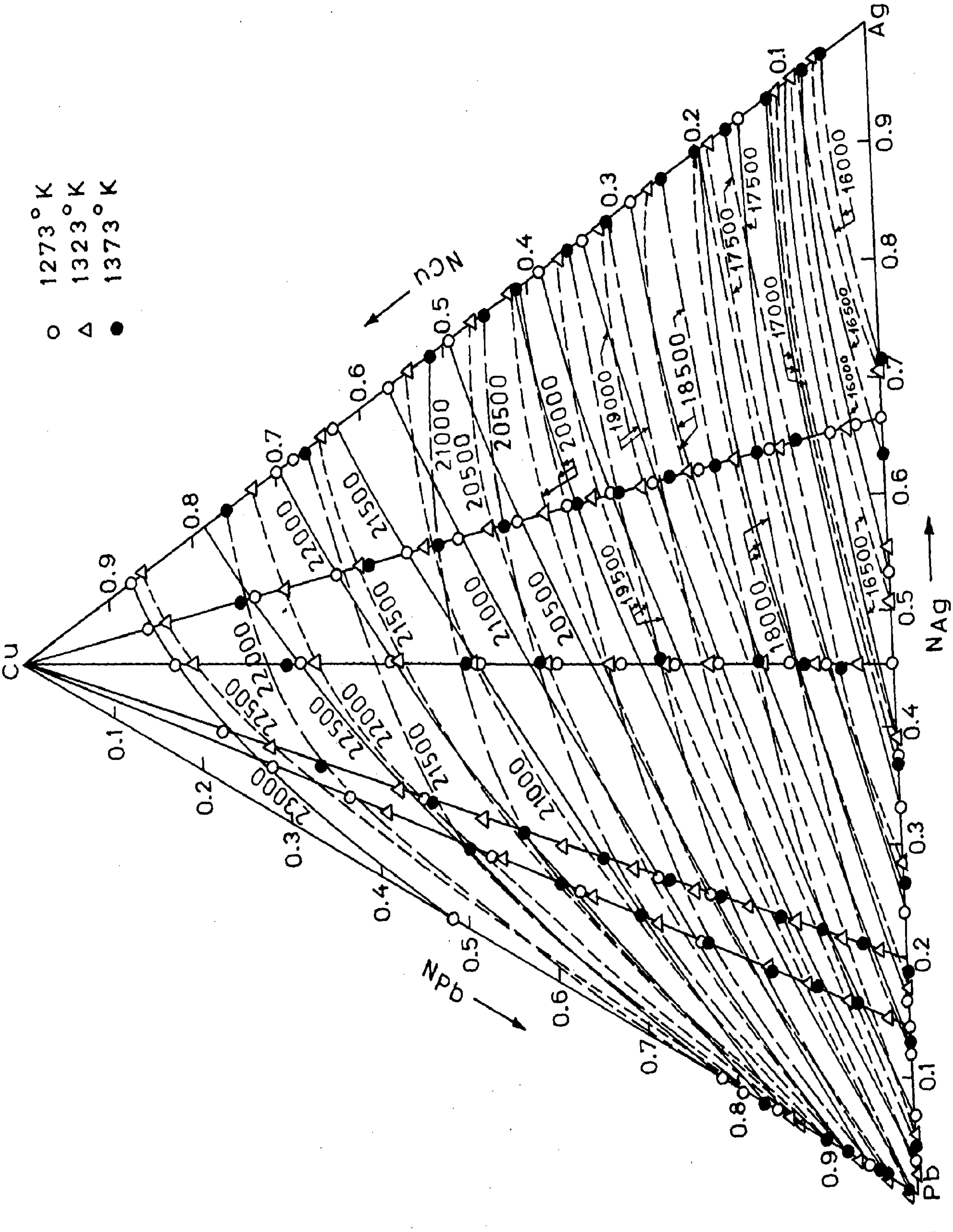

FIG. III.21 ISO-FREE ENERGY CURVES FOR EQUILIBRIA OF SULPHUR IN DIFFERENT Pb-Cu-Ag TERNARY ALLOYS AT DIFFERENT TEMPERATURES. $[\Delta G^{o}_{S}(\text{Pb-Cu-Ag}), \text{cal.}]$

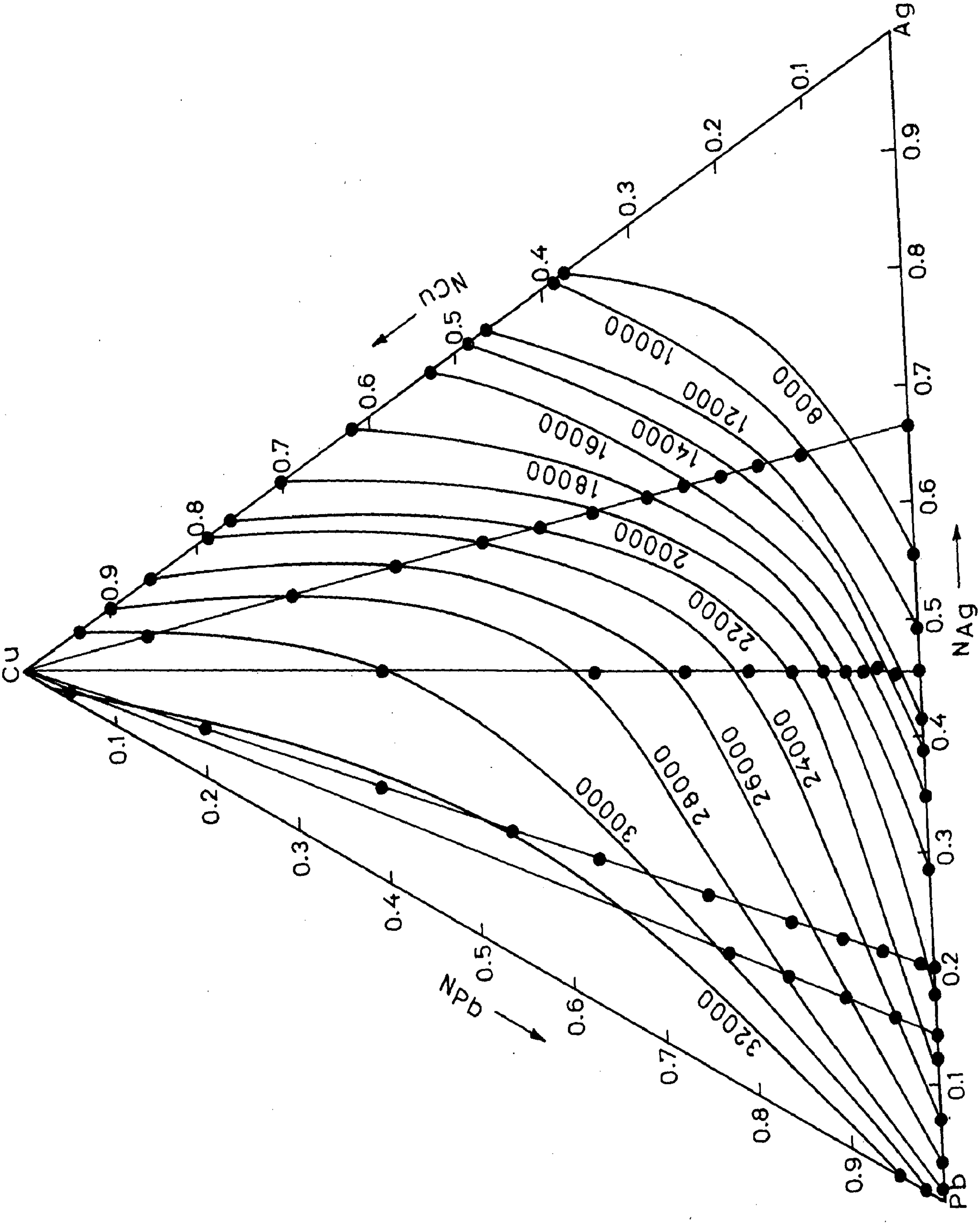

FIG.III.22 ISO-ENTHALPY CURVES FOR EQUILIBRIA OF SULPHUR IN DIFFERENT Pb-Cu-Ag TERNARY ALLOYS.

[ΔH^{o}_{S}(Pb-Cu-Ag) in cal.]

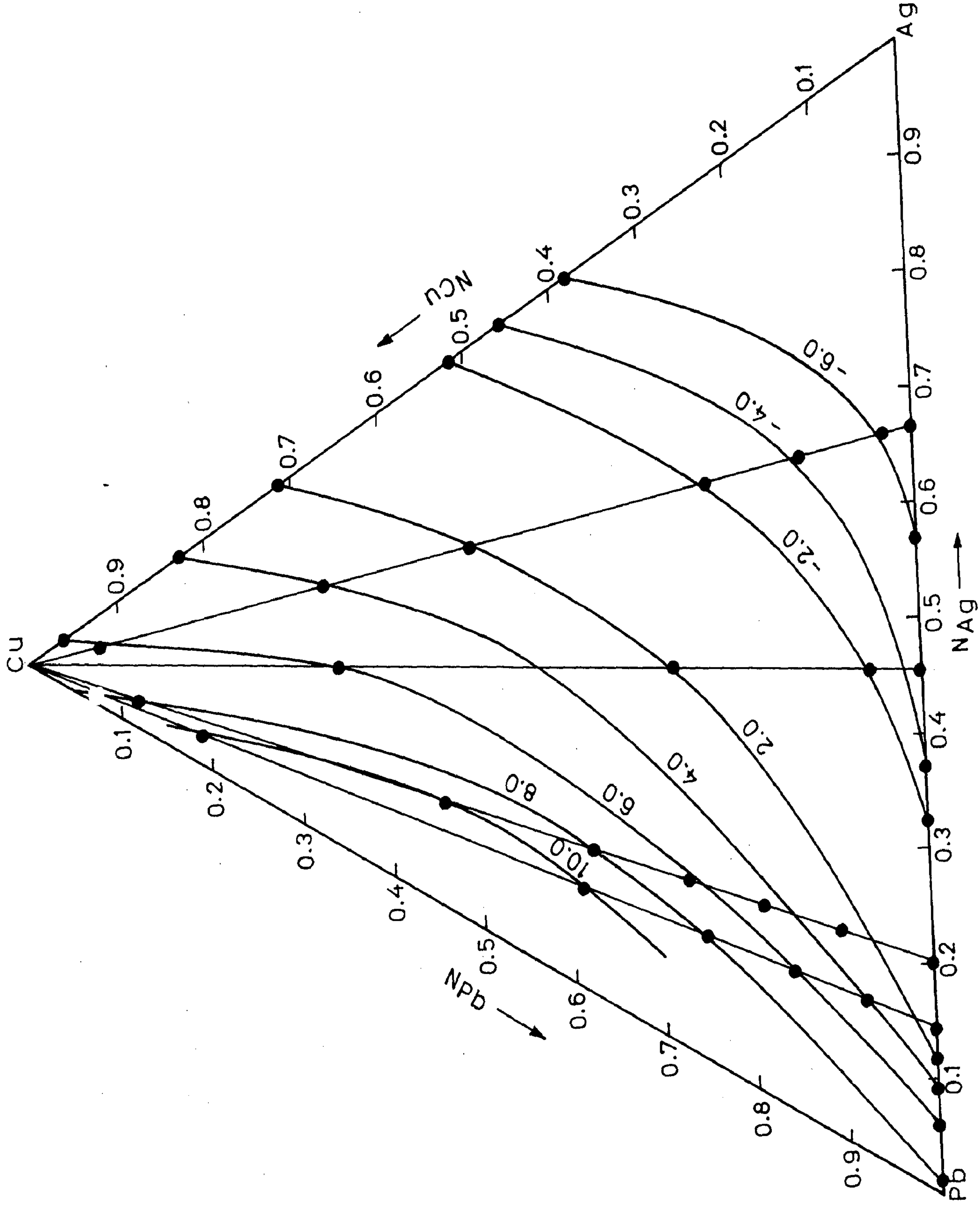

FIG. III. 23 ISO-ENTROPY CURVES FOR EQUILIBRIA OF SULPHUR IN DIFFERENT Pb-Cu-Ag TERNARY ALLOYS. $\left[\Delta S^{\circ}_{S(Pb-Cu-Ag)}\right.$ in e.u.$\left.\right]$

TABLE-37 : Different thermodynamic parameters calculated from experimental data for ternary Pb-Cu-Ag alloy solvents

Composition			Temp°K	ln K_{HS}	$\varepsilon^{S}_{S/Pb-Cu-Ag)}$	$\Delta G^{o}_{S(Pb-Cu-Ag)}$ cals.
N_{Pb}	N_{Cu}	N_{Ag}				
0.135	0.7407	0.1243	1273	-6.37 (±0.23)	-0.516 (±0.03)	22680 (±540)
0.135	0.634	0.231		-6.02 (±0.25)	-0.308 (±0.03)	21790 (±570)
0.135	0.481	0.384		-5.55 (±0.29)	-0.378 (±0.04)	20580 (±620)
0.135	0.247	0.618		-4.65 (±0.22)	-0.401 (±0.05)	18340 (±520)
0.27	0.6327	0.0937		-6.33 (±0.29)	-0.437 (±0.105)	22580 (±620)
0.27	0.5353	0.1947		-5.99 (±0.30	-0.196 (±0.02)	21730 (±630)
0.27	0.4056	0.3244		-5.51 (±0.25)	-0.385 (±0.03)	20500 (±570)
0.27	0.2086	0.5214		-4.64 (±0.27)	-0.297 (±0.03)	18300 (±590)
0.445	0.481	0.074		-6.32 (±0.26)	-0.319 (±0.07)	22540 (±580)
0.445	0.407	0.148		-5.96 (±0.25)	-0.187 (±0.04)	21650 (±550)
0.445	0.308	0.247		-5.48 (±0.22)	-0.237 (±0.04)	20430 (±510)
0.445	0.1586	0.3964		-4.63 (±0.23)	-0.198 (±0.04)	18270 (±530)

Table-37 (Contd.)

Composition			Temp°K	ln K_{HS}	$\varepsilon^{S}_{S(Pb+Cu+Ag)}$	$\Delta G^{o}_{S(Pb+Cu+Ag)}$ cals.
N_{Pb}	N_{Cu}	N_{Ag}				
0.135	0.7407	0.1243	1323	-6.26 (±0.29)	-0.234 (±0.05)	22440 (±610)
0.135	0.634	0.231		-6.04 (±0.23)	-0.287 (+0.04)	21840 (±570)
0.135	0.481	0.384		-5.63 (±0.21)	-0.322 (±0.05)	20770 (±530)
0.135	0.247	0.618		-4.81 (±0.19)	-0.298 (±0.03)	18600 (±500)
0.27	0.6327	0.0937		-6.34 (±0.28)	-0.326 (±0.09)	22640 (±580)
0.27	0.5353	0.1947		-6.08 (±0.28)	-0.172 (±0.03)	21940 (±570)
0.27	0.4056	0.3244		-5.64 (±0.27)	-0.336 (±0.02)	20800 (±570)
0.27	0.2086	0.5214		-4.83 (±0.21)	-0.216 (±0.04)	18670 (±500)
0.445	0.481	0.074		-6.41 (±0.29)	-0.126 (±0.03)	22830 (±600)
0.445	0.407	0.148		-6.11 (±0.25)	-0.150 (±0.03)	22040 (±570)
0.445	0.308	0.247		-5.66 (±0.21)	-0.133 (±0.03)	20850 (±520)
0.445	0.1586	0.3964		-4.85 (±0.23)	-0.117 (±0.05)	18700 (±540)

Table-37 (Contd.)

Composition			Temp^{o}K	ln K_{HS}	$\epsilon^{S}_{S(Pb-Cu-Ag)}$	$\Delta G^{o}_{S(Pb-Cu-Ag)}$ cals.
N_{Pb}	N_{Cu}	N_{Ag}				
0.135	0.7407	0.1243	1373	-6.23 (±0.21)	-0.135 (±0.05)	22380 (±500)
0.135	0.634	0.231		-6.07 (±0.21)	-0.173 (±0.04)	21940 (±510)
0.135	0.481	0.384		-5.73 (±0.23)	0.087 (±0.03)	21010 (±540)
0.135	0.247	0.618		-4.97 (±0.25)	-0.107 (±0.05)	18940 (±560)
0.27	0.6327	0.0937		-6.345 (±0.26)	-0.486 (±0.06)	22690 (±590)
0.27	0.5353	0.1947		-6.12 (±0.25)	-0.187 (±0.05)	22090 (±550)
0.27	0.4056	0.3244		-5.76 (±0.27)	-0.115 (±0.03)	21080 (±570)
0.27	0.2086	0.5214		-4.99 (±0.23)	-0.168 (±0.03)	19010 (±520)
0.445	0.481	0.074		-6.46 (±0.27)	-0.285 (±0.04)	23000 (±570)
0.445	0.407	0.148		-6.20 (±0.25)	-0.116 (±0.02)	22280 (±540)
0.445	0.308	0.247		-5.79 (±0.23)	-0.098 (±0.03)	21170 (±510)
0.445	0.1586	0.3964		-5.02 (±0.21)	-0.073 (±0.03)	19080 (±500)

$\frac{\Delta G^{o}_{S(Pb-Cu-Ag)}}{T}$ Vs. (1/T) plots for these alloys, values of enthalpy and entropy for the reaction given by eq.(III.34) have been evaluated for these alloys. Finally from these values, iso-free energy, iso-enthalpy and iso-entropy plots have been drawn in Figs. III.21 - Fig. 23. The values of different functions computed are shown in Table III.37

It has been inferred from the literature review that no work has so far been carried out on Pb-Cu-Ag ternary alloys for study of behaviour of sulphur.

CHAPTER - IV

STATISTICAL THERMODYNAMIC INTERPRETATION OF RESULTS

IV.1 Introduction:

In the previous chapter, different experimental parameters namely, the interaction parameters and the equilibrium constants for dissolution of sulphur from the gaseous phase in pure liquid metallic solvents and alloy solvents have been calculated from the experimental data. This chapter is devoted to a quantitative interpretation of the experimentally determined values of equilibrium constants. For this purpose, the statistical approach to the study of thermodynamics of solutions is made use of. In such treatments either the composition of the system is arrived at from a knowledge of the chemical potentials of the surroundings or expressions for free energy of solution and the different partial molar properties of each of the constituents are derived for a solution of known composition. In the present case, the later approach shall be followed for the sake of simplicity of treatment although the first approach is considered to be more rigorous. However, the end results obtained in both the cases are found to be the same.

As the experimentally determinable variable is equilibrium constant for the reaction expressed by eq. (III.34) and the different theoretical expressions shall be in terms of the excess partial molar properties of the components of the solution under study, so one would first require a relationship between these two parameters. For its derivation, one proceeds as follows :

Eq. (III.34) is split into the following two reactions.

$$1/2\ S_2 = S(l) \qquad \text{... (IV.1)}$$

and

$$S(l) = \underline{S} \qquad \text{... (IV.2)}$$

The first reaction pertains to the condensation of sulphur from the gaseous phase into a hypothetical atomic liquid sulphur phase. Let $\Delta G_1^o(T)$ be the standard free energy of the reaction, which will obviously be a function of temperature, T. Thus, according to this reaction, the fugacity, $f_{S_2}^o$, of gaseous sulphur in equilibrium with pure liquid sulphur shall be given by the expression

$$f_{S_2}^o = \exp\left[\frac{2.\{\Delta G_1^o(T)\}}{RT} \right] \qquad \text{... (IV.3)}$$

Eq. (IV.2) expresses the dissolution of sulphur from its pure liquid form in the alloy. Hence, if one takes pure liquid sulphur as the standard state, then free energy, ΔG_2, of this reaction shall be given by the expression,

$$\Delta G_2 = RT \ln a_S \qquad \text{... (IV.4)}$$

where, a_S is the activity of sulphur in the solution. For ideal or Raoultian behaviour of sulphur in a melt, the above expression will take the form,

$$\Delta G_2^{id} = RT \ln N_S^{id} \qquad \text{... (IV.5)}$$

whereas, for Henrian behaviour (with infinite dilution as standard state) eq. (IV.4) takes the form,

$$\Delta G_2^{H} = RT \ln \gamma^o + RT \ln N_S^{H} \qquad \text{... (IV.6)}$$

where γ^o is the Henry's law constant and N_S^{id} and N_S^{H} are mole fractions of sulphur in the ideal and Henrian solutions respectively.

With the help of eqs. (IV.3) - (IV.5), one can express the solubility of sulphur for its ideal behaviour under its low partial pressure, P_{S_2}, (at which fugacity can be taken to be equal to partial pressure) by the following expression:

$$N_S^{id} = \left(\frac{p_{S_2}}{f^o_{S_2}}\right)^{1/2}$$

$$= p_{S_2}^{1/2} \cdot \exp\left[-\frac{\Delta G_1^o(T)}{RT}\right] \qquad \text{... (IV.7)}$$

whereas, from eqs. (IV.3), (IV.4) and (IV.6) for a Henrian solution, one can write similarly the following expression,

$$p_{S_2}^{1/2} = \gamma^o \cdot N_S^H \cdot \exp\left[-\frac{\Delta G_1^o(T)}{RT}\right] \qquad \text{... (IV.8)}$$

Eqs. (IV.7) and (IV.8) yield for a given partial pressure of sulphur the following relationship,

$$\gamma^{o} = \frac{N_S^{id}}{N_S^{H}} = \left(\frac{p_{S_2}^{1/2}}{N_S^{H}}\right) \cdot \exp\left[\frac{\Delta G_1^{o}(T)}{RT}\right] \qquad \ldots (IV.9)$$

From eq.(IV.1), it is clear that

$$\left(\frac{p_{S_2}^{1/2}}{N_S}\right)_{p_{S_2} \to o} = K \qquad \ldots (IV.10)$$

and hence $N_S \to o$

Thus the required relationship between the Henry's law constant, γ^{o}, and the equilibrium constant, K, for the reaction(III.34) takes the following form,

$$RT \ln \gamma^{o} = RT \ln K + \Delta G_1^{o}(T) \qquad \ldots (IV.11)$$

or, in terms of free energies,

$$\Delta \bar{G}_{S\,(A+P+C)}^{ex} = - \Delta G_{S(A+P+C)}^{o} + \Delta G_1^{o}(T) \qquad \ldots (IV.12)$$

where, $\Delta \bar{G}_{S(A+P+C)}^{ex}$ is the partial molar excess free energy and $\Delta G_{S(A+P+C)}^{o}$, the standard free energy of solution of sulphur. In the above expression, the value for $\Delta \bar{G}_{S(A+P+C)}^{ex}$ will be derived from theoretical treatment, whereas that of $\Delta G_{S(A+P+C)}^{o}$, for the reaction expressed by eq. (III.34), shall be determined experimentally. Though the value of temperature dependent function, $\Delta G_1^{o}(T)$, can be calculated with the help of thermodynamic properties of sulphur, yet as shall be seen during the course of treatment in the present chapter, this parameter is not required for a correlation of experimental and theoretically computed data.

In the following sections, therefore, first a unified theoretical approach shall be presented for the behaviour of infinitely dilute solutions of sulphur in alloys and from this, under different simplifying assumptions, a set of expressions correlating the function $\Delta G^{o}_{S(A+P+C)}$ with the composition of solution shall be derived. Then in the next section applicability of these expressions shall be tested and discussed.

IV.2 Theory

Though a number of models have been proposed to explain the thermodynamic properties of dilute substitutional as well as interstitial systems, but most of these are based on lattice assumptions and have been applied predominantly to systems in which the solute is present in binary alloy solvents. These approaches have been reviewed comprehensively by Kapoor [68]. The major weakness of these models is that they do not take into account the changes in free volumes on mixing and hence are unable to explain most of the thermodynamic properties of such solutions to a satisfactory degree of accuracy. This is particularly true for the explanation of the changes in entropy on mixing.To overcome this drawback, in the present work, the free volume theory, of which lattice models form a special case, will be made use of for the derivation of different thermodynamic relationships to explain the experimental results. The basic assumptions of free volume theory are as follows:

i) Molecules or atoms present in a solution can be assumed to form a quasi-crystalline lattice with atoms of each of the species being assigned a particular type of site. In case, the atoms of the different constituent species are similar in size, as in the case of the system under study in the present work, each atom can be considered to occupy, as its mean position, one lattice site. However, if the solute atoms are much smaller in size than the solvent atoms, they will occupy the interstitial sites of the quasi-crystalline lattice built by the solvent atoms. This type of solutions are generally referred to as 'interstitial solutions', whereas the former type as the 'substitutional solutions'. This assumption is the same as the one made in the case of lattice models.

ii) The atoms of a solution vibrate around their mean positions in a small space called 'cell'. The volume of such a cell is determined by the interaction of the atom occupying it with its nearest neighbours i.e., those lying in its first 'coordination shell'.

iii) The energy of an atom is a function of the number and types of atoms surrounding it.

Systems studied in the present investigation consisted of a molten metallic solvent (either pure molten metal - lead, copper or silver or their binary alloys consisting of any two of these metals or a ternary alloy consisting of all three of them) and a gaseous phase comprising of a mixture of Hydrogen and Hydrogen sulphide and having a predetermined chemical potential for sulphur. Equilibrium studies have been conducted on such systems. For the purpose of statistical thermodynamic treatment of the solution, one may consider it to form an open system with respect to sulphur (as it can be exchanged by the solution with the surrounding gaseous phase) and closed system with respect to the metallic components (as their volatilisation during the equilibration process has been found experimentally to be negligibly small). Thus for the derivation of different experessions for the amount of sulphur dissolved in the metallic solvents and also for the derivation of expressions for the different thermodynamic properties of such systems, one requires, in principle, constructing a semi-grand partition function, Ξ , for the solution. Such a partition function is defined by the following expression,

$$\Xi = \sum_{n_x} \left[\quad (n_A, n_P, n_C, n_S) \exp \left(\frac{\mu_S \cdot n_S}{NkT} \right) \right] \quad \ldots \text{(IV. 13)}$$

where, n_A, n_P, n_C are respectively the numbers of atoms of silver, lead and copper in the solvent, n_S corresponds to the number of sulphur atoms in the solution, μ_S represents the chemical potential of sulphur in the gaseous phase, N, the Avogadro's number, k, the Boltzmann's constant, T, the absolute temperature and finally $\Omega(n_A, n_P, n_C, n_S)$ represents the ordinary partition function of the solution containing atoms of different species as given in parenthesis. However, as stated earlier, instead of adopting this path, we shall assume a solution of constant composition and construct an ordinary partition function for such a system and derive its thermodynamic properties.

The ordinary partition function, Ω, of an ensemble is defined by the expression,

$$\Omega = \sum_i \left[\exp(-E_i/kT) \cdot \prod_i (v_i) \right] \qquad \ldots \text{(IV.14)}$$

where the summation in the above expression extends over all distinguishable states of the system. The above expression can be written in a more frequently used alternative form. In this form, all distinguishable state of the system having the same energy are written together. Thus, expression for Ω is written as,

$$\Omega = \sum_i^n g(E_i) \cdot \exp(-E_i/kT) \cdot \prod_i (v_i) \qquad \ldots \text{(IV.15)}$$

where $g(E_i)$ is the number of distinguishable states of the system having same total energy E_i. The summation in the above equation now extends over all possible values of total energy E_i. In this case again, the evaluation of Ω is done by replacing the summation by the maximum term in the series given by eq. (IV.15). Thus,

$$\Omega = g_{max} \cdot \exp\left(-\frac{E_{max}}{kT}\right). \qquad (v_{max}) \qquad \ldots (IV.16)$$

where, g_{max} and E_{max} correspond to the values of these variables in the maximum term which can be determined by the standard procedure for optimisation as will be shown later in the course of present treatment. As a first step for the evaluation of this term, one needs expressions for the combinatorial term, g, and energy E.

The energy of the system, E, may be considered to be equal to the sum of the energies of all the atoms present in the system. These atoms can be distinguished, firstly, on the basis of species to which they belong and secondly on the basis of the number and types of other atoms present in their first coordination shells. On this basis, one can classify atoms into following different categories with another simplifying assumption that the coordination number of each atom is z.

i) Silver atoms having no solute atom, i-lead atoms and j-copper atoms in their first coordination shells. Let there be $n_A^{i\,jo}$ such atoms in a particular total energy state of the system. If $W_A^{i\,jo}$ is the energy of one such atom, then the total energy, E_A^o, of all such atoms having no solute atom around them will be given by the expression,

$$E_A^o = \sum_{i=o}^{z} \sum_{j=o}^{(z-i)} W_A^{ijo} \cdot n_A^{ijo} \qquad \ldots \text{(IV.17)}$$

ii) Assuming further the solution to be so dilute in solute that no solvent atom has more than one solute atom in its first coordination shell, that a solute atom does not have an atom of its own species in its first coordination shell and also that there will be few silver atoms having only one solute atom in their first coordination shell, the other atoms will be those of the type of species present in the solvent. If n_A^{kdl} denotes the number of silver atoms having k atoms of lead, d atoms of copper and one atom of sulphur around them and W_A^{kdl} the energy of one such atom, then the total energy, E_A^1, of silver atoms having one sulphur atom shall be given by the expression

$$E_A^1 = \sum_{k=o}^{(z-1)} \sum_{d=o}^{(z-k-1)} W_A^{kdl} \cdot n_A^{kdl} \qquad \ldots \text{(IV.18)}$$

If one denotes by n_A^1, the total number of silver atoms having one solute atom around them and n_A^o, those having no solute atom around them one can write, on the basis of mass balance, the following expressions

$$\sum_{i=o}^{z} \sum_{j=o}^{(z-i)} n_A^{ijo} = n_A^o \qquad \ldots \text{(IV.19)}$$

$$\sum_{k=o}^{(z-1)} \sum_{d=o}^{(z-k-1)} n_A^{kdl} = n_A^1 \qquad \ldots \text{(IV.20)}$$

and,

$$\sum_{i=o}^{z}\sum_{j=o}^{(z-i)} n_A^{i\,jo} + \sum_{k=o}^{(z-1)}\sum_{d=o}^{(z-k-1)} n_A^{kdl} = n_A^o + n_A^1 = n_A \quad \ldots (IV.21)$$

iii) As in (i) above, one can also categorise lead atoms. Thus if one denotes by n_P^{xyo}, lead atoms having x copper atoms and y - silver atoms and no solute (sulphur) atom around, and by W_P^{xyo}, the corresponding energy, one can write the following expressions for the energy, E_P^o, and number, n_P^o, of all lead atoms having no solute atom around them,

$$E_P^o = \sum_{x=o}^{z}\sum_{y=o}^{(z-x)} W_P^{xyo} \cdot n_P^{xyo} \quad \ldots (IV.22)$$

and

$$\sum_{x=o}^{z}\sum_{y=o}^{(z-x)} n_P^{xyo} = n_P^o \quad \ldots (IV.23)$$

iv). As in (ii), classifying the lead atoms, one can write the following expressions,

$$E_P^1 = \sum_{p=o}^{(z-1)}\sum_{q=o}^{(z-p-1)} W_P^{pql} \cdot n_P^{pql} \quad \ldots (IV.24)$$

and,

$$\sum_{p=o}^{(z-1)}\sum_{q=o}^{(z-p-1)} n_P^{pql} = n_P^1 \quad \ldots (IV.25)$$

$$\sum_{x=o}^{z}\sum_{y=o}^{(z-x)} n_P^{xyo} + \sum_{p=o}^{(z-1)}\sum_{q=o}^{(z-p-1)} n_P^{pql} = n_P^o + n_P^1 = n_P. \quad (IV.26)$$

v) Similarly one can write the following expressions for the different types of solvent copper atoms;

$$E_C^o = \sum_{r=o}^{z} \sum_{t=o}^{(z-r)} W_C^{rto} \cdot n_C^{rto} \qquad \ldots \text{(IV.27)}$$

and,

$$\sum_{r=o}^{z} \sum_{t=o}^{(z-r)} n_C^{rto} = n_C^o \qquad \ldots \text{(IV.28)}$$

where n_C^{rto} denotes the number of copper atoms having r-silver, t-lead and no sulphur atoms around them. Further,

$$E_C^1 = \sum_{u=o}^{(z-1)} \sum_{v=o}^{(z-u-1)} W_C^{uv1} \cdot n_C^{uv1} \qquad \ldots \text{(IV.29)}$$

and,

$$\sum_{u=o}^{(z-1)} \sum_{v=o}^{(z-u-1)} n_C^{uv1} = n_C^1 \qquad \ldots \text{(IV.30)}$$

Also,

$$\sum_{r=o}^{z} \sum_{t=o}^{(z-r)} n_C^{rto} + \sum_{u=o}^{(z-1)} \sum_{v=o}^{(z-u-1)} n_C^{uv1} = n_C^o + n_C^1 = n_C . \qquad \text{(IV.31)}$$

vi. Lastly, one requires an expression for the energy, E_S, of the solute atoms. If one assumes that a solute atom having m- silver, w-lead and rest copper atoms in its first coordination shell, has an energy, W_S^{mw}, and if there are n_S^{mw} such atoms in the system, then E_S shall be given by the expression,

$$E_S = \sum_{m=0}^{z} \sum_{w=0}^{(z-m)} W_S^{mw} . n_S^{mw} \qquad \ldots \text{(IV.32)}$$

and ,

$$\sum_{m=0}^{z} \sum_{w=0}^{(z-m)} n_S^{mw} = n_S \qquad \ldots \text{(IV.33)}$$

Thus, with the help of eqs. (IV.17) - (IV.33), one can write the following expression for the total energy, E, of the system,

$$\begin{aligned} E &= E_A^o + E_A^1 + E_P^o + E_P^1 + E_C^o + E_C^1 + E_S \\ &= \sum_{i=o}^{z} \sum_{j=o}^{(z-i)} W_A^{ijo} . n_A^{ijo} + \sum_{k=o}^{(z-1)} \sum_{d=o}^{(z-k-1)} n_A^{kdl} . W_A^{kdl} \\ &+ \sum_{x=o}^{z} \sum_{y=o}^{(z-x)} W_P^{xyo} . n_P^{xyo} + \sum_{p=o}^{(z-1)} \sum_{q=o}^{(z-p-1)} W_P^{pql} . n_P^{pql} \\ &+ \sum_{r=o}^{z} \sum_{t=o}^{(z-r)} n_C^{rto} . W_C^{rto} + \sum_{u=o}^{(z-1)} \sum_{v=o}^{(z-u-1)} n_C^{uvl} . W_C^{uvl} \\ &+ \sum_{m=o}^{z} \sum_{w=o}^{(z-m)} W_S^{mw} . n_S^{mw} \end{aligned} \qquad \ldots \text{(IV.34)}$$

Similarly, one can write the following expression for the product of free volumes of all the atoms present in the system,

$$\begin{aligned} v = & \prod_i \prod_j (v_A^{ijo})^{n_A^{ijo}} . \prod_k \prod_d (v_A^{kdl})^{n_A^{kdl}} . \prod_x \prod_y (v_P^{xyo})^{n_P^{xyo}} \\ & . \prod_p \prod_q (v_P^{pql})^{n_P^{pql}} . \prod_r \prod_t (v_C^{rto})^{n_C^{rto}} . \prod_u \prod_v (v_C^{uvl})^{n_C^{uvl}} . \prod_m \prod_w (v_S^{mw})^{n_S^{mw}} \end{aligned}$$

$$\ldots \text{(IV.35)}$$

As the next step in derivation of the desired relationships one needs an expression for the combinatorial term, 'g'. On the basis of principles of combination and permutation, one can write, for the different configurations of atoms present in the system, the expression,

$$g = h(n_A,n_P,n_C,n_S) \times \frac{(n_A+n_P+n_C+n_S)!}{\prod_i \prod_j \left[\left(n_A^{ij0}/z_{C_i}(z-i)_{C_j}\right)!\right]^{zC_i\,(z-i)C_j}}$$

$$\times \frac{1}{\prod_k \prod_d \left[\left(n_A^{kd1}/(z-1)_{C_k}\cdot(z-k-1)_{C_d}\right)!\right]^{(z-1)_{C_k}(z-k-1)_{C_d}}}$$

$$\times \frac{1}{\prod_x \prod_y \left[\left(n_P^{xy0}/z_{C_x}(z-x)_{C_y}\right)!\right]^{z_{C_x}\cdot(z-x)_{C_y}}}$$

$$\times \frac{1}{\prod_p \prod_q \left[\left(n_P^{pq1}/(z-1)_{C_p}\cdot(z-p-1)_{C_q}\right)!\right]^{(z-1)_{C_p}\cdot(z-p-1)_{C_q}}}$$

$$\times \frac{1}{\prod_r \prod_t \left[\left(n_C^{rt0}/z_{C_r}\cdot(z-r)_{C_t}\right)!\right]^{z_{C_r}\cdot(z-r)_{C_t}}}$$

$$\times \frac{1}{\prod_u \prod_v \left[\left(n_C^{uv1}/(z-1)_{C_u}\cdot(z-u-1)_{C_v}\right)!\right]^{(z-1)_{C_u}\cdot(z-u-1)_{C_v}}}$$

$$\times \frac{1}{\prod_m \prod_w \left[n_S^{mw}/z_{C_m}\cdot(z-m)_{C_w}\right)!\right]^{z_{C_m}\cdot(z-m)_{C_w}}} \quad \ldots \quad (IV.36)$$

where the terms of the type z_{C_x} are defined by the following expression ,

$$ {}^{z}C_{x} = \frac{z!}{(z-x)!x!} \qquad \ldots \text{(IV.37)} $$

The term $h(n_A, n_P, n_C, n_S)$, in eq. (IV.36) is called the 'normalising factor' and as per the procedure laid down in references [77 and 86], is expressed as,

$$
\begin{aligned}
h(n_A,n_P,n_C,n_S) = {} & \frac{1}{n_A!\, n_P!\, n_C!\, n_S!} \cdot \\
& \cdot \prod_{i}\prod_{j}\left[\left(n_A^{*ijo}/{}^{z}C_{i}\cdot{}^{(z-i)}C_{j}\right)!\right]^{{}^{z}C_{i}\,{}^{(z-i)}C_{j}} \\
& \cdot \prod_{k}\prod_{d}\left[\left(n_A^{*kd1}./{}^{(z-1)}C_{k}\cdot{}^{(z-k-1)}C_{d}\right)!\right]^{{}^{(z-1)}C_{k}\cdot{}^{(z-k-1)}C_{d}} \\
& \cdot \prod_{x}\prod_{y}\left[\left(n_P^{*xyo}/.{}^{z}C_{x}\cdot{}^{(z-x)}C_{y}\right)!\right]^{{}^{z}C_{x}\cdot{}^{(z-x)}C_{y}} \\
& \cdot \prod_{p}\prod_{q}\left[\left(n_P^{*pq1}/{}^{(z-1)}C_{p}\cdot{}^{(z-p-1)}C_{q}\right)!\right]^{{}^{(z-1)}C_{p}\cdot{}^{(z-p-1)}C_{q}} \\
& \cdot \prod_{r}\prod_{t}\left[\left(n_C^{*rto}/{}^{z}C_{r}\cdot{}^{(z-r)}C_{t}\right)!\right]^{{}^{z}C_{r}\cdot{}^{(z-r)}C_{t}} \\
& \cdot \prod_{u}\prod_{v}\left[\left(n_C^{*uv1}/{}^{(z-1)}C_{u}\cdot{}^{(z-u-1)}C_{v}\right)!\right]^{{}^{(z-1)}C_{u}\cdot{}^{(z-u-1)}C_{v}} \\
& \cdot \prod_{m}\prod_{w}\left[\left(n_S^{*mw}/{}^{z}C_{m}\cdot{}^{(z-m)}C_{w}\right)!\right]^{{}^{z}C_{m}\cdot{}^{(z-m)}C_{w}} \qquad \ldots \text{(IV.38)}
\end{aligned}
$$

where, the terms with asterisk mark (*), correspond to the values of different types of atoms in a randomly distributed system and are given by the following expressions,

$$ n_A^{*ijo} = {}^{z}C_{i} \cdot {}^{(z-i)}C_{j} \cdot n_A^{(z-i-j)} \cdot n_P^{i} \cdot n_C^{j} \cdot \frac{n_A^{*o}}{(n_A+n_P+n_C)^{z}} \qquad \ldots \text{(IV.39)} $$

$$n_P^{*xyo} = {}^{z}C_x \cdot {}^{(z-x)}C_y \cdot n_A^{y} \cdot n_P^{(z-x-y)} \cdot n_C^{x} \cdot \frac{n_P^{*o}}{(n_A+n_P+n_C)^{z}} \qquad \ldots \text{(IV.40)}$$

$$n_C^{*rto} = {}^{z}C_r \cdot {}^{(z-r)}C_t \cdot n_A^{r} \cdot n_P^{t} \cdot n_C^{(z-r-t)} \cdot \frac{n_C^{*o}}{(n_A+n_P+n_C)^{z}} \qquad \ldots \text{(IV.41)}$$

$$n_A^{*kdl} = z \cdot {}^{(z-1)}C_k \cdot {}^{(z-k-1)}C_d \cdot n_A^{(z-k-d-1)} \cdot n_P^{K} \cdot n_C^{d} \cdot \frac{n_A^{*1}}{(n_A+n_P+n_C)^{z-1}} \qquad \ldots \text{(IV.42)}$$

$$n_P^{*pql} = z \cdot {}^{(z-1)}C_p \cdot {}^{(z-p-1)}C_q \cdot n_A^{q} \cdot n_P^{(z-p-q-1)} \cdot n_C^{p} \cdot \frac{n_P^{*1}}{(n_A+n_P+n_C)^{z-1}} \qquad \ldots \text{(IV.43)}$$

$$n_C^{*uvl} = z \cdot {}^{(z-1)}C_u \cdot {}^{(z-u-1)}C_v \cdot n_A^{u} \cdot n_P^{v} \cdot n_C^{(z-u-v-1)} \cdot \frac{n_C^{*1}}{(n_A+n_P+n_C)^{z-1}} \qquad \ldots \text{(IV.44)}$$

$$n_S^{*mw} = {}^{z}C_m \cdot {}^{(z-m)}C_w \cdot n_A^{m} \cdot n_P^{w} \cdot n_C^{(z-m-w)} \cdot \frac{n_S}{(n_A+n_P+n_C)^{z}} \qquad \ldots \text{(IV.45)}$$

In the above expressions, following equalities hold good,

$$n_A^{*1} = \left(\frac{n_A}{n_A+n_P+n_C}\right) \cdot z\, n_S \qquad \ldots. \text{(IV.46)}$$

$$n_P^{*1} = \left(\frac{n_P}{n_A+n_P+n_C}\right) \cdot z\, n_S \qquad \ldots \text{(IV.47)}$$

$$n_C^{*1} = \left(\frac{n_C}{n_A+n_P+n_C}\right) \cdot z\, n_S \qquad \ldots \text{(IV.48)}$$

and

$$n_A^{*o} = n_A - n_A^{*1} \qquad \text{... (IV.49)}$$

$$n_P^{*o} = n_P - n_P^{*1} \qquad \text{... (IV.50)}$$

$$n_C^{*o} = n_C - n_C^{*1} \qquad \text{... (IV.51)}$$

Substitution of the above expression for $h(n_A, n_P, n_C, n_S)$ and with the help of eqs. (IV.17) - (IV.35), one can write, on application of 'Sterlings approximation', the following expression for $\ln \Omega$.

$$\ln \Omega = (n_A + n_P + n_C + n_S) \ln (n_A + n_P + n_C + n_S) - n_A \ln n_A - n_P \ln n_P - n_C \ln n_C - n_S \ln n_S$$

$$+ \sum_i \sum_j n_A^{*ijo} . \ln (n_A^{*ijo} / z_{C_i} . {}^{(z-i)}C_j) + \sum_k \sum_d n_A^{*kdl} .$$

$$\ln (n_A^{*kdl} / z . {}^{(z-1)}C_k . {}^{(z-k-1)}C_d) + \sum_x \sum_y n_P^{*xyo} .$$

$$\ln (n_P^{*xyo} / z_{C_x} . {}^{(z-x)}C_y) + \sum_p \sum_q n_P^{*pql} . \ln (n_P^{*pql} / z . {}^{(z-1)}C_p . {}^{(z-p-1)}C_q)$$

$$+ \sum_r \sum_t n_C^{*rto} . \ln (n_C^{*rto} / z_{C_r} . {}^{(z-r)}C_t) + \sum_u \sum_v n_C^{*uvl} .$$

$$\ln (n_C^{*uvl} / z . {}^{(z-1)}C_u . {}^{(z-u-1)}C_v) + \sum_m \sum_w n_S^{*mw} .$$

$$\ln (n_S^{*mw} / z_{C_m} . {}^{(z-m)}C_w)$$

lagrangian multiplier method, the following expression for the different atomic species ;

$$n_A^{ij.o} = \alpha_A\ {}^{z}C_{i}\ {}^{(z-i)}C_{j}\ \exp(i\pi_1).\exp(-j\pi_3).\exp\left(-\frac{W_A^{ijo}-kT\ln v_A^{ijo}}{kT}\right) \qquad \ldots \text{(IV.59)}$$

$$n_A^{kdl} = \alpha_A.z.{}^{(z-1)}C_{k}.\ {}^{(z-k-1)}C_{d}\ \exp(k\pi_1).\exp(-d\ \pi_3).\ \exp\left(-\frac{W_A^{kdl}-kT\ \ln\ v_A^{kdl}}{kT}\right) \qquad \ldots \text{(IV.60)}$$

$$n_P^{xyo} = \alpha_P.{}^{z}C_{x}.{}^{(z-x)}C_{y}.\exp(x\pi_2).\exp(-y\pi_1).\exp\left(-\frac{W_P^{xyo}-kT\ \ln\ v_P^{xyo}}{kT}\right) \qquad \ldots \text{(IV.61)}$$

$$n_P^{pql} = \alpha_P.z.{}^{(z-1)}C_{p}.{}^{(z-p-1)}C_{q}.\exp(p\pi_2).\exp(-q\pi_1).\ \exp\left(-\frac{W_P^{pql}-kT\ \ln\ v_P^{pql}}{kT}\right) \qquad \ldots \text{(IV.62)}$$

$$n_C^{rto} = \alpha_C.{}^{z}C_{r}.{}^{(z-r)}C_{t}.\exp(-t\pi_2).\exp(r\pi_3).\exp\left(-\frac{W_C^{rto}-kT\ \ln\ v_C^{rto}}{kT}\right) \qquad \ldots \text{(IV.63)}$$

$$n_C^{uvl} = \alpha_C.z.{}^{(z-1)}C_{u}.{}^{(z-u-1)}C_{v}.\exp(-v\pi_2).\exp(u\pi_3).\ \exp\left(-\frac{W_C^{uvl}-kT\ \ln\ v_C^{uvl}}{kT}\right) \qquad \ldots \text{(IV.64)}$$

$$n_S^{mw} = \alpha_S.{}^{z}C_{m}.{}^{(z-m)}C_{w}.\exp(-m\pi_4).\exp(-w\pi_5).\exp\left\{-(z-m-w)\pi_6\right\}.\ \exp\left(-\frac{W_S^{mw}-kT\ \ln\ v_S^{mw}}{kT}\right) \qquad \ldots \text{(IV.65)}$$

In the above expressions $\ln \alpha_A$, $\ln \alpha_P$, $\ln \alpha_C$ and $\ln \alpha_S$ are the lagrangian multipliers for the eqs. (IV.21), (IV.26), (IV.31) and (IV.33) respectively and π_1, π_2, π_3, π_4, π_5 and π_6 for eqs. (IV.53) - (IV.58) respectively. All these multiplier variables can be determined with the help of following set of nine equations which are obtained by substitution of eqs. (IV.59) - (IV.65) in the sets of material and bond balance equations.

$$\begin{aligned}
\alpha_A &= n_A^o \Big[\sum_{i=o}^{z} \sum_{j=o}^{(z-i)} {}^{z}C_i \,.\, {}^{(z-i)}C_j \,.\exp(i\pi_1).\exp(-j\pi_3)\,. \\
&\qquad \exp\Big(-\frac{W_A^{ijo}-kT\ln v_A^{ijo}}{kT}\Big)\Big]^{-1} \\
&= n_A^1 \Big[\sum_{k=o}^{(z-1)} \sum_{d=o}^{(z-k-1)} z\,.\,{}^{(z-1)}C_k \,.\, {}^{(z-k-1)}C_d .\exp(k\pi_1). \\
&\qquad .\exp(-d\pi_3).\exp\pi_4.\exp\Big(-\frac{W_A^{kd1}-kT\ln v_A^{kd1}}{kT}\Big)\Big]^{-1} \\
&= n_A \Big[\Big\{ \sum_{i=o}^{z} \sum_{j=o}^{(z-i)} {}^{z}C_i \,.\, {}^{(z-i)}C_j \; \exp(i\pi_1).\exp(-j\pi_3)\,. \\
&\qquad \exp\Big(-\frac{W_A^{ijo}-kT\ln v_A^{ijo}}{kT}\Big)\Big\} \\
&\quad + \Big\{ \sum_{k=o}^{(z-1)} \sum_{d=o}^{(z-k-1)} z\,.\,{}^{(z-1)}C_k \,.\, {}^{(z-k-1)}C_d .\exp(k\pi_1)\,. \\
&\qquad \exp(-d\pi_3).\exp\Big(-\frac{W_A^{kd1}-kT\ln v_A^{kd1}}{kT}\Big)\Big\}\Big]^{-1}
\end{aligned}$$

... (IV.66)

$$\alpha_P = n_P^o \Big[\sum_{x=o}^{z} \sum_{y=o}^{(z-x)} {}^{z}C_x . {}^{(z-x)}C_y . \exp(-y\pi_1) . \exp(x\pi_2) .$$

$$\exp(- \frac{W_P^{xyo} - kT \ln v_P^{xyo}}{kT}) \Big]^{-1}$$

$$= n_P^1 \Big[\sum_{p=o}^{(z-1)} \sum_{q=o}^{(z-p-1)} z . {}^{(z-1)}C_p . {}^{(z-p-1)}C_q . \exp(-q\pi_1) .$$

$$\exp(p\pi_2) . \exp\pi_5 \ . \exp(- \frac{W_P^{pq1} - kT \ln v_P^{pq1}}{kT}) \Big]^{-1}$$

$$= n_P \Big[\{ \sum_{x=o}^{z} \sum_{y=o}^{(z-x)} {}^{z}C_x . {}^{(z-x)}C_y . \exp(-y\pi_1) . \exp(x\pi_3)$$

$$\exp(- \frac{W_P^{xyo} - kT \ln v_P^{xyo}}{kT}) \}$$

$$+ \{ \sum_{p=o}^{(z-1)} \sum_{q=o}^{(z-p-1)} z . {}^{(z-1)}C_p . {}^{(z-p-1)}C_q . \exp(-q\pi 1) . \exp(p\pi_2) .$$

$$\exp\pi_5 \ . \exp(- \frac{W_P^{pq1} - kT \ln v_P^{pq1}}{kT}) \} \Big]^{-1} \quad \ldots \text{(IV.67)}$$

$$\alpha_C = n_C^o \Big[\sum_{r=o}^{z} \sum_{t=o}^{(z-r)} {}^{z}C_r . {}^{(z-r)}C_t . \exp(-t\pi_2) . \exp(r\pi_3) .$$

$$\exp(- \frac{W_C^{rto} - kT \ln v_C^{rto}}{kT}) \Big]^{-1}$$

$$= n_C^1 \Big[\sum_{u=o}^{(z-1)} \sum_{v=o}^{(z-u-1)} z . {}^{(z-1)}C_u . {}^{(z-u-1)}C_v . \exp(-v\pi_2)$$

$$\exp(u\pi_3) \ . \exp(- \frac{W_C^{rto} - kT \ln v_C^{rto}}{kT}) \Big]^{-1}$$

$$= n_C \Big[\{ \sum_{r=o}^{z} \sum_{t=o}^{(z-r)} {}^{z}C_r . {}^{(z-r)}C_t . \exp(-t\pi_2) . \exp(r\pi_3) .$$

$$\exp(- \frac{W_C^{rto} - kT \ln v_C^{rto}}{kT}) \} + \{ \sum_{u=o} \sum_{v=o} z . {}^{(z-1)}C_u . {}^{(z-u-1)}C_v .$$

$$.\exp(u\,\pi_3).\exp(-v\pi_2).\exp(\pi_6).\exp\left(-\frac{W_C^{uv1}-kT\ \ln\ v_C^{uv1}}{kT}\right)\Big\}\Big]^{-1}$$

$$\ldots\ (IV.68)$$

$$\alpha_S = n_S\left[\sum_{m=0}^{z}\sum_{w=0}^{z}{}^{z}C_m.{}^{(z-m)}C_w.\exp(-m\pi_4).\exp(-w\pi_5).\right.$$

$$\left.\exp\{-(z-m-w)\}.\exp\left(-\frac{W_x^{mw}-kT\ \ln\ v_x^{mw}}{kT}\right)\right]^{-1}\ldots\ (IV.69)$$

Evaluation of π_1, π_2, π_3, π_4, π_5 and π_6 for the above expressions can follow from the following six simultaneous equations ,

$$n_A\left[\sum_{i=0}^{z}\sum_{j=0}^{(z-i)} i.\ {}^{z}C_i.{}^{(z-i)}C_j.\exp(i\pi_1).\exp(-j\pi_3).\right.$$

$$.\exp\left(-\frac{W_A^{ij0}-kT\ \ln\ v_A^{ij0}}{kT}\right)$$

$$+\sum_{k=0}^{(z-1)}\sum_{d=0}^{(z-k-1)} k.z.{}^{(z-1)}C_k.{}^{(z-k-1)}C_d.\exp(k\pi_1).\exp(-d\pi_3).$$

$$\left.\exp\ \pi_4.\exp\left(-\frac{W_A^{kd1}-kT\ \ln\ v_A^{kd1}}{kT}\right)\right].\left[\sum_{i=0}^{z}\sum_{j=0}^{(z-i)}{}^{z}C_i.{}^{(z-i)}C_j.\right.$$

$$\exp(i\pi_1).\exp(-j\pi_3).\exp\left(-\frac{W_A^{ij0}-kT\ \ln\ v_A^{ij0}}{kT}\right)+\sum_{k=0}^{(z-1)}\sum_{d=0}^{(z-k-1)}$$

$$z.{}^{(z-1)}C_k.{}^{(z-k-1)}C_d.\exp(k\pi_1).\exp(-d\pi_3).\exp(\pi_4).$$

$$\left..\exp\left(-\frac{W_A^{kd1}-kT\ \ln\ v_A^{kd1}}{kT}\right)\right]^{-1}$$

$$-n_P\left[\sum_{x=0}^{z}\sum_{y=0}^{(z-x)} y\ {}^{z}C_x.{}^{(z-x)}C_y.\exp(x\pi_2).\exp(-y\pi_1).\right.$$

$$\exp\left(-\frac{W_P^{xy0}-kT\ \ln\ v_P^{xy0}}{kT}\right)$$

$$+\sum_{p=0}^{(z-1)}\sum_{q=0}^{(z-p-1)} q.z.{}^{(z-1)}C_p.{}^{(z-p-1)}C_q.\exp(p\pi_2).\exp(-q\pi_1)\ .$$

$$\exp(\pi_5).\ \exp\left(-\frac{W_P^{pq1}-kT\ \ln v_P^{pq1}}{kT}\right)\Bigg].\ \Bigg[\sum_{x=0}^{z}\sum_{y=0}^{(z-x)} {}^{z}C_x.{}^{(z-x)}C_y\ .$$

$$\exp(x\pi_2).\exp(-y\pi_1).\exp\left(-\frac{W_P^{xyo}-kT\ \ln v_P^{xyo}}{kT}\right)$$

$$+\sum_{p=0}^{(z-1)}\sum_{q=0}^{(z-p-1)} z.{}^{(z-1)}C_p\ .$$

$${}^{(z-p-1)}C_q.\exp(p\pi_2).\exp(-q\pi_1).\exp(\pi_5).$$

$$\exp\left(-\frac{W_P^{pq1}-kT\ \ln v_P^{pq1}}{kT}\right)\Bigg]^{-1} = 0 \qquad \ldots\ (IV.70)$$

$$n_P\ \Bigg[\sum_{x=0}^{z}\sum_{y=0}^{(z-x)} x.{}^{z}C_x.{}^{(z-x)}C_y.\exp(x\pi_2).\exp(-y\pi_1)\ .$$

$$\exp\left(-\frac{W_P^{xyo}-kT\ \ln v_P^{xyo}}{kT}\right)$$

$$+\sum_{p=0}^{(z-1)}\sum_{q=0}^{(z-p-1)} p.z.{}^{(z-1)}C_p.{}^{(z-p-1)}C_q.\exp(p\pi_2).\exp(-q\pi_1)\ .$$

$$\exp\pi_5.\exp\left(-\frac{W_P^{pq1}-kT\ \ln v_P^{pq1}}{kT}\right)\Bigg].$$

$$\Bigg[\sum_{x=0}^{z}\sum_{y=0}^{(z-x)} {}^{z}C_x.{}^{(z-x)}C_y.\exp(x\pi_2).\exp(-y\pi_1)\ .$$

$$\exp\left(-\frac{W_P^{xyo}-kT\ \ln v_P^{xyo}}{kT}\right)$$

$$+\sum_{p=o}^{(z-1)}\sum_{q=o}^{(z-p-1)} z.{}^{(z-1)}C_p.{}^{(z-p-1)}C_q.\exp(p\pi_2).\exp(-q\pi_1).$$

$$\exp(\pi_5)\;.\exp(-\frac{W_P^{pq1}-kT\ \ln\ v_P^{pq1}}{kT})\Big]\Big]^{-1}$$

$$-n_C\Big[\Big[\sum_{r=o}^{z}\sum_{t=o}^{(z-r)} t.{}^{z}C_r.{}^{(z-r)}C_t.\exp(-t\pi_2).\exp(r\pi_3).$$

$$\exp(-\frac{W_C^{rto}-kT\ \ln\ v_C^{rto}}{kT})$$

$$+\sum_{u=o}^{(z-1)}\sum_{v=o}^{(z-u-1)} v.z.{}^{(z-1)}C_u.{}^{(z-u-1)}C_v.\exp(-v\pi_2).$$

$$\exp(u\pi_3)\;.\exp(\pi_6).$$

$$\exp(-\frac{W_C^{uv1}-kT\ \ln\ v_C^{uv1}}{kT})\Big]\Big].\Big[\sum_{r=o}^{z}\sum_{t=o}^{(z-r)} {}^{z}C_r.{}^{(z-r)}C_t.$$

$$\exp(-t\pi_2).\exp(r\pi_3).$$

$$\exp(-\frac{W_C^{rto}-kT\ \ln\ v_C^{rto}}{kT}) + \sum_{u=o}^{(z-1)}\sum_{v=o}^{(z-u-1)} z.{}^{(z-1)}C_u.$$

$$^{(z-u-1)}C_v.\exp(-v\pi_2).$$

$$\exp(u\pi_3).\exp\pi_6.\exp(-\frac{W_C^{uv1}-kT\ \ln\ v_C^{uv1}}{kT})\Big]\Big]^{-1} = o$$

... (IV.71)

$$n_C\Big[\Big[\sum_{r=o}^{z}\sum_{t=o}^{(z-r)} r.{}^{z}C_r.{}^{(z-r)}C_t.\exp(-t\pi_2).\exp(r\pi_3).$$

$$\exp(-\frac{W_C^{rto}-kT\ \ln\ v_C^{rto}}{kT})$$

$$+\sum_{u=0}^{(z-1)}\sum_{v=0}^{(z-u-1)} u.z.{}^{(z-1)}C_u.{}^{(z-u-1)}C_v.\exp(-v\pi_2)\ .$$

$$.\exp(u\pi_3)\ .\exp\pi_6\ .$$

$$\exp\left(-\frac{W_C^{uvl}-kT\ \ln v_C^{uvl}}{kT}\right)\Big]\Big].\Big[\sum_{r=0}^{z}\sum_{t=0}^{(z-r)} {}^{z}C_r.{}^{(z-r)}C_t\ .$$

$$\exp(-t\ \pi_2)\ .\exp(r\pi_3)\ .$$

$$\exp\left(-\frac{W_C^{rto}-kT\ \ln v_C^{rto}}{kT}\right)+\sum_{u=0}^{(z-1)}\sum_{v=0}^{(z-u-1)} z.{}^{(z-1)}C_u\ .$$

$${}^{(z-u-1)}C_v.\exp(-v\ \pi_2).\exp(u\pi_3)\ .$$

$$\exp\pi_6.\exp\left(-\frac{W_C^{uvl}-kT\ \ln v_C^{uvl}}{kT}\right)\Big]^{-1}-n_A\Big[\sum_{i=0}^{z}\sum_{j=0}^{(z-i)} j\,{}^{z}C_i\ .$$

$${}^{(z-i)}C_j.\exp(i\pi_1)\ .$$

$$\exp(-j\pi_3).\exp\left(-\frac{W_A^{ijo}-kT\ \ln v_A^{ijo}}{kT}\right)+\sum_{h=0}^{(z-1)}\sum_{d=0}^{(z-k-1)} d.z\ .$$

$${}^{(z-1)}C_k.{}^{(z-k-1)}C_d.$$

$$\exp(k\pi_1).\exp(-d\pi_3).\exp(\pi_4).\exp\left(-\frac{W_A^{kdl}-kT\ \ln v_A^{kdl}}{kT}\right)\Big].$$

$$\Big[\sum_{i=0}^{z}\sum_{j=0}^{(z-i)} {}^{z}C_i.{}^{(z-i)}C_j.\exp(i\pi_1).\exp(-j\pi_3)\ .$$

$$\exp\left(-\frac{W_A^{ijo}-kT\ \ln v_A^{ijo}}{kT}\right)$$

$$+\sum_{k=o}^{(z-1)}\sum_{d=o}^{(z-k-1)} z.{}^{(z-1)}C_k.{}^{(z-k-1)}C_d.\exp(k\pi_1).\exp(-d\pi_3).$$

$$\left.\exp(\pi_4).\exp\left(-\frac{W_A^{kdl}-kT\ln v_A^{kdl}}{kT}\right)\right]^{-1} = o$$

$$\ldots\ (IV.72)$$

$$n_A\left[\sum_{k=o}^{(z-i)}\sum_{d=o}^{(z-k-1)} z.{}^{(z-1)}C_k.{}^{(z-k-1)}C_d.\exp(k\pi_1).\exp(-d\pi_3).\exp(\pi_4).\right.$$

$$\left.\exp\left(-\frac{W_A^{kdl}-kT\ln v_A^{kdl}}{kT}\right)\right].\left[\sum_{i=o}^{z}\sum_{j=o}^{(z-i)} {}^{z}C_i.{}^{(z-i)}C_j\right.\ .$$

$$.\exp(i\pi_1).\exp(-j\pi_3)\ .$$

$$\exp\left(-\frac{W_A^{ijo}-kT\ln v_A^{ijo}}{kT}\right)+\sum_{k=o}^{(z-1)}\sum_{d=o}^{(z-k-1)} z.{}^{(z-1)}C_k\ .$$

$$.{}^{(z-k-1)}C_d.\exp(k\pi_1).\exp(-d\pi_3)\ .$$

$$\left.\exp(\pi_4).\exp\left(-\frac{W_A^{kdl}-kT\ln v_A^{kdl}}{kT}\right)\right]^{-1} - n_S\left[\sum_{m=o}^{z}\sum_{w=o}^{(z-m)} m.{}^{z}C_m\right..$$

$$.{}^{(z-m)}C_w\ .$$

$$\exp(-m\pi_4).\exp(-w\pi_5).\exp\left\{-(z-m-w)\pi_6\right\}.$$

$$\left..\exp\left(-\frac{W_S^{mw}-kT\ln v_S^{mw}}{kT}\right)\right]\ .$$

$$\left[\sum_{m=o}^{z}\sum_{w=o}^{(z-m)} {}^{z}C_m.{}^{(z-m)}C_w.\exp(-m\pi_4).\exp(-w\pi_5)\right..$$

$$\left.\exp\left\{-(z-m-w)\pi_6\right\}.\exp\left(-\frac{W_S^{mw}-kT\ln v_S^{mw}}{kT}\right)\right]^{-1} = o$$

$$\ldots\ (IV.73)$$

$$n_P[\sum_{p=0}^{(z-1)}\sum_{q=0}^{(z-p-1)} z.{}^{(z-1)}C_p.{}^{(z-p-1)}C_q.\exp(p\pi_2).\exp(-q\pi_1).\exp(\pi_5).$$

$$\exp(-\frac{W_P^{pq1}-kT\ln v_P^{pq1}}{kT})].[\sum_{x=0}^{z}\sum_{y=0}^{(z-x)} {}^{z}C_x.{}^{(z-x)}C_y.$$

$$\exp(x\pi_2).\exp(-y\pi_1).$$

$$\exp(-\frac{W_P^{xyo}-kT\ln v_P^{xyo}}{kT})+\sum_{p=0}^{(z-1)}\sum_{q=0}^{(z-p-1)} z.{}^{(z-1)}C_p.$$

$${}^{(z-p-1)}C_q.\exp(p\pi_2).$$

$$\exp(-q\pi_1).\exp(\pi_5).\exp(-\frac{W_P^{pq1}-kT\ln v_P^{pq1}}{kT})]^{-1}\varepsilon.$$

$$-n_S[\sum_{m=0}^{z}\sum_{w=0}^{(z-m)} w.{}^{z}C_m.{}^{(z-m)}C_w.\exp(-m\pi_4).$$

$$\exp(-w\pi_5).\exp\{-(z-m-w)\pi_6\}.$$

$$\exp(-\frac{W_S^{mw}-kT\ln v_S^{mw}}{kT})].[\sum_{m=0}^{z}\sum_{w=0}^{(z-m)} {}^{z}C_m.{}^{(z-m)}C_w.\exp(-m\pi_4).$$

$$\exp(-w\pi_5).\exp\{-(z-m-w)\pi_6\}.\exp(-\frac{W_S^{mw}-kT\ln v_S^{mw}}{kT})]^{-1}=0$$

... (IV.74)

$$n_C[\sum_{u=0}^{(z-1)}\sum_{v=0}^{(z-u-1)} z.{}^{(z-1)}C_u.{}^{(z-u-1)}C_v.\exp(-v\pi_2).\exp(u\pi_3).\exp(\pi_6).$$

$$\exp(-\frac{W_C^{uv1}-kT\ln v_C^{uv1}}{kT})].[\sum_{r=0}^{z}\sum_{t=0}^{(z-r)} {}^{z}C_r.{}^{(z-r)}C_t.$$

$$\exp(-t\pi_2).$$

$$.\exp(r\pi_3).\exp\left(-\frac{W_C^{rto}-kT\ \ln\ v_C^{rto}}{kT}\right)+\sum_{u=o}^{(z-1)}\sum_{v=o}^{(z-u-1)} z\ .$$

$${}^{(z-1)}C_v\ .\ {}^{(z-u-1)}C_v\ .$$

$$\left.\exp(-v\pi_2).\exp(u\pi_3).\exp(\pi_6).\exp\left(-\frac{W_C^{uv1}-kT\ \ln\ v_C^{uv1}}{kT}\right)\right]^{-1}$$

$$-\ n_S\left[\sum_{m=o}^{z}\sum_{w=o}^{(z-m)} {}^{z}C_m\ .\ {}^{(z-m)}C_w\ .\ (z-m-w)\ .\exp(-m\pi_4).\exp(-w\pi_5)\ .\right.$$

$$\left.\exp\ \{-(z-m-w)\pi_6\}\ .\exp\left(-\frac{W_S^{mw}-kT\ \ln\ v_S^{mw}}{kT}\right)\right].\left[\sum_{m=o}^{z}\sum_{w=o}^{(z-m)} {}^{z}C_m.\right.$$

$${}^{(z-m)}C_w.\exp(-m\pi_4).\exp(-w\pi_5).\exp\{-(z-m-w)\pi_6\}\ .$$

$$\left.\exp\left(-\frac{W_S^{mw}-kT\ \ln\ v_S^{mw}}{kT}\right)\right]^{-1} = o \quad \ldots \text{(IV.75)}$$

The above set of equations shows that one can solve them simultaneously for evaluating π_1, π_2, π_3, π_4, π_5 and π_6 at any desired temperature provided the energies and free volumes of different atomic species are known. From a knowledge of these lagrangian multipliers, one can calculate α_A, α_P, α_C and α_S and hence the thermodynamic properties of the system. But it is difficult to obtain the values of energies and free volumes of these species from experimental data and hence one tries to express these parameters in terms of empirical and semi-empirical function, so that the number of system dependent constants appearing in the final expression are reduced. In the following sections of this chapter, therefore, some of these functions shall be considered and based on these different final expressions thermodynamic properties shall be derived.

IV.2.1 Approaches Based on Linear Forms of Energy

As the first, most convenient and commonly employed, approximation let us assume that the energies and natural logarithms of free volumes of the different atomic species, present in the system, are linear functions of the types and number of atoms forming the nearest neighbours of the particular species under consideration.

Thus the energy, W_A^{ijo}, of an A atom having i B-atoms, j C-atoms and rest A-atoms around it can be expressed by the following relationship,

$$W_A^{ijo} = i\ \varphi_{AB} + j\ \varphi_{AC} + (z-i-j)\ \varphi_{AA} \qquad \ldots \text{(IV.76)}$$

where, the constants φ_{AB}, φ_{AC} and φ_{AA} can be expressed in terms of certain standard configurations. Thus, from the above equation, one gets by setting both i and j equal to zero, the expression,

$$W_A^{ooo} = z\ \varphi_{AA} \qquad \ldots \text{(IV.77)}$$

and also one gets, from eq. (IV.76), first by putting $i = 1$ and $j = o$ and then $i = o$ and $j = 1$, the following expressions

$$W_A^{100} = \varphi_{AB} + (z-1)\ \varphi_{AA} \qquad \ldots \text{(IV.78)}$$

and ,

$$W_A^{o1o} = \varphi_{AC} + (z-1)\ \varphi_{AA} \qquad \text{... (IV.79)}$$

Elimination of φ_{AA}, φ_{AB} and φ_{AC} from eq. (IV.76) with the help of eqs. (IV.77) - (IV.79), yields the following expression;

$$\begin{aligned} W_A^{ijo} &= W_A^{ooo} + i(W_A^{100}-W_A^{000}) + j(W_A^{010}-W_A^{000}) \\ &= W_A^{000} + i\ \Delta W_A^{100} + j\ \Delta W_A^{010} \qquad \text{... (IV.80)} \end{aligned}$$

where,

$$\Delta W_A^{100} = W_A^{100} - W_A^{000} \qquad \text{... (IV.81)}$$

and

$$\Delta W_A^{010} = W_A^{010} - W_A^{000} \qquad \text{... (IV.82)}$$

Similarly, one can write the following expressions for the energies and also for free volumes of the different species of atoms present in the solution under study;

$$\ln v_A^{ijo} = \ln v_A^{000} + i(\ln v_A^{100} - \ln v_A^{000}) + j(\ln v_A^{010} - \ln v_A^{000}) \qquad \text{... (IV.83)}$$

$$W_A^{kdl} = W_A^{000} + k(W_A^{100}-W_A^{000}) + d(W_A^{010}-W_A^{000}) + (W_A^{001} - W_A^{000}) \qquad \text{... (IV.84)}$$

$$\begin{aligned} \ln v_A^{kdl} &= \ln v_A^{000} + k(\ln v_A^{100} - \ln v_A^{000}) + d(\ln v_A^{010} - \ln v_A^{000}) \\ &\quad + (\ln v_A^{001} - \ln v_A^{000}) \qquad \text{... (IV.85)} \end{aligned}$$

$$W_P^{xyo} = W_P^{000} + x\ (W_P^{100} - W_P^{000}) + y(W_P^{010} - W_P^{000}) \qquad \text{... (IV.86)}$$

$$\ln v_P^{xyo} = \ln v_P^{000} + x(\ln v_P^{100} - \ln v_P^{000}) + y(\ln v_P^{010} - \ln v_P^{000}) \quad \ldots \text{(IV.87)}$$

$$W_P^{pq1} = W_P^{000} + p(W_P^{100} - W_P^{000}) + q(W_P^{010} - W_P^{000}) + (W_P^{001} - W_P^{000}) . \text{(IV.88)}$$

$$\ln v_P^{pq1} = \ln v_P^{000} + p(\ln v_P^{100} - \ln v_P^{000}) + q(\ln v_P^{010} - \ln v_P^{000}) + (\ln v_P^{001} - \ln v_P^{000}) \quad \ldots \text{(IV.89)}$$

$$W_C^{rto} = W_C^{000} + r(W_C^{100} - W_C^{000}) + t(W_C^{010} - W_C^{000}) \quad \ldots \text{(IV.90)}$$

$$\ln v_C^{rto} = \ln v_C^{000} + r(\ln v_C^{100} - \ln v_C^{000}) + t(\ln v_C^{010} - \ln v_C^{000}) \quad \ldots \text{(IV.91)}$$

$$W_C^{uv1} = W_C^{000} + u(W_C^{100} - W_C^{000}) + v(W_C^{010} - W_C^{000}) + (W_C^{001} - W_C^{000}) . \text{(IV.92)}$$

$$\ln v_C^{uv1} = \ln v_C^{000} + u(\ln v_C^{100} - \ln v_C^{000}) + v(\ln v_C^{010} - \ln v_C^{000}) + (\ln v_C^{001} - \ln v_C^{000}) \quad \ldots \text{(IV.93)}$$

$$W_S^{mw} = \frac{m}{z}(W_S^{zo} - W_S) + \frac{W}{z}(W_S^{oz} - W_S) + \frac{(z-m-w)}{z}(W_S^{00} - W_S) + W_S . \quad \text{(IV.94)}$$

$$\equiv \frac{m}{z}\Delta W_S^{zo} + \frac{W}{z}\Delta W_S^{oz} + \frac{z-m-w}{z}\Delta W_S^{00} + W_S \quad \ldots \text{(IV.95)}$$

where W_S is the energy of an S-atom in pure liquid S maintained at the same temperature as that of the solution under study.

Similarly,

$$\ln v_S^{mw} = \frac{m}{z}(\ln v_S^{zo} - \ln v_S) + \frac{w}{z}(\ln v_S^{oz} - \ln v_S) + \frac{(z-m-w)}{z}(\ln v_S^{00} - \ln v_S) + \ln v_S$$

$$\equiv \frac{m}{z}\Delta \ln v_S^{zo} + \frac{w}{z}\Delta \ln v_S^{oz} + \frac{(z-m-w)}{z}\Delta \ln v_S^{00} + \ln v_S \quad \ldots \text{(IV.96)}$$

Although one can solve the set of equations (IV.7o) - (IV.75)with the help of above set of expressions, i.e., from eqs. (IV.80) - (IV.96) and thus arrive at the expressions for different thermodynamic properties of the system under consideration, yet, for certain purposes, one requires simple and quickly computable expressions which can be derived as approximate solutions of the above set. In the following subsections, therefore, several such simplifying assumptions have been made to obtain different simplified expressions:

IV.2.1.1 Randomly distributed system:

For such systems, it is assumed that the distribution of different atomic species in the system is not dependent or based on the effects of energies and free volumes. Thus the eqs. (IV.59) - (IV.65) get modified to a new set of the following alternative forms:

$$n_A^{ijo} = \alpha_A . {}^{z}C_i . {}^{(z-i)}C_j . \exp(i\pi_1) . \exp(-j\pi_3) \qquad \text{... (IV.97)}$$

$$n_A^{kdl} = \alpha_A . z . {}^{(z-1)}C_k . {}^{(z-k-1)}C_d . \exp(k\pi_1) . \exp(-d\pi_3) . \exp(\pi_4) \qquad \text{... (IV.98)}$$

$$n_P^{xyo} = \alpha_P . {}^{z}C_x . {}^{(z-x)}C_y . \exp(x\pi_2) . \exp(-y\pi_1) \qquad \text{... (IV.99)}$$

$$n_P^{pql} = \alpha_P . z . {}^{(z-1)}C_p . {}^{(z-p-1)}C_q . \exp(p\pi_2) . \exp(-q\pi_1) . \exp(\pi_5) \qquad \text{... (IV.100)}$$

$$n_C^{rto} = \alpha_C . {}^zC_r . {}^{(z-r)}C_t . \exp(-t\pi_2) . \exp(r\pi_3) \qquad \ldots \text{(IV.101)}$$

$$n_C^{uvl} = \alpha_C . z . {}^{(z-1)}C_u . {}^{(z-u-1)}C_v . \exp(-v\pi_2) . \exp(u\pi_3) . \exp(\pi_6)$$

... (IV.102)

$$n_S^{mw} = \alpha_S . {}^zC_m . {}^{(z-m)}C_w . \exp(-m\pi_4) . \exp(-w\pi_5) . \exp\{-(z-m-w)\pi_6\}$$

... (IV.103)

where,

$$\alpha_A = n_A\left[\{1+\exp\pi_1+\exp(-\pi_3)\}^z + z\ \exp(\pi_4) . \{1+\exp\pi_1+\exp(-\pi_3)\}^{z-1} \right]^{-1}$$

... (IV.104)

$$\alpha_P = n_P\left[\{1+\exp(-\pi_1)+\exp\pi_2\}^z + z\exp(\pi_5) \cdot \{1+\exp(-\pi_1)+\exp\pi_2\}^{z-1} \right]^{-1}$$

... (IV.105)

$$\alpha_C = n_C\left[\{1+\exp(-\pi_2)+\exp\pi_3\}^z + z\exp(\pi_6) \cdot \{1+\exp(-\pi_2)+\exp\pi_3\}^{z-1} \right]^{-1}$$

... (IV.106)

$$\alpha_S = n_S\left[\exp(-\pi_4)+\exp(-\pi_5)+\exp(-\pi_6)\right]^{-z} \qquad \ldots \text{(IV.107)}$$

Also, from the set of eqs. (IV.70) - (IV.75) one gets the following expressions for the present case,

$$\frac{n_A . \exp\pi_1\left[1+\exp\pi_1+\exp(-\pi_3)+(z-1)\exp\pi_4\right]}{(1+\exp\pi_1+\exp(-\pi_3)+.z\exp\pi_4)\{1+\exp\pi_1+\exp(-\pi_3)\}}$$

$$= \frac{n_P . \exp(-\pi_1)[1+\exp(-\pi_1)+\exp\pi_2+(z-1)\exp\pi_5]}{(1+\exp(-\pi_1)+\exp(\pi_2)+z\exp\pi_5)(1+\exp(-\pi_1)+\exp\pi_2)}$$

... (IV.108)

$$\frac{n_P \cdot \exp\pi_2[1+\exp(-\pi_1)+\exp\pi_2+(z-1)\exp(\pi_5)]}{(1+\exp(-\pi_1)+\exp\pi_2+z\exp\pi_5)(1+\exp(-\pi_1)+\exp\pi_2)}$$

$$= \frac{n_S\ \exp(-\pi_2)\cdot[1+\exp(-\pi_2)+\exp\pi_3+(z-1)\exp\pi_6]}{(1+\exp(-\pi_2)+\exp\pi_3+z\exp\pi_6)(1+\exp(-\pi_2)+\exp\pi_3)} \qquad \ldots \text{(IV.109)}$$

$$\frac{n_S \cdot \exp(\pi_3)[1+\exp(-\pi_2)+\exp\pi_3+(z-1)\exp\pi_6]}{(1+\exp(-\pi_2+\exp(\pi_3)+z\exp\pi_6)\ \{1+\exp(-\pi_1)+\exp\pi_2\}}$$

$$= \frac{n_A \exp(-\pi_3)[1+\exp\pi_1+\exp(-\pi_3)+(z-1)\exp\pi_4]}{(1+\exp\pi_1+\exp(-\pi_3)+z\exp\pi_4)\{1+\exp\pi_1+\exp(-\pi_3)\}} \qquad \ldots \text{(IV.110)}$$

$$\frac{n_A\ \exp\pi_4}{1+\exp\pi_1+\exp(-\pi_3)+z\exp(\pi_4)} = \frac{n_S\ \exp(-\pi_4)}{\exp(-\pi_4)+\exp(-\pi_5)+\exp(-\pi_6)} \qquad \ldots \text{(IV.111)}$$

$$\frac{n_P\ \exp\pi_5}{1+\exp\pi_2+\exp(-\pi_1)+z\exp(\pi_5)} = \frac{n_S\ \exp(-\pi_5)}{\exp(-\pi_4)+\exp(-\pi_5)+\exp(-\pi_6)} \qquad \ldots \text{(IV.112)}$$

$$\frac{n_S\ \exp(\pi_6)}{1+\exp\pi_3+\exp(-\pi_2)+z\exp\pi_6} = \frac{n_S\ \exp(-\pi_6)}{\exp(-\pi_4)+\exp(-\pi_5)+\exp(-\pi_6)} \qquad \ldots \text{(IV.113)}$$

For very dilute solutions of component S in the solvent containing A, P and C, the above set yields the following expressions relating constants π_1, π_2, etc. with different mole fractions;

$$\exp(\pi_1) = \frac{n_P}{n_A} = \frac{N_P}{N_A} \qquad \text{... (IV.114)}$$

$$\exp(\pi_2) = \frac{n_S}{n_P} = \frac{N_S}{N_P} \qquad \text{... (IV.115)}$$

$$\exp(\pi_3) = \frac{n_A}{n_S} = \frac{N_A}{N_S} \qquad \text{... (IV.116)}$$

$$\exp(\pi_4) = \frac{n_S}{n_A} = \frac{N_S}{N_A} \qquad \text{... (IV.117)}$$

$$\exp(\pi_5) = \frac{n_S}{n_P} = \frac{N_S}{N_P} \qquad \text{... (IV.118)}$$

$$\exp(\pi_6) = \frac{n_S}{n_C} = \frac{N_S}{N_C} \qquad \text{... (IV.119)}$$

Substitution of eqs. (IV.114) - (IV.119) in eqs. (IV.97) - (IV.107)and of resulting expressions and of eqs. (IV.80) - (IV.96) in eq. (IV.52), yields on simplification the following expression for arriving at the value of partition function of the solution under study,

$$\begin{aligned} kT \ln \Omega = {} & (n_A+n_P+n_C+n_S) \ln (n_A+n_P+n_C+n_S) \\ & - n_A \ln n_A - n_P \ln n_P - n_C \ln n_C - n_S \ln n_S . \\ & - \frac{zn_A}{(n_A+n_P+n_C+n_S)} \Big[n_P (\Delta W_A^{100} - kT\ \Delta\ln v_A^{100}) + n_C (\Delta W_A^{010} - kT\ \Delta \ln v_A^{010}) \\ & \qquad + n_S (\Delta W_A^{001} - kT\ \Delta \ln v_A^{001}) \Big] \\ & - \frac{z\ n_P}{(n_A+n_P+n_C+n_S)} \Big[n_A (\Delta W_P^{010} - kT\ \Delta \ln v_P^{010}) + n_C (\Delta W_P^{100} - kT\ \Delta \ln v_P^{100}) \\ & \qquad + n_S (\Delta W_P^{001} - kT\ \Delta \ln v_P^{001}) \Big] \end{aligned}$$

$$+ (\Delta W_P^{010} - kT \Delta \ln v_P^{010})] - zN\ N_P N_S [(\Delta W_P^{100} - kT \Delta \ln v_P^{100})$$

$$+ (\Delta W_S^{010} - kT \Delta \ln v_S^{010})] - zN\ N_A N_S [(\Delta W_A^{010} - kT \Delta \ln v_A^{010})$$

$$+ (\Delta W_S^{100} - kT \Delta \ln v_S^{100})]$$

$$- N\ N_A [z(\Delta W_A^{001} - kT \Delta \ln v_A^{001}) + (\Delta W_S^{zo} - kT \Delta \ln v_S^{zo})]$$

$$- N\ N_P [z(\Delta W_P^{001} - kT \Delta \ln v_P^{001}) + (\Delta W_S^{oz} - kT \Delta \ln v_S^{oz})]$$

$$- N\ N_C [z(\Delta W_C^{001} - kT \Delta \ln v_C^{001}) + (\Delta W_S^{vo} - kT \Delta \ln v_S^{00})] \quad \ldots \text{(IV.122)}$$

Though the above expression forms the final relationship, one aimed at in the beginning of this theoretical treatment, yet for the purpose of testing its applicability and, also, to make its use for the actual systems, one needs expressing the energy and free volume parameters (i.e., W and v terms) in terms of experimentally determinable functions. These functions can be expressed in terms of the thermodynamic properties of the solvent and also the thermodynamic behaviour of the solute component, S, in each of the pure component A, P and C. To achieve this aim, let us first deduce these properties from eqs. (IV.120) and (IV.122) as follows;

$$\Delta G^{ex}_{mix(A+P+C)} = -(N.k.T.\ln\Omega)/(n_A+n_P+n_C)$$

$$- N.k.T.(N_A \ln N_A + N_P \ln N_P + N_C \ln N_C)$$

$$= zN.N_A.N_P.[(\Delta W_A^{100} - kT \Delta \ln v_A^{100}) + (\Delta W_P^{010} - kT \Delta \ln v_P^{010})]$$

$$+ z.N.N_A.N_C.[(\Delta W_A^{010} - kT \Delta \ln v_A^{010}) + (\Delta W_C^{100} - kT \Delta \ln v_C^{100})]$$

$$+ z.N.N_P.N_C[(\Delta W_P^{100} - kT \Delta \ln v_P^{100}) + (\Delta W_C^{010} - kT \Delta \ln v_C^{010})] \quad \ldots \text{(IV.123)}$$

$$\Delta \bar{G}^{ex,\infty}_{S(A)} = - N[z.(\Delta W_A^{001} - kT \ \ln v_A^{001}) + (\Delta W_S^{zo} - kT \Delta \ln v_S^{zo})] \qquad \ldots (IV.124)$$

$$\Delta \bar{G}^{ex,\infty}_{S(P)} = - N[z.(\Delta W_P^{001} - kT \Delta \ln v_P^{001}) + (\Delta W_S^{oz} - kT \Delta \ln v_S^{oz})] \qquad \ldots (IV.125)$$

$$\Delta \bar{G}^{ex,\infty}_{S(C)} = - N[z(\Delta W_C^{001} - kT \Delta \ln v_C^{001}) + (\Delta W_S^{00} - kT \Delta \ln v_S^{00})] \qquad \ldots (IV.126)$$

With the help of eqs. (IV.123) - (IV.126), one can write eq. (IV.122) in the following alternative form containing only the experimentally determinable parameters.

$$\begin{aligned} \Delta \bar{G}^{ex,\infty}_{S(A+P+C)} &= N_A \Delta \bar{G}^{ex,\infty}_{S(A)} + N_P \Delta \bar{G}^{ex,\infty}_{S(P)} + N_C \Delta \bar{G}^{ex,\infty}_{S(C)} - \Delta \bar{G}^{ex,\infty}_{Mix(A+P+C)} \\ &= N_A [\Delta \bar{G}^{ex,\infty}_{S(A)} - \Delta \bar{G}^{ex}_{A(A+P+C)}] + N_P [\Delta \bar{G}^{ex,\infty}_{S(P)} - \Delta \bar{G}^{ex}_{P\,(A+P+C)}] \\ &+ N_C [\Delta \bar{G}^{ex,\infty}_{S(C)} - \Delta \bar{G}^{ex}_{C(A+P+C)}] \end{aligned} \qquad \ldots (IV.127)$$

As a generalisation of the above expression, by induction, to determine the properties of the solute in an n-component solvent, one can write the following expression,

$$\Delta \bar{G}^{ex,\infty}_{S(1,2,\ldots n)} = \sum_{i=1}^{n} N_i [\Delta \bar{G}^{ex,\infty}_{S(i)} - \Delta \bar{G}^{ex}_{i(1,2,\ldots.n)}] \qquad \ldots (IV.128)$$

Thus for a binary solvent containing components A and B, one can write the following expression for the infinite dilution property of the solvent 'S',

$$\Delta\bar{G}^{ex,\infty}_{S(A+B)} = N_A[\Delta\bar{G}^{ex,\infty}_{S(A)} - \Delta\bar{G}^{ex}_{A(A+B)}] + N_B[\Delta\bar{G}^{ex,\infty}_{S(B)} - \Delta\bar{G}^{ex}_{B(A+B)}] \qquad \ldots \text{(IV.129)}$$

The above expression for binary solvent systems was first derived by Alcock and Richardson [87], using the concept and treatment based on classical thermodynamics.

IV.2.1.2 Randomly Distributed Solvent with Preferentially Distributed Solute

For this case, the interactions among the constituent solvent molecules or atoms are assumed not to affect the distribution of different type of atoms in the system. Thus, for this case, the set of eqs. (IV.59)- (IV.65) take the following modified forms :

$$n_A^{ijo} = \alpha_A . {}^{z}C_i . {}^{(z-i)}C_j . \exp(i\pi_1) . \exp(-j\pi_3) \qquad \ldots \text{(IV.130)}$$

$$n_A^{kdl} = \alpha_A . z . {}^{(z-1)}C_k . {}^{(z-k-1)}C_d . \exp(k\pi_1) . \exp(-d\pi_3) . \exp(\pi_4) : \exp\left(- \frac{\Delta W_A^{001} - kT\, \Delta \ln v_A^{001}}{kT}\right) \qquad \ldots \text{(IV.131)}$$

$$n_P^{xyo} = \alpha_P . {}^{z}C_x . {}^{(z-x)}C_y . \exp(x\pi_2) . \exp(-y\pi_1) \qquad \ldots \text{(IV.132)}$$

$$n_P^{pq1} = \alpha_P . z . {}^{(z-1)}C_P . {}^{(z-p-1)}C_q . \exp(p\pi_2) . \exp(-q\pi_1) .$$
$$\exp(\pi_5) . \exp\left(- \frac{\Delta W_P^{001} - kT\, \Delta \ln v_P^{001}}{kT}\right) \qquad \ldots \text{(IV.133)}$$

$$n_C^{rto} = \alpha_C . {}^{z}C_r . {}^{(z-r)}C_t . \exp(-t\pi_2) . \exp(r\pi_3) \qquad \ldots \text{(IV.134)}$$

$$n_C^{uv1} = \alpha_C . z . {}^{(z-1)}C_u . {}^{(z-u-1)}C_v . \exp(-v\pi_2) . \exp(u\pi_3) .$$
$$\exp(\pi_6) , \exp\left(- \frac{\Delta W_C^{001} - kT\, \Delta \ln v_C^{001}}{kT}\right) \qquad \ldots \text{(IV.135)}$$

$$n_S^{mw} = \alpha_S . {}^{z}C_m . {}^{(z-m)}C_w . \exp(-m\pi_4) . \exp(-w\pi_5) .$$
$$\exp\{ -(z-m-w)\pi_6 \} . \exp\left(- \frac{m\, \Delta W_S^{z,o} + w\, \Delta W_S^{oz} + (z-m-w)\Delta W_S^{00}}{z\ kT}\right) .$$
$$\exp[(m\, \Delta \ln v_S^{z,o} + w\, \Delta \ln v_S^{oz} + (z-m-w)\, \Delta \ln v_S^{oo})/z]$$
$$\ldots \text{(IV.136)}$$

where,

$$\alpha_A = n_A^o[1 + \exp\pi_1 + \exp(-\pi_3)]^{-z} \qquad \ldots \text{(IV.137a)}$$
$$= n_A^1 . \ z . \exp(\pi_4) . \exp\left(- \frac{\Delta W_A^{001} - kT\, \Delta \ln v_A^{001}}{kT}\right) .$$
$$\cdot [1 + \exp\pi_1 + \exp(-\pi_3)]^{-(z-1)} \qquad \ldots \text{(IV.137b)}$$

$$= n_A[\{1 + \exp\pi_1 + \exp(-\pi_3)\}^{z} + z . \exp(\pi_4) .$$
$$\exp\left(- \frac{W_A^{001} - kT\, \Delta \ln v_A^{001}}{kT}\right) \{1 + \exp\pi_1 + \exp(-\pi_3)\}^{(z-1)}]^{-1}$$
$$\ldots \text{(IV.137c)}$$

$$\alpha_P = n_P^o\,[1+\exp(-\pi_1)+\exp\pi_2]^{-z} \qquad \ldots\ (IV.138a)$$

$$= n_P^1\,[1+\exp(-\pi_1)+\exp\pi_2]^{-(z-1)}[z.\exp(\pi_5).$$

$$\exp\left(-\frac{\Delta W_P^{001}-kT\,\Delta\ln v_P^{001}}{kT}\right)]^{-1} \qquad \ldots\ (IV.138b)$$

$$= n_P[\{1+\exp(-\pi_1)+\exp\pi_2\}^{z}+z.\exp.\pi_5\exp\left(-\frac{\Delta W_P^{001}-kT\,\Delta\ln v_P^{001}}{kT}\right).$$

$$\{1+\exp(-\pi_1)+\ \exp\pi_2\}^{(z-1)}]^{-1} \qquad \ldots\ (IV.138c)$$

$$\alpha_C = n_C^o\,[1+\exp(-\pi_2)+\exp.\pi_3]^z \qquad \ldots\ (IV.139a)$$

$$= n_C^1\,[z.\exp(\pi_5).\exp\left(-\frac{\Delta W_C^{001}-kT\ \Delta\ln v_C^{001}}{kT}\right).$$

$$\{1+\exp(-\pi_2)+\exp\pi_3\}^{(z-1)}]^{-1} \qquad \ldots\ (IV.139b)$$

$$= n_C[\{1+\exp(-\pi_2)+\exp\pi_3\}^{z}+z.\exp(\pi_6).\exp\left(-\frac{\Delta W_C^{001}-kT\,\Delta\ln v_C^{001}}{kT}\right).$$

$$\{1+\exp(-\pi_2)+\exp\pi_3\}^{(z-1)}]^{-1} \qquad \ldots\ (IV.139c)$$

and,

$$\alpha_S = n_S[\exp(-\pi_4).\exp\left(-\frac{\Delta W_S^{zo}-kT\ \Delta\ln v_S^{zo}}{kT}\right)+\exp(-\pi_5).$$

$$\exp\left(-\frac{\Delta W_S^{oz}-kT\ \Delta\ln v_S^{oz}}{kT}\right)+\exp(-\pi_6).\exp\left(-\frac{\Delta W_S^{00}\ -kT\ \Delta\ln v_S^{00}}{kT}\right)]^{-z}$$

$$\ldots\ (IV.140)$$

where, the symbols n_A^o, n_P^o, n_C^o represent respectively the number of atoms of silver, lead and copper not surrounded by the atoms of solute component S i.e., sulphur in the present investigation. Further the symbols n_A^1, n_P^1 and n_S^1

represent respectively the numbers of atoms of these metals having one sulphur atom in their first coordination shell.

The bond balance eqs. (IV.70) - (IV.75) also take the following modified forms :

$$n_A\cdot\frac{\exp\pi_1[1+\exp\pi_1+\exp(-\pi_3)+(z-1).\exp(\pi_4).\exp(-\frac{\Delta W_A^{001}-kT\Delta\ln v_A^{001}}{kT})]}{\{(1+\exp\pi_1+\exp(-\pi_3)\}.[1+\exp\pi_1+\exp(-\pi_3)+z.\exp(\pi_4)\cdot\exp(-\frac{\Delta W_A^{001}-kT\Delta\ln v_A^{001}}{kT})]}$$

$$=n_P\cdot\frac{\exp(-\pi_1)[1+\exp(-\pi_1)+\exp\pi_2+(z-1).\exp(\pi_5).\exp(-\frac{\Delta W_P^{001}-kT\Delta\ln v_P^{001}}{kT})]}{\{1+\exp(-\pi_1)+\exp\pi_2\}.[1+\exp(-\pi_1)+\exp\pi_2+z\exp(\pi_5).\exp(-\frac{\{\Delta W_P^{001}-kT\Delta\ln v_P^{001}}{kT})]}\quad\ldots\text{(IV.141)}$$

$$n_P\cdot\frac{\exp\pi_2[1+\exp\pi_2+\exp(-\pi_1)+(z-1).\exp(\pi_5).\exp(-\frac{\Delta W_P^{001}-kT\Delta\ln v_P^{001}}{kT})]}{\{1+\exp(-\pi_1)+\exp\pi_2\}.[1+\exp(-\pi_1)+\exp\pi_2+z.\exp(\pi_5).\exp(-\frac{\Delta W_P^{001}-kT\Delta\ln v_P^{001}}{kT})]}$$

$$=n_C\cdot\frac{\exp(-\pi_2).[1+\exp(-\pi_2)+\exp\pi_3+(z-1).\exp(\pi_6)\exp(-\frac{\Delta W_C^{001}-kT\Delta\ln v_C^{001}}{kT})]}{\{1+\exp(-\pi_2)+\exp\pi_3\}.[1+\exp(-\pi_2)+\exp\pi_3 z.\exp(\pi_6).\exp(-\frac{\Delta W_C^{001}-kT\Delta\ln v_C^{001}}{kT})]}\quad\ldots\text{(IV.142)}$$

$$n_C \cdot \frac{\exp(\pi_3).[1+\exp(-\pi_2)+\exp\pi_3+(z-1).\exp(\pi_6).\exp(-\frac{\Delta W_C^{001}-kT\,\Delta \ln v_C^{001}}{kT})]}{\{1+\exp(-\pi_2)+\exp\pi_3\}.[1+\exp(-\pi_2)+\exp\pi_3+z.\exp(\pi_6).\exp(-\frac{\Delta W_C^{001}-kT\,\Delta \ln v_C^{001}}{kT})]}$$

$$=n_A \cdot \frac{\exp(-\pi_3).[1+\exp\pi_1+\exp(-\pi_3)+(z-1).\exp(\pi_4).\exp(-\frac{\Delta W_A^{001}-kT\,\Delta \ln v_A^{001}}{kT})]}{\{1+\exp\pi_1+\exp(-\pi_3)\}.[1+\exp\pi_1+\exp(-\pi_3)+z.\exp(\pi_4).\exp(-\frac{\Delta W_A^{001}-kT\,\Delta \ln v_A^{001}}{kT})]} \quad \ldots \text{(IV.143)}$$

$$n_A^1 = \frac{n_A.[z.\exp(\pi_4).\exp(-\frac{\Delta W_A^{001}-kT\,\Delta \ln v_A^{001}}{kT})]}{[1+\exp\pi_1+\exp(-\pi_3)+z.\exp(\pi_4).\exp(-\frac{\Delta W_A^{001}-kT\,\Delta \ln v_A^{001}}{kT})]}$$

$$= \frac{z n_S.\exp(-\pi_4).\exp(-\frac{\Delta W_S^{zo}-kT\,\Delta \ln v_S^{z.o}}{zkT})}{[\exp(-\pi_4).\exp(-\frac{\Delta W_S^{zo}-kT\,\Delta \ln v_S^{zo}}{z\,kT})+\exp(-\pi_5).\exp(-\frac{\Delta W_S^{oz}-kT\,\Delta \ln v_S^{oz}}{z\,kT})+\exp(-\pi_6).\exp(-\frac{\Delta W_S^{00}-kT\,\Delta \ln v_S^{00}}{z\,kT})]}$$

$$\ldots \text{(IV.144)}$$

$$n_P^1 = \frac{n_P.[\exp(\pi_5).\exp(-\frac{\Delta W_P^{001}-kT\,\Delta \ln v_P^{001}}{kT})]}{[1+\exp(-\pi_4)+\exp\pi_2+z.\exp(\pi_5).\exp(-\frac{\Delta W_P^{001}-kT\,\Delta \ln v_P^{001}}{kT})]}$$

$$= \frac{z n_S \cdot \exp(-\pi_5) \cdot \exp\left(-\frac{\Delta W_S^{oz} - kT\,\Delta \ln v_S^{oz}}{zkT}\right)}{\left[\exp(-\pi_4) \cdot \exp\left(-\frac{\Delta W_S^{zo} - kT\,\Delta \ln v_S^{zo}}{zkT}\right) + \exp(-\pi_5) \cdot \exp\left(-\frac{\Delta W_S^{oz} - kT\,\Delta \ln v_S^{oz}}{zkT}\right) + \exp(-\pi_6) \cdot \exp\left(-\frac{\Delta W_S^{00} - kT\,\Delta \ln v_S^{00}}{zkT}\right)\right]} \quad \ldots \text{(IV.145)}$$

and finally,

$$n_C^1 = \frac{n_C \cdot \left[z \cdot \exp(\pi_6) \cdot \exp\left(-\frac{\Delta W_C^{001} - kT\,\Delta \ln v_C^{001}}{kT}\right)\right]}{\left[1 + \exp(-\pi_2) + \exp\pi_3 + z \cdot \exp(\pi_6) \cdot \exp\left(-\frac{\Delta W_C^{001} - kT\,\Delta \ln v_C^{001}}{kT}\right)\right]}$$

$$= \frac{z \cdot n_S \cdot \exp(-\pi_6) \cdot \exp\left(-\frac{\Delta W_S^{00} - kT\,\Delta \ln v_S^{00}}{zkT}\right)}{\left[\exp(-\pi_4) \cdot \exp\left(-\frac{\Delta W_S^{zo} - kT\,\Delta \ln v_S^{zo}}{zkT}\right) + \exp(-\pi_5) \cdot \exp\left(-\frac{\Delta W_S^{oz} - kT\,\Delta \ln v_S^{oz}}{zkT}\right) + \exp(-\pi_6) \cdot \exp\left(-\frac{\Delta W_S^{00} - kT\,\Delta \ln v_S^{00}}{zkT}\right)\right]} \quad \ldots \text{(IV.146)}$$

For infinitely dilute solution of component S in the ternary solvent containing components A, P and C, the above set of equations yield the following expressions for parameters π_1, π_2... etc., in terms of mole fractions of different constituents of the solution;

$$\exp(\pi_1) = \frac{z\ n_P - n_P^1}{z\ n_A - n_A^1} \quad \ldots \text{(IV.147)}$$

$$\exp(\pi_2) = \frac{z\, n_C - n_C^1}{z n_P - n_P^1} \qquad \ldots \text{(IV.148)}$$

$$\exp(\pi_3) = \frac{z\, n_A - n_A^1}{z\, n_C - n_C^1} \qquad \ldots \text{(IV.149)}$$

$$\exp(\pi_4) = \frac{N_A^1}{N_A} \cdot \frac{n_S}{n_A} \cdot \exp\left(\frac{\Delta W_A^{001} - kT\, \Delta \ln v_A^{001}}{kT}\right) \qquad \ldots \text{(IV.150)}$$

$$\exp(\pi_5) = \frac{N_P^1}{N_P} \cdot \frac{n_S}{n_P} \cdot \exp\left(\frac{\Delta W_P^{001} - kT\, \Delta \ln v_P^{001}}{kT}\right) \qquad \ldots \text{(IV.151)}$$

and,

$$\exp(\pi_6) = \frac{N_C^1}{N_C} \cdot \frac{n_S}{n_C} \cdot \exp\left(\frac{\Delta W_C^{001} - kT\, \Delta \ln v_C^{001}}{kT}\right) \qquad \ldots \text{(IV.152)}$$

where the values of N_A^1, N_P^1 and N_C^1 are derived with the help of set of eqs. (IV.144) - (IV.146) and eqs. (IV.150) - (IV.152) and are given by the following expression,

$$\frac{{N_A^1}^2}{N_A^2 \cdot \exp\left(-\frac{\Delta W_S^{zo} - kT\, \Delta \ln v_S^{zo}}{zkT}\right) \cdot \exp\left(-\frac{\Delta W_A^{001} - kT\, \Delta \ln v_A^{001}}{kT}\right)}$$

$$= \frac{{N_P^1}^2}{N_P^2 \cdot \exp\left(-\frac{\Delta W_S^{oz} - kT\, \Delta \ln v_S^{oz}}{zkT}\right) \cdot \exp\left(-\frac{\Delta W_P^{001} - kT\, \Delta \ln v_P^{001}}{kT}\right)}$$

$$= \frac{N_C^{1^2}}{n_C^2 \cdot \exp\left(-\frac{\Delta W_S^{00} - kT\ \Delta \ln v_S^{00}}{zkT}\right) \cdot \exp\left(-\frac{\Delta W_C^{001} - kT\ \Delta \ln v_C^{001}}{kT}\right)} \quad \ldots \text{(IV.153)}$$

With the help of eqs. (IV.133) - (IV.153) one can write eq. (IV.52) for the partition function of the system in the following forms,

$$\begin{aligned}
\ln \Omega = {} & (n_A+n_P+n_C+n_S) \ln (n_A+n_P+n_C+n_S) + z n_A \ln n_A \\
& - z\, n_A \ln (n_A+n_P+n_C+n_S) + z n_P \ln n_P - z n_P \ln(n_A+n_P+n_C+n_S) \\
& + z n_C \ln n_C - z n_C \ln(n_A+n_P+n_C+n_S) + z\, n_S \ln n_S \\
& - z n_S \ln(n_A+n_P+n_C+n_S) - n_A^o \ln \alpha_A - n_A^1 \ln \alpha_A - n_P^o \ln \alpha_P \\
& - n_P^1 \ln \alpha_P - n_C^o \ln \alpha_C - n_C^1 \ln \alpha_C - n_S \ln \alpha_S \\
& - \sum_{i=o}^{z} i\ n_A^{ijo}\left(\frac{\Delta W_A^{100} - kT\ \Delta \ln v_A^{100}}{kT}\right) \\
& - \sum_{j=o}^{(z-i)} j n_A^{ijo}\left(\frac{\Delta W_A^{010} - kT\ \Delta \ln v_A^{010}}{kT}\right) - \sum_{k=o}^{(z-1)} k \\
& \quad n_A^{kdl}\left(\frac{\Delta W_A^{100} - kT\ \Delta \ln v_A^{100}}{kT}\right) \\
& - \sum_{d=o}^{(z-k-1)} d\ n_A^{kdl}\left(\frac{\Delta W_A^{010} - kT\ \Delta \ln v_A^{010}}{kT}\right) - \sum_{x=o}^{z} x \\
& \quad n_P^{xyo}\left(\frac{\Delta W_P^{100} - kT\ \Delta \ln v_P^{100}}{kT}\right) \\
& - \sum_{y=o}^{(z-x)} y\ n_P^{xyo}\left(\frac{\Delta W_P^{010} - kT\ \Delta \ln v_P^{010}}{kT}\right) - \sum_{p=o}^{(z-1)} p\ . \\
& \quad n_P^{pq1}\left(\frac{\Delta W_P^{100} - kT\ \Delta \ln v_P^{100}}{kT}\right)
\end{aligned}$$

$$- \sum_{q=o}^{(z-p-1)} q \cdot n_P^{pq1} \cdot \left(\frac{\Delta W_P^{010} - kT\, \Delta \ln\, v_P^{010}}{kT}\right) - \sum_{r=o}^{z} r \cdot n_C^{rto} \cdot$$

$$\left(\frac{\Delta W_C^{100} - kT\, \Delta \ln\, v_C^{100}}{kT}\right)$$

$$- \sum_{t=o}^{(z-r)} t \cdot n_C^{rto} \cdot \left(\frac{\Delta W_C^{010} - kT\, \Delta \ln\, v_C^{010}}{kT}\right) - \sum_{u=o}^{(z-1)} u\, n_C^{uv1} \cdot \left(\frac{\Delta W_C^{100} - kT \Delta \ln\, v_C^{100}}{kT}\right)$$

$$- \sum_{v=o}^{(z-u-1)} v \cdot n_C^{uv1} \cdot \left(\frac{\Delta W_C^{010} - kT\, \Delta \ln\, v_C^{010}}{kT}\right) \qquad \ldots \quad (IV.154)$$

The above expression is further simplified as,

$$\begin{aligned}
\ln \Omega = {} & (n_A + n_P + n_C + n_S) \ln (n_A + n_P + n_C + n_S) + z n_A \ln n_A \\
& - z n_A \ln (n_A + n_P + n_C + n_S) + z n_P \ln n_P - z n_P \ln (n_A + n_P + n_C + n_S) \\
& + z n_C \ln n_C - z n_C \ln (n_A + n_P + n_C + n_S) + z n_S \ln n_S \\
& - z n_S \ln (n_A + n_P + n_C + n_S) \\
& - (n_A - z n_S N_A^1) \ln (n_A - z n_S N_A^1) + z n_A \ln \left(\frac{n_A + n_P + n_C - n_S}{n_A - N_A^1 \cdot n_S}\right) \\
& - 2\, z n_S N_A^1 \ln n_A^1 - z n_S N_A^1 \ln \left(\frac{n_A + n_P + n_C - n_S}{n_A - N_A^1 \cdot n_S}\right) \\
& - (n_P - z n_S N_P^1) \ln (n_P - z n_S N_P^1) + z n_P \ln \left(\frac{n_A + n_P + n_C - n_S}{n_P - N_P^1 \cdot n_S}\right) \\
& - 2\, z n_S N_P^1 \ln N_P^1 - z n_S N_P^1 \ln \left(\frac{n_A + n_P + n_C - n_S}{n_P - N_P^1 \cdot n_S}\right) \\
& - (n_C - z n_S N_C^1) \ln (n_C - z n_S N_C^1) + z n_C \ln \left(\frac{n_A + n_P + n_C - n_S}{n_C - N_C^1\, n_S}\right) \\
& - 2\, z n_S N_C^1 \ln N_C^1 - z\, n_S N_C^1 \ln \left(\frac{n_A + n_P + n_C - n_S}{n_C - N_C^1\, n_S}\right)
\end{aligned}$$

$$- n_S \ln n_S - z n_S N_A^1 \left(\frac{\Delta W_A^{001} - kT \, \Delta \ln v_A^{001}}{kT} \right) - z \; n_S N_P^1 \left(\frac{\Delta W_P^{001} - kT \, \Delta \ln v_P^{001}}{kT} \right)$$

$$- z n_S N_C^1 \left(\frac{\Delta W_C^{001} - kT \Delta \ln v_C^{001}}{kT} \right) - z n_S N_A^1 \left(\frac{\Delta W_S^{z\;o} - kT \, \Delta \ln v_S^{zo}}{z kT} \right)$$

$$- z n_S N_P^1 \left(\frac{\Delta W_S^{oz} - kT \Delta \ln v_S^{oz}}{z kT} \right) - z n_S N_C^1 \left(\frac{\Delta W_S^{00} - kT \, \Delta \ln v_S^{00}}{z kT} \right)$$

$$- z n_A \left(\frac{n_P - n_S N_P^1}{n_A + n_P + n_C - n_S} \right) \left(\frac{\Delta W_A^{100} - kT \, \Delta \ln v_A^{100}}{kT} \right)$$

$$- z n_A \left(\frac{n_C - n_S N_C^1}{n_A + n_P + n_C + n_S} \right) \left(\frac{\Delta W_A^{010} - kT \, \Delta \ln v_A^{010}}{kT} \right)$$

$$- z n_P \left(\frac{n_C - n_S N_C^1}{n_A + n_P + n_C - n_S} \right) \left(\frac{\Delta W_P^{100} - kT \, \Delta \ln v_P^{100}}{kT} \right)$$

$$- z n_P \left(\frac{n_A - n_S N_A^1}{n_A + n_P + n_C - n_S} \right) \left(\frac{\Delta W_P^{010} - kT \, \Delta \ln v_P^{010}}{kT} \right)$$

$$- z n_C \left(\frac{n_A - n_S \; N_A^1}{n_A + n_P + n_C - n_S} \right) \left(\frac{\Delta W_C^{100} - kT \, \Delta \ln v_C^{100}}{kT} \right)$$

$$- z n_C \left(\frac{n_P - n_S N_P^1}{n_A + n_P + n_C - n_S} \right) \left(\frac{\Delta W_C^{010} - kT \, \Delta \ln v_C^{010}}{kT} \right)$$

$$+ z N_A^1 n_S \left(\frac{n_P - N_P^1 n_S}{n_A + n_P + n_C - n_S} \right) \left(\frac{\Delta W_A^{100} - kT \, \Delta \ln v_A^{100}}{kT} \right)$$

$$+ z N_A^1 n_S \left(\frac{n_C - N_C^1 n_S}{n_A + n_P + n_C - n_S} \right) \left(\frac{\Delta W_A^{010} - kT \, \Delta \ln v_A^{010}}{kT} \right)$$

$$+ z N_P^1 n_S \left(\frac{n_C - N_C^1 n_S}{n_A + n_P + n_C - n_S} \right) \left(\frac{\Delta W_P^{100} - kT \, \Delta \ln v_P^{100}}{kT} \right)$$

$$+ z N_P^1 n_S \left(\frac{n_A - N_A^1 n_S}{n_A + n_P + n_C - n_S} \right) \left(\frac{\Delta W_P^{010} - kT \, \Delta \ln v_P^{010}}{kT} \right)$$

$$+ z N_C^1 n_S \left(\frac{n_A - N_A^1 n_S}{n_A + n_P + n_C - n_S} \right) \left(\frac{\Delta W_C^{100} - kT \Delta \ln v_C^{100}}{kT} \right) + z n_C^1 n_S \left(\frac{n_P - N_P^1 n_S}{n_A + n_P + n_C - n_S} \right)$$

$$\left(\frac{\Delta W_C^{010} - kT \, \Delta \ln v_C^{010}}{kT} \right) \qquad \ldots \text{(IV.155)}$$

and therefore,

$$\begin{aligned}
\left(\frac{\partial \ln\Omega}{\partial n_S}\right)_{n_S\to o} = {} & 2zN_A^1 \ln \frac{N_A}{N_A^1} + 2z\, N_P^1 \ln \frac{N_P}{N_P^1} + 2z\, N_C^1 \ln \frac{N_C}{N_C^1} \\
& - zN_A^1\left(\frac{\Delta W_A^{001} - kT\, \Delta \ln v_A^{001}}{kT}\right) - zN_P^1\left(\frac{\Delta W_P^{001} - kT\, \Delta \ln v_P^{001}}{kT}\right) \\
& - zN_C^1\left(\frac{\Delta W_C^{001} - kT\, \Delta \ln v_C^{001}}{kT}\right) - zN_A^1\left(\frac{\Delta W_S^{zo} - kT\, \Delta \ln v_S^{zo}}{zkT}\right) \\
& - zN_P^1\left(\frac{\Delta W_S^{oz} - kT\, \Delta \ln v_S^{oz}}{zkT}\right) - zN_C^1\left(\frac{\Delta W_S^{00} - kT\, \Delta \ln v_S^{00}}{zkT}\right) \\
& - zN_A(N_P - N_P^1)\left(\frac{\Delta W_A^{100} - kT\, \Delta \ln v_A^{100}}{kT}\right) - zN_A(N_C - N_C^1)\left(\frac{\Delta W_A^{010} - kT\, \Delta \ln v_A^{010}}{kT}\right) \\
& - zN_P(N_C - N_C^1)\left(\frac{\Delta W_P^{100} - kT\, \Delta \ln v_P^{100}}{kT}\right) - zN_P(N_A - N_A^1)\left(\frac{\Delta W_P^{010} - kT\, \Delta \ln v_P^{010}}{kT}\right) \\
& - zN_C(N_A - N_A^1)\left(\frac{\Delta W_C^{100} - kT\, \Delta \ln v_C^{100}}{kT}\right) - zN_C(N_P - N_P^1)\left(\frac{\Delta W_C^{010} - kT\, \Delta \ln v_C^{010}}{kT}\right) \\
& + zN_A^1 N_P\left(\frac{\Delta W_A^{100} - kT\, \Delta \ln v_A^{100}}{kT}\right) + zN_A^1 N_C\left(\frac{\Delta W_A^{010} - kT\, \Delta \ln v_A^{010}}{kT}\right) \\
& + zN_P^1 N_C\left(\frac{\Delta W_P^{100} - kT\, \Delta \ln v_P^{100}}{kT}\right) + zN_P^1 N_A\left(\frac{\Delta W_P^{010} - kT\, \Delta \ln v_P^{010}}{kT}\right) \\
& + zN_C^1 N_A\left(\frac{\Delta W_C^{100} - kT\, \Delta \ln v_C^{100}}{kT}\right) + zN_C^1 N_P\left(\frac{\Delta W_C^{010} - kT\, \Delta \ln v_C^{010}}{kT}\right)
\end{aligned} \quad \ldots \text{(IV.156)}$$

From the eq. (IV.155), one gets an expression for the integral molar property by setting n_S equal to zero and the following expressions for partial molar properties of the solvent components.

$$\begin{aligned}
\Delta \bar{G}^{ex}_{A(A+P+C)} = {} & zN\, N_P[(\Delta W_A^{100} - kT\, \Delta \ln v_A^{100}) + (\Delta W_P^{010} - kT\, \Delta \ln v_P^{010})] \\
& + zNN_C[(\Delta W_A^{010} - kT\, \Delta \ln v_A^{010}) + (\Delta W_C^{100} - kT\, \Delta \ln v_C^{100})]
\end{aligned}$$

$$
\begin{aligned}
& - zNN_AN_P[(\Delta W_A^{100}-kT\,\Delta\ln v_A^{100})+(\Delta W_P^{010}-kT\,\Delta\ln v_P^{010})] \\
& - zN.N_AN_C[(\Delta W_A^{010}-kT\,\Delta\ln v_A^{010})+(\Delta W_C^{100}-kT\,\Delta\ln v_C^{100})] \\
& - zNN_PN_S[(\Delta W_P^{100}-kT\,\Delta\ln v_P^{100})+(\Delta W_C^{010}-kT\,\Delta\ln v_C^{010})]
\end{aligned}
\qquad \ldots \quad (IV.157)
$$

$$
\begin{aligned}
\Delta\bar{G}^{ex}_{P(A+P+C)} = {} & zNN_A[(\Delta W_A^{100}-kT\,\Delta\ln v_A^{100})+(\Delta W_P^{010}-kT\,\Delta\ln v_P^{010})] \\
& + z\,NN_C[(\Delta W_P^{100}-kT\,\Delta\ln v_P^{100})+(\Delta W_C^{010}-kT\,\Delta\ln v_C^{010})] \\
& - z\,NN_AN_P[(\Delta W_A^{100}-kT\,\Delta\ln v_A^{100})+(\Delta W_P^{010}-kT\,\Delta\ln v_P^{010})] \\
& - z\,NN_AN_C[(\Delta W_A^{010}-kT\,\Delta\ln v_A^{010})+(\Delta W_C^{100}-kT\,\Delta\ln v_C^{100})] \\
& - z\,NN_PN_C[(\Delta W_P^{100}-kT\,\Delta\ln v_P^{100})+(\Delta W_C^{010}-kT\,\Delta\ln v_C^{010})]
\end{aligned}
\qquad \ldots \quad (IV.158)
$$

and finally,

$$
\begin{aligned}
\Delta\bar{G}^{ex}_{C(A+P+C)} = {} & z\,NN_A[(\Delta W_A^{010}-kT\,\Delta\ln v_A^{010})+(\Delta W_C^{100}-kT\Delta\ln v_C^{100})] \\
& + z\,NN_P[(\Delta W_P^{100}-kT\,\Delta\ln v_P^{100})+(\Delta W_C^{010}-kT\,\Delta\ln v_C^{010})] \\
& - z\,NN_AN_P[(\Delta W_A^{100}-kT\,\Delta\ln v_A^{100})+(\Delta W_P^{010}-kT\,\Delta\ln v_P^{010})] \\
& - z\,NN_AN_C[(\Delta W_A^{010}-kT\,\Delta\ln v_A^{010})+(\Delta W_C^{100}-kT\,\Delta\ln v_C^{100})] \\
& - z\,NN_PN_C[(\Delta W_P^{100}-kT\,\Delta\ln v_P^{100})+(\Delta W_C^{010}-kT\,\Delta\ln v_C^{010})]
\end{aligned}
\qquad \ldots \quad (IV.159)
$$

One can also arrive at eqs. (IV.124)-(IV.126) from eq. (IV.156) for expressing the properties of the solute S in pure solvents A, P and C.

Elimination of energy and free volume terms from eq. (IV.156) with the help of eqs. (IV.157)-(IV.159) and (IV.124) - (IV.126) yields the following expression,

$$\Delta \bar{G}^{ex,\infty}_{S(A+P+C)} = 2zRT[N^1_A \ln \frac{N^1_A}{N_A} + N^1_P \ln \frac{N^1_P}{N_P} + N^1_C \ln \frac{N^1_C}{N_C}]$$
$$+ N^1_A[\Delta \bar{G}^{ex,\infty}_{S(A)} - \Delta \bar{G}^{ex}_{A(A+P+C)}] + N^1_P[\Delta \bar{G}^{ex,\infty}_{S(P)} - \Delta \bar{G}^{ex}_{P(A+P+C)}]$$
$$+ N^1_C[\Delta \bar{G}^{ex,\infty}_{S(C)} - \Delta \bar{G}^{ex}_{C(A+P+C)}] \quad \ldots \quad (IV.160)$$

where, the terms N^1_A, N^1_P and N^1_C are given by the following expressions,

$$N^1_A = \frac{k_A.N_A}{k_A.N_A+k_P.N_P+k_C.N_C} \quad \ldots \quad (IV.161)$$

$$N^1_P = \frac{k_P.N_P}{k_A.N_A+k_P.N_P+k_C.N_C} \quad \ldots \quad (IV.162)$$

$$N^1_C = \frac{k_C.N_C}{k_A.N_A+k_P.N_P+k_C.N_C} \quad \ldots \quad (IV.163)$$

and according to eq. (IV.155)

$$k_A = \exp[-\frac{\Delta \bar{G}^{ex,\infty}_{S(A)}}{2\ zRT}] \quad \ldots \quad (IV.164)$$

$$k_P = \exp[-\frac{\Delta \bar{G}^{ex,\infty}_{S(P)}}{2\ zRT}] \quad \ldots \quad (IV.165)$$

and

$$k_C = \exp[-\frac{\Delta \bar{G}^{ex,\infty}_{S(C)}}{2\ zRT}] \quad \ldots \quad (IV.166)$$

One can write from the above sets of equations, the following expression for the property of solute in a binary solvent containing components A and B only,

$$\Delta \bar{G}^{ex,\infty}_{S(A+B)} = 2\ zRT[N^1_A \ln \frac{N^1_A}{N_A} + N^1_B \ln \frac{N^1_B}{N_B}]$$

$$+ N^1_A [\Delta \bar{G}^{ex,\infty}_{S(A)} - \Delta \bar{G}^{ex}_{A(A+B)}] + N^1_B [\Delta \bar{G}^{ex,\infty}_{S(B)} - \Delta \bar{G}^{ex}_{B(A+B)}] \qquad \ldots (IV.167)$$

where,

$$N^1_A = \frac{k_A \cdot N_A}{k_A \cdot N_A + k_B \cdot N_B} \qquad \ldots (IV.168)$$

and

$$N^1_B = \frac{k_B \cdot N_B}{k_A \cdot N_A + k_B \cdot N_B} \qquad \ldots (IV.169)$$

with the functions k_A and k_B given by the following expressions,

$$k_A = \exp [- \frac{\Delta \bar{G}^{ex,\infty}_{S(A)}}{2\ zRT}] \qquad \ldots (IV.170)$$

and

$$k_B = \exp [- \frac{\Delta \bar{G}^{ex,\infty}_{S(B)}}{2\ zRT}] \qquad \ldots (IV.171)$$

Similarly for a multicomponent system containing components 1,2,3,...,n , one can write by induction the following generallized expressions ,

$$\Delta \bar{G}^{ex,\infty}_{S(1+2+\ldots+n)} = 2\ zRT [\sum_{i=1}^{n} N^1_i \ln \frac{N^1_i}{N_i}]$$

$$+ \sum_{i=1}^{n} N^1_i [\Delta \bar{G}^{ex,\infty}_{S(i)} - \Delta \bar{G}^{ex}_{i(1+2+\ldots+n)}] \qquad \ldots (IV.172)$$

where,

$$N^1_i = \frac{k_i\ N_i}{\sum_{i=1}^{n} k_i\ N_i} \qquad \ldots (IV.173)$$

and,

$$k_i = \exp [- \frac{\Delta \bar{G}^{ex,\infty}_{S(i)}}{2\ zRT.}] \qquad \ldots (IV.174)$$

IV.2.1.3 Preferentially Distributed System

In this case the distribution of both the solute and the solvent molecules or atoms is affected by the interaction among the neighbouring atoms. Thus with the help of eqs. (IV.80) - (IV.96), the set of eqs. (IV.59) - (IV.65) take the following modified forms,

$$n_A^{ijo} = \alpha_A \cdot {}^{z}C_i \cdot {}^{(z-i)}C_j \cdot \exp\left[i\left(\pi_1 - \frac{\Delta W_A^{100} - kT\,\Delta \ln v_A^{100}}{kT}\right)\right] \cdot$$

$$\cdot\ \exp\left[-j\left(\pi_3 + \frac{\Delta W_A^{010} - kT\,\Delta \ln v_A^{010}}{kT}\right)\right] \qquad \ldots \text{(IV.175)}$$

$$n_A^{kdl} = \alpha_A . z . {}^{(z-1)}C_k . {}^{(z-k-1)}C_d . \exp\left[k\left(\pi_1 - \frac{\Delta W_A^{100} - kT\,\Delta \ln v_A^{100}}{kT}\right)\right] \cdot$$

$$\cdot\ \exp\left[-d\left(\pi_3 + \frac{\Delta W_A^{010} - kT\,\Delta \ln v_A^{010}}{kT}\right)\right] \cdot$$

$$\cdot\ \exp\left[\pi_4 - \left(\frac{\Delta W_A^{001} - kT\,\Delta \ln v_A^{001}}{kT}\right)\right] \qquad \ldots \text{(IV.176)}$$

$$n_P^{xyo} = \alpha_P \cdot {}^{z}C_x \cdot {}^{(z-x)}C_y \cdot \exp\left[x\left(\pi_2 - \frac{\Delta W_P^{100} - kT\,\Delta \ln v_P^{100}}{kT}\right)\right] \cdot$$

$$\cdot\ \exp\left[-y\left(\pi_1 + \frac{\Delta W_P^{010} - kT\,\Delta \ln v_P^{010}}{kT}\right)\right] \qquad \ldots \text{(IV.177)}$$

$$n_P^{pql} = \alpha_P . z . {}^{(z-1)}C_p . {}^{(z-p-1)}C_q . \exp\left[p\left(\pi_2 - \frac{\Delta W_P^{100} - kT\,\Delta \ln v_P^{100}}{kT}\right)\right] \cdot$$

$$\cdot\ \exp\left[-q\left(\pi_1 + \frac{\Delta W_P^{010} - kT\,\Delta \ln v_P^{010}}{kT}\right)\right] . \exp(\pi_5) \cdot$$

$$\cdot\ \exp\left[-\frac{\Delta W_P^{001} - kT\,\Delta \ln v_P^{001}}{kT}\right] \qquad \ldots \text{(IV.178)}$$

$$n_C^{rto} = \alpha_C \cdot {}^{z}C_r \cdot {}^{(z-r)}C_t \cdot \exp\left[r\left(\pi_3 - \frac{\Delta W_C^{100} - kT\,\Delta \ln v_C^{100}}{kT}\right)\right] \cdot$$

$$\cdot \exp\left[-t\left(\pi_2 + \frac{\Delta W_C^{010} - kT\,\Delta \ln v_C^{010}}{kT}\right)\right] \qquad \ldots \text{(IV.179)}$$

$$n_C^{uvl} = \alpha_C \cdot z \cdot {}^{(z-1)}C_u \cdot {}^{(z-u-1)}C_v \cdot \exp\left[u\left(\pi_3 - \frac{\Delta W_C^{100} - kT\,\Delta \ln v_C^{100}}{kT}\right)\right] \cdot$$

$$\cdot \exp\left[-v\left(\pi_2 + \frac{\Delta W_C^{010} - kT\,\Delta \ln v_C^{010}}{kT}\right)\right]$$

$$\cdot \exp\left[\pi_6 - \left(\frac{\Delta W_C^{001} - kT\,\Delta \ln v_C^{001}}{kT}\right)\right] \qquad \ldots \text{(IV.180)}$$

where,

$$\alpha_\Lambda = n_\Lambda^0 \left[1 + \exp\left(\pi_1 - \frac{\Delta W_\Lambda^{100} - kT\Delta \ln v_\Lambda^{100}}{kT}\right)\right.$$

$$\left. + \exp\left(-\pi_3 - \frac{\Delta W_\Lambda^{010} - kT\,\Delta \ln v_\Lambda^{010}}{kT}\right)\right]^{-z} \qquad \ldots \text{(IV.181)}$$

$$= \frac{n_\Lambda^1}{z} \exp\left(-\pi_4 + \frac{\Delta W_\Lambda^{001} - kT\,\Delta \ln v_\Lambda^{001}}{kT}\right) \cdot$$

$$\cdot \left[1 + \exp\left(\pi_1 - \frac{\Delta W_\Lambda^{100} - kT\,\Delta \ln v_\Lambda^{100}}{kT}\right)\right.$$

$$\left. + \exp\left(-\pi_3 - \frac{\Delta W_\Lambda^{010} - kT\,\Delta \ln v_\Lambda^{010}}{kT}\right)\right]^{(-z+1)} \qquad \ldots \text{(IV.181a)}$$

$$= n_\Lambda \cdot \left[1 + \exp\left(\pi_1 - \frac{\Delta W_\Lambda^{100} - kT\,\Delta \ln v_\Lambda^{100}}{kT}\right)\right.$$

$$\left. + \exp\left(-\pi_3 - \frac{\Delta W_\Lambda^{010} - kT\,\Delta \ln v_\Lambda^{010}}{kT}\right)\right]^{-(z-1)} \cdot$$

$$\cdot \left[1 + \exp\left(\pi_1 - \frac{\Delta W_\Lambda^{100} - kT\,\Delta \ln v_\Lambda^{100}}{kT}\right) + \right.$$

$$+ \exp\left(-\pi_3 - \frac{\Delta W_\Lambda^{010} - kT\,\Delta \ln v_\Lambda^{010}}{kT}\right)$$

$$\left. + z \exp\left(\pi_4 - \frac{\Delta W_\Lambda^{001} - kT\,\Delta \ln v_\Lambda^{001}}{kT}\right)\right]^{-1} \qquad \ldots \text{(IV.181b)}$$

$$\alpha_P = n_P^o \left[1+\exp\left(-\pi_1 - \frac{\Delta W_P^{010} - kT\,\Delta \ln v_P^{010}}{kT}\right) + \exp\left(\pi_2 - \frac{\Delta W_P^{100} - kT\,\Delta \ln v_P^{100}}{kT}\right)\right]^{-z} \quad \ldots \quad (IV.182)$$

$$= \frac{n_P^1}{z} \left[1+\exp\left(-\pi_1 - \frac{\Delta W_P^{010} - kT\,\Delta \ln v_P^{010}}{kT}\right) + \exp\left(\pi_2 - \frac{\Delta W_P^{100} - kT\,\Delta \ln v_P^{100}}{kT}\right)\right]^{-(z-1)} \cdot \exp\left(-\pi_5 + \frac{\Delta W_P^{001} - kT\,\Delta \ln v_P^{001}}{kT}\right) \quad \ldots \quad (IV.182a)$$

$$= n_P \left[1+\exp\left(-\pi_1 - \frac{\Delta W_P^{010} - kT\,\Delta \ln v_P^{010}}{kT}\right) + \exp\left(\pi_2 - \frac{\Delta W_P^{100} - kT\,\Delta \ln v_P^{100}}{kT}\right)\right]^{-(z-1)}$$

$$\cdot \left[1+\exp\left(-\pi_1 - \frac{\Delta W_P^{010} - kT\,\Delta \ln v_P^{010}}{kT}\right) + \exp\left(\pi_2 - \frac{\Delta W_P^{100} - kT\,\Delta \ln v_P^{100}}{kT}\right) + z \exp\left(\pi_5 - \frac{\Delta W_P^{001} - kT\,\Delta \ln v_P^{001}}{kT}\right)\right]^{-1} \quad \ldots \quad (IV.182b)$$

$$\alpha_C = n_C^o \left[1+\exp\left(-\pi_2 - \frac{\Delta W_C^{010} - kT\,\Delta \ln v_C^{010}}{kT}\right) + \exp\left(\pi_3 - \frac{\Delta W_C^{100} - kT\,\Delta \ln v_C^{100}}{kT}\right)\right]^{-z} \quad \ldots \quad (IV.183)$$

$$= \frac{n_C^1}{z} \left[1+\exp\left(-\pi_2 - \frac{\Delta W_C^{010} - kT\,\Delta \ln v_C^{010}}{kT}\right) + \exp\left(\pi_3 - \frac{\Delta W_C^{100} - kT\,\Delta \ln v_C^{100}}{kT}\right)\right]^{-(z-1)} \cdot \exp\left(-\pi_6 + \frac{\Delta W_C^{001} - kT\,\Delta \ln v_C^{001}}{kT}\right) \quad \ldots \quad (IV.183a)$$

$$= n_C\Big[1+\exp\Big(-\pi_2-\frac{\Delta W_C^{010}-kT\ \Delta\ln\ v_C^{010}}{kT}\Big)$$

$$+\exp\Big(\pi_3-\frac{\Delta W_C^{100}-kT\ \Delta\ln\ v_C^{100}}{kT}\Big)\Big]^{-(z-1)}\cdot$$

$$\cdot\Big[1+\exp\Big(-\pi_2-\frac{\Delta W_C^{010}-kT\ \Delta\ln\ v_C^{010}}{kT}\Big)+\exp\Big(\pi_3-\frac{\Delta W_C^{100}-kT\ \Delta\ln v_C^{100}}{kT}\Big)$$

$$+z\ \exp\Big(\pi_5-\frac{\Delta W_C^{001}-kT\ \Delta\ln\ v_C^{001}}{kT}\Big)\Big]^{-1} \qquad \ldots \quad (IV.183b)$$

The bond balance expressions viz., eqs. (IV.70) - (IV. 75) also take the following modified forms;

$$n_A\Big[\exp\Big(\pi_1-\frac{\Delta W_A^{100}-kT\ \Delta\ln\ v_A^{100}}{kT}\Big)\Big].\Big[1+\exp\Big(\pi_1-\frac{\Delta W_A^{100}-kT\ \Delta\ln\ v_A^{100}}{kT}\Big)$$

$$+\exp\Big(-\pi_3-\frac{\Delta W_A^{010}-kT\ \Delta\ln\ v_A^{010}}{kT}\Big)+(z-1).\exp(\pi_4)\cdot$$

$$.\exp\Big(-\frac{\Delta W_A^{001}-kT\ \Delta\ln\ v_A^{001}}{kT}\Big)\Big]\cdot$$

$$\cdot\Big[1+\exp\Big(\pi_1-\frac{\Delta W_A^{100}-kT\Delta\ln v_A^{100}}{kT}\Big)+\exp\Big(-\pi_3-\frac{\Delta W_A^{010}-kT\ \Delta\ln\ v_A^{010}}{kT}\Big)\Big]^{-1}\cdot$$

$$\cdot\Big[1+\exp\Big(\pi_1-\frac{\Delta W_A^{100}-kT\ \Delta\ln\ v_A^{100}}{kT}\Big)+\exp\Big(-\pi_3-\frac{\Delta W_A^{010}-kT\ \Delta\ln\ v_A^{010}}{kT}\Big)$$

$$+z\ \exp(\pi_4)\ .\ \exp\Big(-\frac{\Delta W_A^{001}-kT\ \Delta\ln\ v_A^{001}}{kT}\Big)\Big]^{-1}$$

$$= n_P\Big[\exp\Big(-\pi_1-\frac{\Delta W_P^{010}-kT\ \Delta\ln\ v_P^{010}}{kT}\Big)\Big].\Big[1+\exp\Big(-\pi_1-\frac{\Delta W_P^{010}-kT\ \Delta\ln v_P^{010}}{kT}\Big)$$

$$+\exp\Big(\pi_2-\frac{\Delta W_P^{100}-kT\ \Delta\ln\ v_P^{100}}{kT}\Big)+(z-1)\exp\Big(\pi_5-\frac{\Delta W_P^{001}-kT\ \Delta\ln\ v_P^{001}}{kT}\Big)\Big]\cdot$$

$$\cdot\Big[1+\exp\Big(-\pi_1-\frac{\Delta W_P^{010}-kT\ \Delta\ln\ v_P^{010}}{kT}\Big)+\exp\Big(\pi_2-\frac{\Delta W_P^{100}-kT\ \Delta\ln\ v_P^{100}}{kT}\Big)\Big]^{-1}$$

$$\cdot[1+\exp(-\pi_1-\frac{\Delta W_P^{010}-kT\ \Delta\ln\ v_P^{010}}{kT})+\exp(\pi_2-\frac{\Delta W_P^{100}-kT\ \Delta\ \ln\ v_P^{100}}{kT}$$

$$+z\ \exp(\pi_5-\frac{\Delta W_P^{001}-kT\ \Delta\ \ln\ v_P^{001}}{kT})]^{-1} \qquad \ldots \quad (IV.184)$$

$$n_P[\exp(\pi_2-\frac{\Delta W_P^{100}-kT\ \Delta\ln\ v_P^{100}}{kT})].[1+\exp(-\pi_1-\frac{\Delta W_P^{010}-kT\ \Delta\ \ln\ v_P^{010}}{kT})$$

$$+\exp(\pi_2-\frac{\Delta W_P^{100}-kT\ \Delta\ln\ v_P^{100}}{kT})+(z-1)\exp(\pi_5-\frac{\Delta W_P^{001}-kT\ \Delta\ \ln\ v_P^{001}}{kT})]\cdot$$

$$\cdot[1+\exp(-\pi_1-\frac{\Delta W_P^{010}-kT\ \Delta\ln\ v_P^{010}}{kT})+\exp(\pi_2-\frac{\Delta W_P^{100}-kT\ \Delta\ln\ v_P^{100}}{kT})]^{-1}\cdot$$

$$\cdot[1+\exp(-\pi_1-\frac{\Delta W_P^{010}-kT\ \Delta\ \ln\ v_P^{010}}{kT})+\exp(\pi_2-\frac{\Delta W_P^{100}-kT\ \Delta\ln\ v_P^{100}}{kT})$$

$$+z\ \exp(\pi_5-\frac{\Delta W_P^{001}-kT\ \Delta\ln\ v_P^{001}}{kT})]^{-1}$$

$$=n_C[\exp\ (-\pi_2-\frac{\Delta W_C^{010}-kT\ \Delta\ln\ v_C^{010}}{kT})].[1+\exp(-\pi_2-\frac{\Delta W_C^{010}-kT\ \Delta\ln\ v_C^{010}}{kT})$$

$$+\ \exp(\pi_3-\frac{\Delta W_C^{100}-kT\ \Delta\ \ln\ v_C^{100}}{kT})+(z-1).\exp(\pi_6-\frac{\Delta W_C^{001}-kT\ \Delta\ln\ v_C^{001}}{kT})]\cdot$$

$$\cdot[1+\exp(-\pi_2-\frac{\Delta W_C^{010}-kT\ \Delta\ \ln v_C^{010}}{kT})+\exp(\pi_3-\frac{\Delta W_C^{100}-kT\ \Delta\ln\ v_C^{100}}{kT})]^{-1}\cdot$$

$$\cdot[1+\exp(-\pi_2-\frac{\Delta W_C^{010}-kT\ \Delta\ \ln\ v_C^{010}}{kT})+\exp(\pi_3-\frac{\Delta W_C^{100}-kT\ \Delta\ln\ v_C^{100}}{kT})$$

$$+z.\exp(\pi_6-\frac{\Delta W_C^{001}-kT\ \Delta\ \ln\ v_C^{001}}{kT})]^{-1} \qquad \ldots \quad (IV.185)$$

$$n_C[\exp(\pi_3-\frac{\Delta W_C^{100}-kT\ \Delta\ln\ v_C^{100}}{kT})].[1+\exp(-\pi_2-\frac{\Delta W_C^{010}-kT\ \Delta\ln\ v_C^{010}}{kT})$$

$$+\exp(\pi_3-\frac{\Delta W_C^{100}-kT\ \Delta\ln\ v_C^{100}}{kT})+(z-1).\exp(\pi_6-\frac{\Delta W_C^{001}-kT\ \Delta\ln\ v_C^{001}}{kT})]\cdot$$

$$[1+\exp(-\pi_2-\frac{\Delta W_C^{010}-kT\ \Delta\ \ln\ v_C^{010}}{kT})+\exp(\pi_3-\frac{\Delta W_C^{100}-kT\ \Delta\ln\ v_C^{100}}{kT})]^{-1}$$

$$\cdot\left[1+\exp\left(-\pi_2-\frac{\Delta W_C^{010}-kT\,\Delta\ln v_C^{010}}{kT}\right)+\exp\left(\pi_3-\frac{\Delta W_C^{100}-kT\,\Delta\ln v_C^{100}}{kT}\right)\right.$$

$$\left.+z.\exp\left(\pi_6-\frac{\Delta W_C^{001}-kT\,\Delta\ln v_C^{001}}{kT}\right)\right]^{-1}$$

$$=n_A\left[\exp\left(-\pi_3-\frac{\Delta W_A^{010}-kT\,\Delta\ln v_A^{010}}{kT}\right)\right].\left[1+\exp\left(\pi_1-\frac{\Delta W_A^{100}-kT\,\Delta\ln v_A^{100}}{kT}\right)\right.$$

$$\left.+\exp\left(-\pi_3-\frac{\Delta W_A^{010}-kT\,\Delta\ln v_A^{010}}{kT}\right)+(z-1).\exp\left(\pi_4-\frac{\Delta W_A^{001}-kT\,\Delta\ln v_A^{001}}{kT}\right)\right]$$

$$\cdot\left[1+\exp\left(\pi_1-\frac{\Delta W_A^{100}-kT\,\Delta\ln v_A^{100}}{kT}\right)+\exp\left(-\pi_3-\frac{\Delta W_A^{010}-kT\,\Delta\ln v_A^{010}}{kT}\right)\right]^{-1}$$

$$\cdot\left[1+\exp\left(\pi_1-\frac{\Delta W_A^{100}-kT\,\Delta\ln v_A^{100}}{kT}\right)+\exp\left(-\pi_3-\frac{\Delta W_A^{010}-kT\,\Delta\ln v_A^{010}}{kT}\right)\right.$$

$$\left.+z.\exp\left(\pi_4-\frac{\Delta W_A^{001}-kT\,\Delta\ln v_A^{001}}{kT}\right)\right]^{-1} \qquad \ldots\ (\mathrm{IV}.186)$$

$$n_A^1=\frac{n_A\cdot\left[\left(z.\exp\left(\pi_4-\frac{\Delta W_A^{001}-kT\,\Delta\ln v_A^{001}}{kT}\right)\right]\right.}{\left[1+\exp\left(\pi_1-\frac{\Delta W_A^{100}-kT\,\Delta\ln v_A^{100}}{kT}\right)+\exp\left(-\pi_3-\frac{\Delta W_A^{010}-kT\,\Delta\ln v_A^{010}}{kT}\right)+z\,\exp\left(\pi_4-\frac{\Delta W_A^{001}-kT\,\Delta\ln v_A^{001}}{kT}\right)\right]} \qquad \ldots\ (\mathrm{IV}.187)$$

$$=\frac{z.n_S.\exp\left(-\pi_4-\frac{\Delta W_S^{zo}-kT\,\Delta\ln v_S^{zo}}{zkT}\right)}{\left[\exp(-\pi_4)-\frac{\Delta W_S^{zo}-kT\,\Delta\ln v_S^{zo}}{zkT}\right)+\exp\left(-\pi_5-\frac{\Delta W_S^{oz}-kT\,\Delta\ln v_S^{oz}}{zkT}\right)+\exp\left(-\pi_6-\frac{\Delta W_S^{00}-kT\,\Delta\ln v_S^{00}}{zkT}\right)\right]} \qquad \ldots\ (\mathrm{IV}.187a)$$

$$n_P^1=\frac{n_P\cdot\left[z\,\exp\left(\pi_5-\frac{\Delta W_P^{001}-kT\,\Delta\ln v_P^{001}}{kT}\right)\right]}{\left[1+\exp\left(-\pi_1-\frac{\Delta W_P^{010}-kT\,\Delta\ln v_P^{010}}{kT}\right)+\exp\left(\pi_2-\frac{\Delta W_P^{100}-kT\,\Delta\ln v_P^{100}}{kT}\right)+z\,\exp\left(\pi_5-\frac{\Delta W_P^{001}-kT\,\Delta\ln v_P^{001}}{kT}\right)\right]} \qquad \ldots\ (\mathrm{IV}.188)$$

$$= \frac{z.n_S.\exp(-\pi_5 - \frac{\Delta W_S^{oz} - kT\,\Delta \ln v_S^{oz}}{zkT})}{[\exp(-\pi_4 - \frac{\Delta W_S^{zo} - kT\,\Delta \ln v_S^{zo}}{zkT}) + \exp(-\pi_5 - \frac{\Delta W_S^{oz} - kT\,\Delta \ln v_S^{oz}}{zkT}) + \exp(-\pi_6 - \frac{\Delta W_S^{00} - kT\,\Delta \ln v_S^{00}}{zkT})]} \quad \ldots \quad (IV.188a)$$

$$n_C^1 = \frac{n_C[z\ \exp(\pi_6 - \frac{\Delta W_C^{001} - kT\,\Delta \ln v_C^{001}}{kT})]}{[1 + \exp(-\pi_2 - \frac{\Delta W_C^{010} - kT\,\Delta \ln v_C^{010}}{kT}) + \exp(\pi_3 - \frac{\Delta W_C^{100} - kT\,\Delta \ln v_C^{100}}{kT}) + z\ \exp(\pi_6 - \frac{\Delta W_C^{001} - kT\,\Delta \ln v_C^{001}}{kT})]} \quad \ldots \quad (IV.189)$$

$$= \frac{z.n_S.\exp(-\pi_6 - \frac{\Delta W_S^{00} - kT\,\Delta \ln v_S^{00}}{zkT})}{[\exp(-\pi_4 - \frac{\Delta W_S^{zo} - kT\,\Delta \ln v_S^{zo}}{zkT}) + \exp(-\pi_5 - \frac{\Delta W_S^{oz} - kT\,\Delta \ln v_S^{oz}}{zkT}) + \exp(-\pi_6 - \frac{\Delta W_S^{00} - kT\,\Delta \ln v_S^{00}}{zkT})]} \quad \ldots \quad (IV.189a)$$

Further, according to eqs. (IV.187) - (IV.189a), one gets the following relationships,

$$\frac{n_A^1}{\exp(-\pi_4).\exp(-\frac{\Delta W_S^{zo} - kT\,\Delta \ln v_S^{zo}}{zkT})} = \frac{n_P^1}{\exp(-\pi_5).\exp(-\frac{\Delta W_S^{oz} - kT\,\Delta \ln v_S^{oz}}{zkT})}$$

$$= \frac{n_C^1}{\exp(-\pi_6).\exp(-\frac{\Delta W_S^{00} - kT\,\Delta \ln v_S^{00}}{zkT})} \quad \ldots \quad (IV.190)$$

where,

$$\exp(-\pi_4) = \frac{z.n_A^0}{n_A^1}\ .\exp(-\frac{\Delta W_A^{001} - kT\,\Delta \ln v_A^{001}}{kT}).$$

$$\cdot[1+\exp(\pi_1-\frac{\Delta W_A^{100}-kT\,\Delta\ln\,v_A^{100}}{kT})+\exp(-\pi_3-\frac{\Delta W_A^{010}-kT\,\Delta\ln\,v_A^{010}}{kT})]$$

... (IV.191)

$$=\frac{z.n_A^0}{n_A^1}\cdot(\frac{\alpha_A}{n_A^0})^{1/z}\cdot\exp(-\frac{\Delta W_A^{001}-kT\,\Delta\ln\,v_A^{001}}{kT})$$

.... (IV.191a)

$$\exp(-\pi_5)=\frac{z\,n_P^0}{n_P^1}\cdot\exp(-\frac{\Delta W_P^{001}-kT\,\Delta\ln\,v_P^{001}}{kT})\cdot$$

$$\cdot[1+\exp(-\pi_1-\frac{\Delta W_P^{010}-kT\,\Delta\ln\,v_P^{010}}{kT})+\exp(\pi_2-\frac{\Delta W_P^{100}-kT\,\Delta\ln\,v_P^{100}}{kT})]$$

... (IV.192)

$$=\frac{z.n_P^0}{n_P^1}\cdot(\frac{\alpha_P}{n_P^0})^{1/z}\cdot\exp(-\frac{\Delta W_P^{001}-kT\,\Delta\ln\,v_P^{001}}{kT})$$

... (IV.192a)

and,

$$\exp(-\pi_6)=\frac{z.n_C^0}{n_C^1}\cdot\exp(-\frac{\Delta W_C^{001}-kT\,\Delta\ln\,v_C^{001}}{kT})\cdot$$

$$\cdot[1+\exp(-\pi_2-\frac{\Delta W_C^{010}-kT\,\Delta\ln\,v_C^{010}}{kT})+\exp(\pi_3-\frac{\Delta W_C^{100}-kT\,\Delta\ln\,v_C^{100}}{kT})]$$

... (IV.193)

$$=\frac{z.n_C^0}{n_C^1}\cdot(\frac{\alpha_C}{n_C^0})^{1/z}\cdot\exp(-\frac{\Delta W_C^{001}-kT\,\Delta\ln\,v_C^{001}}{kT})$$

... (IV.193a)

With the help of above expressions one can simplify eqn. (IV. 52) to the following form,

$$\begin{aligned}\ln\Omega &= (n_A+n_P+n_C+n_S)\ln(n_A+n_P+n_C+n_S)+zn_A\,\ln\,n_A\\ &- zn_A\,\ln(n_A+n_P+n_C+n_S)+zn_P\,\ln\,n_P-zn_P\,\ln(n_A+n_P+n_C+n_S)\\ &+ zn_C\,\ln\,n_C-zn_C\,\ln(n_A+n_P+n_C+n_S)+zn_S\,\ln\,n_S\\ &- zn_S\,\ln(n_A+n_P+n_C+n_S)-n_A^0\,\ln\,\alpha_A-n_A^1\,\ln\,\alpha_A\end{aligned}$$

$$- n_P^o \cdot \ln \alpha_P - n_P^1 \ln \alpha_P - n_C^o \ln \alpha_C - n_C^1 \ln \alpha_C - n_S \ln \alpha_S \quad \ldots \quad (IV.194)$$

Further, using eqs. (IV.181) - (IV.183b) the above expression can be modified into the following alternative form,

$$\begin{aligned}
\ln\Omega = {} & (n_A+n_P+n_C+n_S) \ln (n_A+n_P+n_C+n_S) + z\, n_A \ln n_A \\
& - zn_A \ln(n_A+n_P+n_C+n_S) + zn_P \ln n_P - zn_P \ln(n_A+n_P+n_C+n_S) \\
& + zn_C \ln n_C - zn_C \ln(n_A+n_P+n_C+n_S) \\
& - zn_S \ln(n_A+n_P+n_C+n_S) - n_A^o \ln \alpha_A - 2n_A^1 \ln N_A^1 \\
& - n_A^1 \left(\frac{\Delta W_A^{001} - kT\,\Delta \ln v_A^{001}}{kT}\right) + \left(\frac{z-1}{z}\right) n_A^1 \ln (n_A^o/\alpha_A) - n_P^o \ln \alpha_P \\
& - 2n_P^1 \ln N_P^1 - n_P^1 \left(\frac{\Delta W_P^{001} - kT\,\Delta \ln v_P^{001}}{kT}\right) + \left(\frac{z-1}{z}\right) \ln (n_P^o/\alpha_P) \\
& - n_C^o \ln \alpha_C - 2n_C^1 \ln N_C^1 - n_C^1 \left(\frac{\Delta W_C^{001} - kT\,\Delta \ln v_C^{001}}{kT}\right) + \left(\frac{z-1}{z}\right) \ln(n_C^o/\alpha_C) \\
& - n_S \ln n_S - n_A^1 \left(\frac{\Delta W_S^{zo} - kT\,\Delta \ln v_S^{zo}}{zkT}\right) - n_P^1 \left(\frac{\Delta W_S^{oz} - kT\,\Delta \ln v_S^{oz}}{zkT}\right) \\
& - n_C^1 \left(\frac{\Delta W_S^{00} - kT\,\Delta \ln v_S^{00}}{zkT}\right) \qquad \ldots \quad (IV.195)
\end{aligned}$$

Differentiation of this expression with respect to n_S leads to the following expression for partial molar free energy of solute component S at infinite dilution,

$$\begin{aligned}
- \frac{1}{kT} \Delta \bar{G}_{S(A+P+C)}^{ex,\infty} & = \left[\left(\frac{\partial \ln\Omega}{n_S} \right)_{n_S \to o} + \ln N_S \right] \\
& = z\, n_A^1 \ln N_A - 2zN_A^1 \ln N_A^1 - zN_A^1 \left(\frac{\Delta W_A^{001} - kT\,\Delta \ln v_A^{001}}{kT}\right) \\
& - zn_A^1 \ln \Big\{ 1 + \exp\Big(\pi_1 - \frac{\Delta W_A^{100} - kT\,\Delta \ln v_A^{100}}{kT}\Big) \\
& \qquad + \exp\Big(-\pi_3 - \frac{\Delta W_A^{010} - kT\,\Delta \ln v_A^{010}}{kT}\Big) \Big\}
\end{aligned}$$

$$+ zN_P^1 \ln N_P - 2\, zN_P^1 \ln N_P^1 - zN_P^1 \left(\frac{\Delta W_P^{001} - kT\, \Delta \ln v_P^{001}}{kT}\right)$$

$$- zN_P^1 \ln\left\{ 1+\exp\left(-\pi_1 - \frac{\Delta W_P^{010} - kT\, \Delta \ln v_P^{010}}{kT}\right) + \exp\left(\pi_2 - \frac{\Delta W_P^{100} - kT\, \Delta \ln v_P^{100}}{kT}\right)\right\}$$

$$+ zN_C^1 \ln N_C - 2\, zN_C^1 \ln N_C^1 - zN_C^1 \left(\frac{\Delta W_C^{001} - kT\, \Delta \ln v_C^{001}}{kT}\right)$$

$$- zN_C^1 \ln \left\{1+\exp\left(-\pi_2 - \frac{\Delta W_C^{010} - kT\, \Delta \ln v_C^{010}}{kT}\right) + \exp\left(\pi_3 - \frac{\Delta W_C^{100} - kT\, \Delta \ln v_C^{100}}{kT}\right)\right\}$$

$$- zN_A^1 \left(\frac{\Delta W_S^{zo} - kT\, \Delta \ln v_S^{zo}}{zkT}\right) - zN_P^1 \left(\frac{\Delta W_S^{oz} - kT\, \Delta \ln v_S^{oz}}{zkT}\right) - zN_C^1 \left(\frac{\Delta W_S^{00} - kT\, \Delta \ln v_S^{00}}{zkT}\right. \quad \ldots \text{(IV.196)}$$

From this equation, one gets eqs. (IV.124) - (IV.126) for the excess partial molar free energies of solute 'S' in pure solvents silver, lead and copper respectively. Further, for the partial molar properties of components A, P and C in the solvent, one gets from eq. (IV.195), the following expressions,

$$\Delta \bar{G}^{ex}_{A(A+P+C)} = - z\, RT \ln N_A - zRT \ln \left\{1+\exp\left(\pi_1 - \frac{\Delta W_A^{100} - kT\, \Delta \ln v_A^{100}}{kT}\right) + \exp\left(-\pi_3 - \frac{\Delta W_A^{010} - kT\, \Delta \ln v_A^{010}}{kT}\right)\right\} \quad \ldots \text{(IV.197)}$$

$$\Delta \bar{G}^{ex}_{P(A+P+C)} = - zRT \ln N_P - zRT \ln \left\{ 1+\exp\left(-\pi_1 - \frac{\Delta W_P^{010} - kT\, \Delta \ln v_P^{010}}{kT}\right) + \exp\left(\pi_2 - \frac{\Delta W_P^{100} - kT\, \Delta \ln v_P^{100}}{kT}\right)\right\} \quad \ldots \text{(IV.198)}$$

and,

$$\Delta \bar{G}^{ex}_{C(A+P+C)} = - zRT \ln N_C - zRT \ln \left\{ 1+\exp\left(-\pi_2 - \frac{\Delta W_C^{010} - kT\, \Delta \ln n_C^{010}}{kT}\right) + \exp\left(\pi_3 - \frac{\Delta W_C^{100} - kT\, \Delta \ln v_C^{100}}{kT}\right)\right\} \quad \ldots \text{(IV.199)}$$

For practical applications of these relationships, as done in earlier two cases also, elimination of energy and free volume terms with the help of above equations and those of excess properties of component 'S' at infinite dilution in pure solvents leads to the following expression;

$$\Delta\bar{G}^{ex,\infty}_{S(A+P+C)} = 2z.\,RT\left(N^1_A \ln \frac{N^1_A}{N_A} + N^1_P \ln \frac{N^1_P}{N_P} + N^1_C \ln \frac{N^1_C}{N_C}\right) + N^1_A[\Delta\bar{G}^{ex,\infty}_{S(A)} - \Delta\bar{G}^{ex}_{A(A+P+C)}] + N^1_P[\Delta\bar{G}^{ex,\infty}_{S(P)} - \Delta\bar{G}^{ex}_{P(A+P+C)} + N^1_C[\Delta\bar{G}^{ex,\infty}_{S(C)} - \Delta\bar{G}^{ex}_{C(A+P+C)}] \quad \ldots \quad (IV.200)$$

where, the terms N^1_A, N^1_P and N^1_C are given by the following expressions,

$$N^1_A = \frac{N_A\ k_A}{N_A k_A + N_P k_P + N_C k_C} \quad \ldots \quad (IV.201a)$$

$$N^1_P = \frac{N_P\ k_P}{N_A k_A + N_P k_P + N_C k_C} \quad \ldots \quad (IV.201b)$$

and,

$$N^1_C = \frac{N_C\ k_C}{N_A k_A + N_P k_P + N_C k_C} \quad \ldots \quad (IV.201c)$$

In these expressions, k_A, k_P and k_C are given by the following expressions:

$$k_A = \exp\left\{\frac{1}{2z}\left(\frac{\Delta\bar{G}^{ex}_{A(A+P+C)} - \Delta\bar{G}^{ex,\infty}_{S(A)}}{RT}\right)\right\} \quad \ldots \quad (IV.202a)$$

$$k_P = \exp\left\{\frac{1}{2z}\left(\frac{\Delta\bar{G}^{ex}_{P(A+P+C)} - \Delta\bar{G}^{ex,\infty}_{S(P)}}{RT}\right)\right\} \quad \ldots \quad (IV.202b)$$

and

$$k_C = \exp\left\{\frac{1}{2z}\left(\frac{\Delta\bar{G}^{ex}_{C(A+P+C)} - \Delta\bar{G}^{ex,\infty}_{S(C)}}{RT}\right)\right\} \quad \ldots \quad (IV.202c)$$

From the above expressions one can deduce the following relationships for the properties of an infinitely dilute solution of a solute 'S' in a binary solvent containing components A and B.

$$\Delta\bar{G}^{ex,\infty}_{S(A+B)} = 2\,zRT\left(N^1_A \ln \frac{N^1_A}{N_A} + N^1_B \ln \frac{N^1_B}{N_B}\right)$$

$$+ N^1_A[\Delta\bar{G}^{ex,\infty}_{S(A)} - \Delta\bar{G}^{ex}_{A(A+B)}] + N^1_B[\Delta\bar{G}^{ex,\infty}_{S(B)} - \Delta\bar{G}^{ex,\infty}_{B(A+B)}] \qquad \text{... (IV.203)}$$

where N^1_A and N^1_B are defined by the expressions,

$$N^1_A = \frac{N_A\ k_A}{N_A k_A + N_B k_B} \qquad \text{... (IV.204a)}$$

and,

$$N^1_B = \frac{N_B\ k_B}{N_A k_A + N_B k_B} \qquad \text{... (IV.204b)}$$

$$\text{where, } k_A = \exp\left\{\frac{1}{2z}\left(\frac{\Delta\bar{G}^{ex}_{A(A+B)} - \Delta\bar{G}^{ex,\infty}_{S(A)}}{RT}\right)\right\} \qquad \text{... (IV.205a)}$$

$$\text{and, } k_B = \exp\left\{\frac{1}{2z}\left(\frac{\Delta\bar{G}^{ex}_{B(A+B)} - \Delta\bar{G}^{ex,\infty}_{S(B)}}{RT}\right)\right\} \qquad \text{... (IV.205b)}$$

Similarly for a multicomponent system one can arrive at the following set of expressions,

$$\Delta\bar{G}^{ex,\infty}_{S(A+2+..+n)} = 2z\ RT\left(\sum_{i=1}^{n} N^1_i \ln \frac{N^1_i}{N_i}\right)$$

$$+ \sum_{i=1}^{n} N^1_i(\Delta\bar{G}^{ex,\infty}_{S(i)} - \Delta\bar{G}^{ex}_{i(1+2+..+n)} \qquad \text{... (IV.206)}$$

where,

$$N^1_i = \frac{N_i\ k_i}{\sum_{i=1}^{n} N_i k_i} \qquad \text{... (IV.207)}$$

and

$$k_i = \exp\left\{\frac{\Delta\bar{G}^{ex}_{i(1+2+..+n)} - \Delta\bar{G}^{ex,\infty}_{S(i)}}{2zRT}\right\} \quad \ldots \text{(IV.208)}$$

Alcock and Richardson [50] also derived a set of expressions, for a binary solvent, which are similar to the expressions derived above, i.e., eq. (IV.203). But in their analysis they have assumed, without proof, that eqs. (IV.207) and (IV.208) are followed by the system. In the present case these equations follow from the rigorous, yet general, and unified treatment of the main equation which formulates the partition function.

IV.2.2 Approaches Based on Non-Linear Forms of Energy

In section (IV.2.1), it has been assumed that the energy of an atom is a linear function of the number of different types of atoms in its first coordination shell. But such a relationship is just empirical and fails in most of the cases involving metallic solutions. Further, linear relationships lead to certain symmetries in the derived expressions for thermodynamic properties, but these symmetries are found to be completely absent in most metallic systems. In order to explain the behaviour of metallic systems, therefore, Mathieu et al.[77,78] made use of the following empirical quadratic forms for energies, W, and vibrational partition functions, q, of atoms in case of any binary solution containing component A and B.

$$W_A^i = W_A^o + \eta_A . i(2\ z_s - i) \qquad \ldots \text{(IV.209)}$$

$$W_B^k = W_B^o + \eta_B . k(2\ z_s - k) \qquad \ldots \text{(IV.210)}$$

$$\mathrm{lw}\ q_A^i = \mathrm{lw} q_A^o + \xi_A . i.(2\ z_s - i) \qquad \ldots \text{(IV.211)}$$

$$\mathrm{lw}\ q_B^k = \mathrm{lw} q_B^o + \xi_B . k.(2\ z_s - k) \qquad \ldots \text{(IV.212)}$$

where, η_A, η_B, ξ_A and ξ_B are constants

With the help of above expressions the partition function of binary system, A-B, can be evaluated and expressions for the different thermodynamic properties can be derived. Brion et al. [88] extended this treatment to ternary systems also. Though these empirical expressions were able to explain the behaviour of both binary and ternary solutions to a better degree of accuracy, yet they failed in relation to the following aspects.

(i) Expressions for the energy and vibrational partition function, though empirical, are not of a general nature because of their inability to explain the behaviour of regular solutions and also the symmetrical behaviour shown by solutions of some organic substances, and,

(ii) Analytical solution of the expressions developed is very tedius and cannot be reduced to simple forms, thereby prohibiting the application of the proposed model to most of the practical cases.

It has, therefore, become necessary to develop suitable expressions for the energy and free volumes of the different atoms present in the system. In the following treatment, this will be done making use of a few semi-empirical considerations characterising metallic solutions.

In the present case, we are concerned with binary and ternary solvents. Let us, therefore, consider for the derivation of an expression for the energy, W_A^{ijo}, of an atom of component A having i-atoms of component P, j-atoms of component C and no solute atom S around it. Now let us remove an atom of component P from its surroundings and replace it by an A atom. The energy of the central A atom under consideration shall change because of this replacement. This change will be due to (i) the difference in electronegativities of A and P atoms, (ii) change in the potential fields in which the conduction-band electrons will move and (iii) change in Van der Waal's forces. Further, as a result of such a replacement, the free volume of the central A atom will also change. Let us denote by the symbol ΔW_A^{ijo}, the change in energy of 'A' atom as a result of this replacement. Thus one can write the following expression for ΔW_A^{ij}

$$\Delta W_A^{ijo} = W_A^{ijo} - W_A^{(i-1)jo} \qquad \ldots \text{(IV.213a)}$$

Similarly, one can write

$$\Delta W_A^{(i-1)jo} = W_A^{(i-1)jo} - W_A^{(i-2)jo} \qquad \ldots \text{(IV.213b)}$$

$$\Delta W_A^{(i-2)jo} = W_A^{(i-2)jo} - W_A^{(i-3)jo} \qquad \ldots \text{(IV.213c)}$$

$$\begin{array}{cccccc} \ldots & \ldots & \ldots & \ldots & \ldots & \ldots \\ \ldots & \ldots & \ldots & \ldots & \ldots & \ldots \\ \ldots & \ldots & \ldots & \ldots & \ldots & \ldots \end{array}$$

$$\Delta W_A^{2jo} = W_A^{2jo} - W_A^{1jo} \qquad \ldots \text{(IV.213i-1)}$$

$$\Delta W_A^{1jo} = W_A^{1jo} - W_A^{ojo} \qquad \ldots \text{(IV.213 i)}$$

The consecutive effect of replacement of subsequent P atoms by A atoms on energy of central A atom shall be different, as among others, the electron exchange capacity of the central A atom with each replacement shall change to a different degree. But such a difference in change referred to above is expected to be small and hence one can conveniently assume it to be a constant, thus

$$\Delta W_A^{ijo} - \Delta W_A^{(i-1)jo} = \Delta W_A^{(i-1)jo} - \Delta W_A^{(i-2)jo} = \ldots$$

$$\ldots = \Delta W_A^{2jo} - \Delta W_A^{1jo} = \Delta W_A^{1jo} - \Delta W_A^{ojo} = h_{AP} \qquad \ldots \text{(IV.214)}$$

where, h_{AP} is an empirical constant, representing the small change referred to above due to replacement of one P atom from the surrounding of a central A atom.

Substitution of the expressions for ΔW_A^{ijo} $\Delta W_A^{(i-1)jo}$ ... etc. from eqns. (IV.213a) - (IV.213i) in the above expression yields

$$W_A^{ijo} - 2W_A^{(i-1)jo} + W_A^{(i-2)jo} = h_{AP} \qquad \ldots \text{(IV.215.1)}$$

$$W_A^{(i-1)jo} - 2W_A^{(i-2)jo} + W_A^{(i-3)jo} = h_{AP} \qquad \ldots \text{(IV.215.2)}$$

$$\vdots \qquad \vdots \qquad \vdots \qquad \vdots$$

$$W_A^{3\,jo} - 2W_A^{2\,jo} + W_A^{1jo} = h_{AP} \qquad \ldots \text{(IV.215i-2)}$$

$$W_A^{2\,jo} - 2W_A^{1\,jo} + W_A^{o\,jo} = h_{AP} \qquad \ldots \text{(IV.215i-1)}$$

Elimination of $W_A^{(i-1)\,jo}$, $W_A^{(i-2)\,jo}$,...., $W_A^{2\,jo}$ from the above set of expressions yields.

$$W_A^{i\,jo} - iW_A^{1\,jo} + (i-1)\,W_A^{o\,jo} = \frac{i(i-1)}{2}\,h_{AP}. \qquad \text{(IV.216)}$$

As next step, let us consider the replacement of a C atom from the first coordination shell of an A atom by atoms of component A. Following the above mentioned procedure, one can write for this case also the following expressions.

$$W_A^{ijo} - 2W_A^{1(j-1)o} + W_A^{1(j-2)o} = h_{AC} \qquad \ldots \text{(IV.217.1)}$$

$$W_A^{1(j-1)o} - 2W_A^{1(j-2)o} + W_A^{1(j-3)o} = h_{AC} \qquad \ldots \text{(IV.217.2)}$$

$$\vdots \qquad \vdots \qquad \vdots \qquad \vdots \qquad \vdots$$

$$W_A^{120} - 2W_A^{110} + W_A^{100} = h_{AC} \qquad \ldots \text{(IV.217.i-1)}$$

Elimination of $W_A^{1(j-1)o}$, $W_A^{1(j-2)o}$ ...., $W_A^{1\,20}$ from the above expression, yields

$$W_A^{1\,jo} - j.W_A^{1\,10} + (j-1)\,W_A^{100} = \frac{i(j-1)}{2}\,h_{AC}. \text{(IV.218)}$$

Similarly,

$$W_A^{o\,jo} - jW_A^{0\,10} + (j-1)\,W_A^{000} = \frac{i(j-1)}{2}\,h_{AC}\ . \ \text{(IV.218a)}$$

Combination of eqs. (IV.216), (IV.218) and (IV.218a) yields

$$W_A^{ijo} = ij(\Delta W_A^{110} - \Delta W_A^{100} - \Delta W_A^{010}) + i.\ \Delta W_A^{100} + j\ \Delta W_A^{010} + W_A^{000} + \frac{i.(i-1)}{2} h_{AP} + \frac{i.(j-1)}{2} h_{AC} \qquad \text{... (IV.219)}$$

where,

$$\Delta W_A^{100} = W_A^{100} - W_A^{000} \qquad \text{... (IV.220)}$$

other energy terms appearing in these expressions would be defined accordingly as eq. (IV.220). Similarly for atoms of species P and C one can write the expressions

$$W_P^{xyo} = xy(\Delta W_P^{110} - \Delta W_P^{100} - \Delta W_P^{010}) + x\ \Delta W_P^{100} + y\ \Delta W_P^{010} + W_P^{000} + \frac{x.(x-1)}{2} h_{PC} + \frac{y.(y-1)}{2} h_{PA} \qquad \text{... (IV.221)}$$

and,

$$W_C^{rto} = rt(\Delta W_C^{110} - \Delta W_C^{100} - \Delta W_C^{010}) + r.\ \Delta W_C^{100} + t.\ \Delta W_C^{010} + W_C^{000} + \frac{r(r-1)}{2} h_{CA} + \frac{t(t-1)}{2} h_{CP} \qquad \text{... (IV.222)}$$

Following Wagner's [79] approach for the enthalpy of a solute component in a binary solvent Kapoor [81] derived an expression for the enthalpy of a solute in a ternary solvent. On the basis of such a derivation, one can write the following expressions for the energy and free volume of an atom of solute component S having m atoms of component A, W atoms of component P and (z-m-W) atoms of component C around it.

$$\Delta W_S^{mw} = \{m.\ \Delta W_S^{zo} + w.\ \Delta W_S^{oz} + (z-m-w).\ \Delta W_S^{00}\}/z + m.w.h_{S,AP} + w.(z-m-w)h_{S,PC} + m.(z-m-w)h_{S,AC}. \qquad \text{(IV.223)}$$

where, $h_{S,AP}$, $h_{S,AC}$ and $h_{S,PC}$ are constants and are computed from the following expressions

$$\Delta W_S^{(m-1)\rightarrow m,w} - \Delta W_S^{m\rightarrow(m+1),(w-1)} = h_{S,AP} \qquad \ldots \text{(IV.224)}$$

$$\Delta W_S^{(w-1)\rightarrow w,(z-m-w)} - \Delta W_S^{w\rightarrow(w+1),(z-m-w-1)} = h_{S,PC} \qquad \text{(IV.225)}$$

$$\Delta W_S^{m.(z-m-w-1)\rightarrow(z-m-w)} - \Delta W_S^{(m-1),(z-m-w)\rightarrow(z-m-w+1)} = h_{S,CA} \qquad \ldots \text{(IV.226)}$$

where,

$$\Delta W_S^{(m-1)\rightarrow m,w} = W_S^{(m-1),w} - W_S^{m,w} \qquad \ldots \text{(IV.227)}$$

and so on.

Following the above procedure one can write the following expressions;

$$\begin{aligned} W_A^{kdl} = {} & kd(\Delta W_A^{111} - \Delta W_A^{110} - \Delta W_A^{101} - \Delta W_A^{011} + \Delta W_A^{100} + \Delta W_A^{010} + \Delta W_A^{001}) \\ & + kd(\Delta W_A^{110} - \Delta W_A^{100} - \Delta W_A^{010}) \\ & + d.(\Delta W_A^{011} - \Delta W_A^{010} - \Delta W_A^{001}) + k.(\Delta W_A^{101} - \Delta W_A^{100} - \Delta W_A^{001}) \\ & + k.\,\Delta W_A^{100} + d.\,\Delta W_A^{010} \\ & + \Delta W_A^{001} + W_A^{000} + \frac{k(k-1)}{2} h_{AP} + \frac{d(d-1)}{2} h_{AC}. \end{aligned} \qquad \ldots \text{(IV.228)}$$

$$\begin{aligned} W_P^{pql} = {} & p.q.(\Delta W_P^{111} - \Delta W_P^{110} - \Delta W_P^{101} - \Delta W_P^{011} + \Delta W_P^{100} + \Delta W_P^{010} + \Delta W_P^{001}) \\ & + p.q.(\Delta W_P^{110} - \Delta W_P^{100} - \Delta W_P^{010}) \\ & + q.(\Delta W_P^{011} - \Delta W_P^{010} - \Delta W_P^{001}) + p.(\Delta W_P^{101} - \Delta W_P^{100} - \Delta W_P^{001}) \\ & + p.\,\Delta W_P^{100} + q.\,\Delta W_P^{010} + \Delta W_P^{001} \\ & + W_P^{000} + \frac{p.(p-1)}{2}\,.\,h_{PC} + \frac{q.(q-1)}{2}\,.\,h_{PA} \end{aligned} \ldots \text{(IV.229)}$$

$$\begin{aligned} W_C^{uvl} &= u.v.(\Delta W_C^{111} - \Delta W_C^{110} - \Delta W_C^{101} - \Delta W_C^{011} + \Delta W_C^{100} + \Delta W_C^{010} + \Delta W_C^{001}) \\ &+ u.v.(\Delta W_C^{110} - \Delta W_C^{100} - \Delta W_C^{010}) \\ &+ v.(\Delta W_C^{011} - \Delta W_P^{010} - \Delta W_C^{001}) + u.(\Delta W_P^{101} - \Delta W_C^{100} - \Delta W_C^{001}) \\ &+ u.\Delta W_C^{100} + v.\Delta W_C^{010} + \Delta W_C^{001} \\ &+ W_C^{000} + \frac{u.(u-1)}{2}.h_{CA} + \frac{v(v-1)}{2}h._{CP} \qquad \ldots (IV.230) \end{aligned}$$

In the above expressions for energies of different types of atoms of components A, P and C, the energy terms having quadratic forms are assumed to be negligible as their contribution to the total energy of the system is negligibly small.

Similarly for the change in free volumes of solvent components A, P and C and solute component S one can write the following expressions:

$$\begin{aligned} \ln v_A^{ijo} &= i.\Delta\ln v_A^{100} + j\,\Delta\ln v_A^{010} + \ln v_A^{000} + \frac{i.(i-1)}{2}\beta_{AP} \\ &+ \frac{i.(j-1)}{2}.\beta_{AC} \qquad \ldots (IV.231) \end{aligned}$$

$$\begin{aligned} \ln v_A^{kdl} &= k.\Delta\ln v_A^{100} + d.\Delta\ln v_A^{010} + \Delta\ln v_A^{001} + \ln v_A^{000} \\ &+ \frac{k(k-1)}{2}\beta_{AP} + \frac{d(d-1)}{2}.\beta_{AC} \qquad \ldots (IV.232) \end{aligned}$$

$$\begin{aligned} \ln v_P^{xyo} &= x.\Delta\ln v_P^{100} + y.\Delta\ln v_P^{010} + \ln v_P^{000} + \frac{x(x-1)}{2}.\beta_{PC} \\ &+ \frac{y(y-1)}{2}\beta_{PA}. \qquad \ldots (IV.233) \end{aligned}$$

$$\begin{aligned} \ln v_P^{pql} &= p.\Delta\ln v_P^{100} + q.\Delta\ln v_P^{010} + \Delta\ln v_P^{001} + \ln v_P^{000} \\ &+ \frac{p(p-1)}{2}.\beta_{PC} + \frac{q(q-1)}{2}.\beta_{PA} \qquad \ldots (IV.234) \end{aligned}$$

$$\ln v_C^{rto} = r.\Delta \ln v_C^{100} + t.\Delta \ln v_C^{010} + \ln v_C^{000} + \frac{r(r-1)}{2}.\beta_{CA} + \frac{t.(t-1)}{2}.\beta_{CP} \quad \ldots (IV.235)$$

$$\ln v_C^{uvl} = u.\Delta \ln v_C^{100} + v.\Delta \ln v_C^{010} + \Delta \ln v_C^{001} + \frac{u.(u-1)}{2}\beta_{CA} + \frac{v(v-1)}{2}.\beta_{CP} \quad \ldots (IV.236)$$

$$\Delta \ln v_S^{(m-1)\rightarrow m,w} - \Delta \ln v_S^{m\rightarrow (m+1),(w-1)} = \beta_{S,AP} \quad \ldots (IV.237)$$

$$\Delta \ln v_S^{(w-1)\rightarrow w,(z-m-w)} - \Delta \ln v_S^{w\rightarrow (w+1),(z-m-w-1)} = \beta_{S,PC} \quad \ldots (IV.238)$$

$$\Delta \ln v_S^{m,(z-m-w-1)\rightarrow (z-m-w)} - \Delta \ln v_S^{(m-1),(z-m-w)\rightarrow (z-m-w+1)} = \beta_{S,CA} \quad \ldots (IV.239)$$

where,

$$\Delta \ln v_S^{(m-1),(w+1)} = \ln v_S^{(m-1),(w+1)} - \ln v_S^{m,(w+1)} \quad \ldots (IV.240)$$

With the help of above expressions for energy and free volumes, one can now proceed for the evaluation of partition function under different assumptions as done in the last section (Sec.2.1).

IV.2.2.1 Randomly Distributed System

As in the previous case let us consider, first of all, a system in which the atoms of all species are randomly distributed. Under this condition, the number of atoms of different types of atoms shall be given by the eqs.(IV. 97) - (IV.103). Further, the lagrangian multipliers shall be given by the eqs. (IV.104) - (IV.119). With these expressions and also expressions for energy eqs. (IV.219) - (IV.230) and free volumes (IV.231) - (IV.240), eqs (IV. 52) for partition function of the system takes the following form ,

$$\ln\Omega = (n_A+n_P+n_C+n_S)\ln\,(n_A+n_P+n_C+n_S)-n_A\ \ln\ n_A-n_P\ \ln\ n_P$$

$$-\ n_C\ \ln\ n_C\ -\ n_S\ \ln\ n_S$$

$$-\ zn_A[N_P\cdot(\frac{\Delta W_A^{100}-kT\ \Delta\ln\ v_A^{100}}{kT})+N_C\cdot(\frac{\Delta W_A^{010}-kT\ \Delta\ln\ v_A^{010}}{kT})$$

$$+\ N_S\cdot(\frac{\Delta W_A^{001}-kT\ \Delta\ln\ v_A^{001}}{kT})]$$

$$-\ zn_P[N_A\cdot(\frac{\Delta W_P^{010}-kT\ \Delta\ln\ v_P^{010}}{kT})+N_C\cdot(\frac{\Delta W_P^{100}-kT\ \Delta\ln\ v_P^{100}}{kT})$$

$$+\ N_S\cdot(\frac{\Delta W_P^{001}-kT\ \Delta\ln\ v_P^{001}}{kT})]$$

$$-\ zn_C[N_A\cdot(\frac{\Delta W_C^{100}-kT\ \Delta\ln\ v_C^{100}}{kT})+N_P(\frac{\Delta W_C^{010}-kT\ \Delta\ln\ v_C^{010}}{kT})$$

$$+\ N_S\cdot(\frac{\Delta W_C^{001}-kT\ \Delta\ln\ v_C^{001}}{kT})]$$

$$-\ z.(z-1)n_A N_P^2\ (\frac{h_{AP}-kT\ \beta_{AP}}{2kT})-z(z-1)n_A N_C^2\ (\frac{h_{AC}-kT\ \beta_{AC}}{2kT})$$

$$-\ z.(z-1)n_P N_C^2(\frac{h_{PC}-kT\ \beta_{PC}}{2kT})-z.(z-1)n_P N_A^2(\frac{h_{PA}-kT\ \beta_{PA}}{2kT})$$

$$-z.\ (z-1)n_C N_A^2(\frac{h_{CA}-kT\ \beta_{CA}}{2kT})-z.(z-1)n_C N_P^2(\frac{h_{CP}-kT\ \beta_{CP}}{2kT})$$

$$-z.\ (z-1)N_A.N_P.n_S(\frac{h_{S,AP}-kT\ \beta_{S,AP}}{2kT})-z.(z-1).N_A N_C.$$

$$.n_S(\frac{h_{S,CA}-kT\ \beta_{S,CA}}{2kT})$$

$$-z.\ (z-1)N_P N_C\cdot ns\ (\frac{h_{S,PC}-kT\ \beta_{S,PC}}{2kT}) \qquad \ldots\ (IV.241)$$

From the above equation, one can arrive at the following expression for the excess partial molar free energy of the solute component, S, at infinite dilution in the ternary solvent.

$$
\begin{aligned}
\Delta\bar{G}^{ex,\infty}_{S(A+P+C)} &= N_A[\ \Delta\bar{G}^{ex,\infty}_{S(A)} - \Delta\bar{G}^{ex}_{A(A+P+C)}] \\
&\quad + N_P[\ \Delta\bar{G}^{ex,\infty}_{S(P)} - \ \Delta\bar{G}^{ex}_{P(A+P+C)}] + N_C[\ \Delta\bar{G}^{ex,\infty}_{S(C)}\ \ \Delta\bar{G}^{ex}_{C(A+P+C)}] \\
&\quad - z(z-1)N.N_A N_P^2\left(\frac{h_{AP}-kT\ \beta_{AP}}{2}\right) - z(z-1)N.N_A N_C^2\left(\frac{h_{AC}-kT\ \beta_{AC}}{2}\right) \\
&\quad - z(z-1)N.N_P N_C^2\left(\frac{h_{PC}-kT\ \beta_{PC}}{2}\right) - z(z-1)N.N_P N_A^2\left(\frac{h_{PA}-kT\ \beta_{PA}}{2}\right) \\
&\quad - z(z-1)N.N_C N_A^2\left(\frac{h_{CA}-kT\ \beta_{CA}}{2}\right) - z(z-1).N.N_C N_P^2\left(\frac{h_{CP}-kT\ \beta_{CP}}{2}\right) \\
&\quad + z(z-1)N.N_A N_P\left(\frac{h_{S.AP}-kT\ \beta_{S.AP}}{2}\right) + z(z-1)N.N_A.N_C\left(\frac{h_{S.CA}\ kT\ \beta_{S.CA}}{2}\right) \\
&\quad + z(z-1)N.N_P N_C\left(\frac{h_{S.PC}-kT\ \beta_{S.PC}}{2}\right) \qquad \ldots\ (IV.242)
\end{aligned}
$$

It is seen from the above expression, as compared to eq. (IV.127), that it contains few additional terms which can neither be expressed in terms of properties of solute in pure solvents, A, P or C or properties only of the solvents. In order to express the above expression in terms of experimentally determinable parameters one has to take help of the interaction parameters. With the introduction of these parameters, the above equation takes the following alternative form,

$$
\begin{aligned}
\Delta\bar{G}^{ex,\infty}_{S(A+P+C)} = {} & N_A[\Delta\bar{G}^{ex,\infty}_{S(A)} - \Delta\bar{G}^{ex}_{A(A+P+C)}] \\
& + N_P[\Delta\bar{G}^{ex,\infty}_{S(P)} - \Delta\bar{G}^{ex}_{P(A+P+C)}] + N_C[\Delta\bar{G}^{ex,\infty}_{S(C)} - \Delta\bar{G}^{ex}_{C(A+P+C)}] \\
& + \frac{N_A N_P^2}{N_A+N_P}[RT\,\varepsilon^{A}_{S(P)} - \Delta\bar{G}^{ex,\infty}_{S(A)} + \Delta\bar{G}^{ex,\infty}_{S(P)} + \Delta\bar{G}^{ex,\infty}_{A(P)}] \\
& + \frac{N_A^2 N_P}{N_A+N_P}[RT\varepsilon^{P}_{S(A)} - \Delta\bar{G}^{ex,\infty}_{S(P)} + \Delta\bar{G}^{ex,\infty}_{S(A)} + \Delta\bar{G}^{ex,\infty}_{P(A)}] \\
& + \frac{N_P N_C^2}{N_P+N_C}[RT\varepsilon^{P}_{S(C)} - \Delta\bar{G}^{ex,\infty}_{S(P)} + \Delta\bar{G}^{ex,\infty}_{S(C)} + \Delta\bar{G}^{ex,\infty}_{P(C)}] \\
& + \frac{N_P^2 N_C}{N_P+N_C}[RT\varepsilon^{C}_{S(P)} - \Delta\bar{G}^{ex,\infty}_{S(C)} + \Delta\bar{G}^{ex,\infty}_{S(P)} + \Delta\bar{G}^{ex,\infty}_{C(P)}] \\
& + \frac{N_C N_A^2}{N_C+N_A}[RT\,\varepsilon^{C}_{S(A)} - \Delta\bar{G}^{ex,\infty}_{S(C)} + \Delta\bar{G}^{ex,\infty}_{S(A)} + \Delta\bar{G}^{ex,\infty}_{C(A)}] \\
& + \frac{N_C^2 N_A}{N_C+N_A}[RT\varepsilon^{A}_{S(C)} - \Delta\bar{G}^{ex,\infty}_{S(A)} + \Delta\bar{G}^{ex,\infty}_{S(C)} + \Delta\bar{G}^{ex,\infty}_{A(C)}] \\
& + \frac{N_A N_P N_C}{N_A+N_P}[N_A \cdot \Delta\bar{G}^{ex,\infty}_{P(A)} + N_P \cdot \Delta\bar{G}^{ex,\infty}_{A(P)}] \\
& + \frac{N_A N_P N_C}{N_P+N_C}[N_P \cdot \Delta\bar{G}^{ex,\infty}_{C(P)} + N_C \cdot \Delta\bar{G}^{ex,\infty}_{P(C)}] \\
& + \frac{N_A N_P N_C}{N_A+N_C}[N_C\,\Delta\bar{G}^{ex,\infty}_{A(C)} + N_A \cdot \Delta\bar{G}^{ex,\infty}_{C(A)}] \qquad \ldots \text{(IV.243)}
\end{aligned}
$$

where, the different terms used in this expression have their usual meaning.

From the above expression one can write for the excess partial molar free energy at infinite dilution of the solute component, S, in a binary substitutional solvent comprising of components A and B, the expression,

$$\Delta\bar{G}^{ex,\infty}_{S(A+B)} = N_A[\Delta\bar{G}^{ex,\infty}_{S(A)} - \Delta\bar{G}^{ex}_{A(A+B)}] + N_B[\Delta\bar{G}^{ex,\infty}_{S(B)} - \Delta\bar{G}^{ex}_{B(A+B)}]$$

$$+ N_A N_B^2[RT\varepsilon^{A}_{S(B)} - \Delta\bar{G}^{ex,\infty}_{S(A)} + \Delta\bar{G}^{ex,\infty}_{S(B)} + \Delta\bar{G}^{ex,\infty}_{A(B)}]$$

$$+ N_A^2 N_B[RT\varepsilon^{B}_{S(A)} - \Delta\bar{G}^{ex,\infty}_{S(B)} + \Delta\bar{G}^{ex,\infty}_{S(A)} + \Delta\bar{G}^{ex,\infty}_{B(A)}] \quad \ldots \text{(IV.244)}$$

The above expression was first derived by Kumar et al.[89].

For such solutions, in which the solvent components have linear forms of energy and solute component has non-linear forms of energy the expression given by eq. (IV.243) takes the following form,

$$\Delta\bar{G}^{ex,\infty}_{S(A+P+C)} = N_A[\Delta\bar{G}^{ex,\infty}_{S(A)} - \Delta\bar{G}^{ex}_{A(A+P+C)}]$$

$$+ N_P[\Delta\bar{G}^{ex,\infty}_{S(P)} - \Delta\bar{G}^{ex,}_{P(A+P+C)}] + N_C[\Delta\bar{G}^{ex,\infty}_{S(C)} - \Delta\bar{G}^{ex,}_{C(A+P+C)}]$$

$$+ \frac{N_A N_P^2}{N_A+N_P}[RT\varepsilon^{A}_{S(P)} - \Delta\bar{G}^{ex,\infty}_{S(A)} + \Delta\bar{G}^{ex,\infty}_{S(P)} + \Delta\bar{G}^{ex,\infty}_{A(P)}]$$

$$+ \frac{N_A^2 N_P}{N_A+N_P}[RT\varepsilon^{P}_{S(A)} - \Delta\bar{G}^{ex,\infty}_{S(P)} + \Delta\bar{G}^{ex,\infty}_{S(A)} + \Delta\bar{G}^{ex,\infty}_{P(A)}]$$

$$+ \frac{N_P N_C^2}{N_P+N_C}[RT\varepsilon^{P}_{S(C)} - \Delta\bar{G}^{ex,\infty}_{S(P)} + \Delta\bar{G}^{ex,\infty}_{S(C)} + \Delta\bar{G}^{ex,\infty}_{P(C)}]$$

$$+ \frac{N_P^2 N_C}{N_P+N_C}[RT\varepsilon^{C}_{S(P)} - \Delta\bar{G}^{ex,\infty}_{S(C)} + \Delta\bar{G}^{ex,\infty}_{S(P)} + \Delta\bar{G}^{ex,\infty}_{C(P)}]$$

$$+ \frac{N_C N_A^2}{N_C+N_A} [RT\varepsilon^{C}_{S(A)} - \Delta \bar{G}^{ex,\infty}_{S(C)} + \Delta \bar{G}^{ex,\infty}_{S(A)} + \Delta \bar{G}^{ex,\infty}_{C(A)}]$$

$$+ \frac{N_C^2 N_A}{N_C+N_A} [RT\varepsilon^{A}_{S(C)} - \Delta \bar{G}^{ex,\infty}_{S(A)} + \Delta \bar{G}^{ex,\infty}_{S(C)} + \Delta \bar{G}^{ex,\infty}_{A(C)}] \quad \ldots \text{(IV.245)}$$

It is clear from the basic assumptions made for this derivation that this expression shall be applicable to the dilute solutions of such solute components, in a weakly interacting multicomponent solvent, which have approximately similar values of excess partial molar free energy in each of the pure components of the solvents.

IV. 2.2.2 Randomly Distributed Solvent with Preferentially Distributed Solute

For this case using eqs. (IV. 130) - (IV. 136), the expression for the partition function (IV. 52), takes the following alternate form

$$\ln\Omega = (n_A+n_P+n_C+n_S) \ln (n_A+n_P+n_C+n_S) + z\, n_A \ln n_A$$

$$- z\, n_A \ln (n_A+n_P+n_C+n_S) + zn_P \ln n_P - zn_P \ln(n_A+n_P+n_C+n_S)$$

$$+ z\, n_C \ln n_C - zn_C \ln (n_A+n_P+n_C+n_S) - zn_S \ln (n_A+n_P+n_C+n_S)$$

$$- n_A^o \ln n_A^o + zn_A \ln\left(\frac{n_A+n_P+n_C-n_S}{n_A-n_S N_A^1}\right) - 2n_A^1 \ln N_A^1 - n_A^1 \ln\left(\frac{n_A+n_P+n_C-n_S}{n_A-n_S N_A^1}\right)$$

$$- n_P^o \ln n_P^o + zn_P \ln\left(\frac{n_A+n_P+n_C-n_S}{n_P-n_S N_P^1}\right) - 2n_P^1 \ln N_P^1 - n_P^1 \ln\left(\frac{n_A+n_P+n_C-n_S}{n_P-n_S N_P^1}\right)$$

$$- n_C^o \ln n_C^o + zn_C \ln(\frac{n_A+n_P+n_C-n_S}{n_C-n_SN_C^1}) - 2n_C^1 \ln N_C^1 - n_C^1 \ln(\frac{n_A+n_P+n_C-n_S}{n_C-n_SN_C^1})$$

$$- n_S \ln n_S - n_A^1(\frac{\Delta W_A^{001}-kT\ \Delta \ln v_A^{001}}{kT}) - n_P^1(\frac{\Delta W_P^{001}-kT\ \Delta \ln v_P^{001}}{kT})$$

$$- n_C^1(\frac{\Delta W_C^{001}-kT\ \Delta \ln v_C^{001}}{kT}) - n_A^1(\frac{\Delta W_S^{zo}-kT\ \Delta \ln v_S^{zo}}{zkT}) - n_P^1(\frac{\Delta W_S^{oz}-kT\ \Delta \ln v_S^{oz}}{zkT})$$

$$- n_C^1(\frac{\Delta W_S^{00}-kT\ \Delta \ln v_S^{00}}{zkT}) - zn_A(\frac{n_P-N_P^1 \cdot n_S}{n_A+n_P+n_C-n_S}) . (\frac{\Delta W_A^{100}-kT\ \Delta \ln v_A^{100}}{kT})$$

$$-zn_A(\frac{n_C-N_C^1n_S}{n_A+n_P+n_C-n_S})(\frac{\Delta W_A^{010}-kT\ \Delta \ln v_A^{010}}{kT}) - zn_P(\frac{n_C-N_C^1n_S}{n_A+n_P+n_C-n_S}) .$$

$$. (\frac{\Delta W_P^{100}-kT\ \Delta \ln v_P^{100}}{kT}) - zn_P(\frac{n_A-N_A^1n_S}{n_A+n_P+n_C-n_S})\ (\frac{\Delta W_P^{010}-kT\ \Delta \ln v_P^{010}}{kT})$$

$$- zn_C(\frac{n_A-N_A^1n_S}{n_A+n_P+n_C-n_S})(\frac{\Delta W_C^{100}-kT\ \Delta \ln v_C^{100}}{kT}) - zn_C(\frac{n_P-N_P^1n_S}{n_A+n_P+n_C-n_S}) .$$

$$. (\frac{\Delta W_C^{010}-kT\ \Delta \ln v_C^{010}}{kT}) - z(z-1)n_A(\frac{n_P-N_P^1n_S}{n_A+n_P+n_C-n_S})^2(\frac{h_{AP}-kT\ \beta_{AP}}{2kT})$$

$$- z(z-1)n_A(\frac{n_C-N_C^1n_S}{n_A+n_P+n_C-n_S})^2 . (\frac{h_{AC}-kT\ \beta_{AC}}{2kT}) - z(z-1)n_P(\frac{n_C-N_C^1n_S}{n_A+n_P+n_C-n_S})^2$$

$$. (\frac{h_{PC}-kT\ \beta_{PC}}{2kT}) - z(z-1)n_P(\frac{n_A-N_A^1n_S}{n_A+n_P+n_C-n_S})^2 . (\frac{h_{PA}-kT\ \beta_{PA}}{2kT})$$

$$- z(z-1)n_C(\frac{n_A-N_A^1n_S}{n_A+n_P+n_C-n_S})^2 . (\frac{h_{CA}-kT\ \beta_{CA}}{2kT}) - z(z-1).n_C.(\frac{n_P-N_P^1n_S}{n_A+n_P+n_C-n_S})^2$$

$$. (\frac{h_{CP}-kT\ \beta C_P}{2kT})$$

$$+\ n_A^1\left(\frac{n_P-N_P^1n_S}{n_A+n_P+n_C-n_S}\right)\cdot\left(\frac{\Delta W_A^{100}-kT\ \Delta\ln\ v_A^{100}}{kT}\right)+n_A^1\left(\frac{n_C-N_C^1n_S}{n_A+n_P+n_C-n_S}\right)$$

$$\cdot\left(\frac{\Delta W_A^{010}-kT\ \Delta\ln\ v_A^{010}}{kT}\right)$$

$$+n_P^1\cdot\left(\frac{n_C-N_C^1\cdot n_S}{n_A+n_P+n_C-n_S}\right)\cdot\left(\frac{\Delta W_P^{100}-kT\ \Delta\ln\ v_P^{100}}{kT}\right)+n_P^1\cdot\left(\frac{n_A-N_A^1n_S}{n_A+n_P+n_C-n_S}\right)$$

$$\cdot\left(\frac{\Delta W_P^{010}-kT\ \Delta\ln\ v_P^{010}}{kT}\right)$$

$$+n_C^1\cdot\left(\frac{n_A-N_A^1n_S}{n_A+n_P+n_C-n_S}\right)\cdot\left(\frac{\Delta W_C^{100}-kT\ \Delta\ln\ v_C^{100}}{kT}\right)+n_C^1\cdot\left(\frac{n_P-N_P^1n_S}{n_A+n_P+n_C-n_S}\right)$$

$$\cdot\left(\frac{\Delta W_C^{010}-kT\ \Delta\ln\ v_C^{010}}{kT}\right)$$

$$+(z-1)\cdot n_A^1\cdot\left(\frac{n_P-N_P^1n_S}{n_A+n_P+n_C-n_S}\right)^2\cdot\left(\frac{h_{AP}-kT\ \beta_{AP}}{kT}\right)+(z-1)\cdot n_A^1\cdot\left(\frac{n_C-N_C^1\cdot n_S}{n_A+n_P+n_C-n_S}\right)^2$$

$$\cdot\left(\frac{h_{AC}-kT\ \beta_{AC}}{kT}\right)$$

$$+(z-1)\cdot n_P^1\cdot\left(\frac{n_C-N_C^1n_S}{n_A+n_P+n_C-n_S}\right)^2\cdot\left(\frac{h_{PC}-kT\ \beta_{PC}}{kT}\right)+(z-1)\cdot n_P^1\cdot\left(\frac{n_A-N_A^1\cdot n_S}{n_A+n_P+n_C-n_S}\right)^2$$

$$\cdot\left(\frac{h_{PA}-kT\ \beta_{PA}}{kT}\right)$$

$$+(z-1)n_C^1\cdot\left(\frac{n_A-N_A^1n_S}{n_A+n_P+n_C-n_S}\right)^2\cdot\left(\frac{h_{CA}-kT\ \beta_{CA}}{k\ T}\right)+(z-1)\cdot n_C^1\cdot\left(\frac{n_P-N_P^1n_S}{n_A+n_P+n_C-n_S}\right)^2$$

$$\cdot\left(\frac{h_{CP}-kT\ \beta_{CP}}{kT.}\right)$$

$$-z(z-1)N_A^1N_P^1\cdot n_S\cdot\left(\frac{h_{S,AP}-kT\ \beta_{S,AP}}{2kT}\right)-z(z-1)N_P^1\cdot N_C^1\cdot n_S\cdot\left(\frac{h_{S,PC}-kT\ \beta_{S,PC}}{2kT}\right)$$

$$-z(z-1)N_C^1\cdot N_A^1\cdot n_S\ \left(\frac{h_{S,CA}-kT\ \beta_{S,CA}}{2kT}\right) \qquad \ldots\ (IV.246)$$

From the above expression, one can arrive at the following relationships for the partial molar free energy of component, S, at infinite dilution in a solvent containing components A. P and C.

$$\Delta\bar{G}^{ex,\infty}_{S(A+P+C)} = 2\ zRT.[N^1_A \ln \frac{N^1_A}{N_A} + N^1_P \ln \frac{N^1_P}{N_P} + N^1_C \ln \frac{N^1_C}{N_C}]$$

$$+ N^1_A.[\Delta\bar{G}^{ex,\infty}_{S(A)} - \Delta\bar{G}^{ex}_{A(A+P+C)}] + N^1_P.[\Delta\bar{G}^{ex,\infty}_{S(P)} - \Delta\bar{G}^{ex}_{P(A+P+C)}]$$

$$+ N^1_C.[\Delta\bar{G}^{ex,\infty}_{S(C)} - \Delta\bar{G}^{ex}_{C(A+P+C)}]$$

$$-z(z-1)N.N^1_A.N^2_P.(\frac{h_{AP}-kT\ \beta_{AP}}{2}) - z(z-1)N.N^1_A.N^2_C.(\frac{h_{AC}-kT\ \beta_{AC}}{2})$$

$$-z(z-1)N.N^1_P.N^2_C.(\frac{h_{PC}-kT\ \beta_{PC}}{2}) - z(z-1)N.N^1_P.N^2_A.(\frac{h_{PA}-kT\ \beta_{PA}}{2})$$

$$-z(z-1)N.N^1_C.N^2_A.(\frac{h_{CA}-kT\ \beta_{CA}}{2}) - z(z-1)N.N^1_C.N^2_P.(\frac{h_{CP}-kT\ \beta_{CP}}{2})$$

$$-z(z-1).N.N^1_A.N^1_P.(\frac{h_{S,AP}-kT\ \beta_{S,AP}}{2}) + z(z-1).N.N^1_P.N^1_C(\frac{h_{S,PC}-kT\beta_{S,PC}}{2})$$

$$+z(z-1).N.N^1_C N^1_A(\frac{h_{S,CA}-kT\ \beta_{S,CA}}{2}) \qquad \text{... (IV.247)}$$

where N^1_A, N^1_P and N^1_C are expressed by the eqs. (IV.161) - (IV.163).

With the help of expressions derived for the partial molar properties of components from eq. (IV.246), one can arrive at the following relationship for the partial molar free energy of component S at infinite dilution in terms of the experimentally determinable parameters.

$$\Delta\bar{G}^{ex,\infty}_{S(A+P+C)} = 2z\,RT[N_A^{1'} \ln \frac{N_A^1}{N_A} + N_P^1 \ln \frac{N_P^1}{N_P} + N_C^1 \ln \frac{N_C^1}{N_C}]$$

$$+ N_A^1 [\Delta\bar{G}^{ex,\infty}_{S(A)} - \Delta\bar{G}^{ex}_{A(A+P+C)}] + N_P^1[\Delta\bar{G}^{ex,\infty}_{S(P)} - \Delta\bar{G}^{ex}_{P(A+P+C)}]$$

$$+ N_C^1[\Delta\bar{G}^{ex,\infty}_{S(C)} - \Delta\bar{G}^{ex}_{C(A+P+C)}]$$

$$+ \frac{N_A^1 \cdot N_P^{1^2}}{N_A^1+N_P^1} \cdot [\frac{k_P}{k_A} \cdot RT\ \varepsilon^A_{S(P)} - \Delta\bar{G}^{ex,\infty}_{S(A)} + \Delta\bar{G}^{ex,\infty}_{S(P)} + \Delta\bar{G}^{ex,\infty}_{A(P)} - 2z\,RT.$$

$$(\ln \frac{k_A}{k_P} + \frac{k_P-k_A}{k_A})]$$

$$+ \frac{N_A^{1^2} \cdot N_P^1}{N_A^1+N_P^1} \cdot [\frac{k_A}{k_P} \cdot RT\ \varepsilon^P_{S(A)} - \Delta\bar{G}^{ex,\infty}_{S(P)} + \Delta\bar{G}^{ex,\infty}_{S(A)} + \Delta\bar{G}^{ex,\infty}_{P(A)} - 2\,zRT.$$

$$(\ln \frac{k_P}{k_A} + \frac{k_A-k_P}{k_P})]$$

$$+ \frac{N_P^1 \cdot N_C^{1^2}}{N_P^1+N_C^1} \cdot [\frac{k_C}{k_P} \cdot RT\ \varepsilon^P_{S(C)} - \Delta\bar{G}^{ex,\infty}_{S(P)} + \Delta\bar{G}^{ex,\infty}_{S(C)} + \Delta\bar{G}^{ex,\infty}_{P(C)} - 2z\,RT.$$

$$(\ln \frac{k_P}{k_C} + \frac{k_C-k_P}{k_P})]$$

$$+ \frac{N_P^{1^2} \cdot N_C^1}{N_P^1+N_C^1} \cdot [\frac{k_P}{k_C} \cdot RT\ \varepsilon^C_{S(P)} - \Delta\bar{G}^{ex,\infty}_{S(C)} + \Delta\bar{G}^{ex,\infty}_{S(P)} + \Delta\bar{G}^{ex,\infty}_{C(P)} - 2z\,RT.$$

$$(\ln \frac{k_C}{k_P} + \frac{k_P-k_C}{k_C})]$$

$$+ \frac{N_C^1 \cdot N_A^{1^2}}{N_C^1+N_A^1} \cdot [\frac{k_A}{k_C} \cdot RT\ \varepsilon^C_{S(A)} - \Delta\bar{G}^{ex,\infty}_{S(C)} + \Delta\bar{G}^{ex,\infty}_{S(A)} + \Delta\bar{G}^{ex,\infty}_{C(A)}$$

$$-2\,zRT(\ln \frac{k_C}{k_A} + \frac{k_A-k_C}{k_C})] + \frac{N_C^{1^2} \cdot N_A^1}{N_C^1+N_A^1} \cdot [\frac{k_C}{k_A} \cdot RT\ \varepsilon^A_{S(C)} - \Delta\bar{G}^{ex,\infty}_{S(A)}$$

$$+ \Delta\bar{G}^{ex,\infty}_{S(C)} + \Delta\bar{G}^{ex,\infty}_{A(C)} - 2z\,RT(\ln \frac{k_A}{k_C} + \frac{k_C-k_A}{k_A})]$$

$$- (N_A^1 N_P^2 - \frac{N_A^1 N_P^{1^2}}{N_A^1+N_P^1}) \Delta\bar{G}^{ex,\infty}_{A(P)} - (N_P^1\ N_A^2 - \frac{N_A^{1^2} N_P^1}{N_A^1+N_P^1}). \Delta\bar{G}^{ex,\infty}_{P(A)}$$

$$- (N_P^1\ N_C^2 - \frac{N_P^1 N_C^{1^2}}{N_P^1+N_C^1}). \Delta\bar{G}^{ex,\infty}_{P(C)} - (N_C^1\ N_P^2 - \frac{N_C^1\ N_P^{1^2}}{N_P^1+N_C^1}). \Delta\bar{G}^{ex,\infty}_{C(P)}$$

$$- (N_A^1\ N_C^2 - \frac{N_A^1\ N_C^{1^2}}{N_A^1+N_C^1}). \Delta\bar{G}^{ex,\infty}_{A(C)} - (N_C^1 N_A^2 - \frac{N_C^1\ N_A^{1^2}}{N_C^1+N_A^1}). \Delta\bar{G}^{ex,\infty}_{C(A)} .$$

... (IV.248)

From this expression, eq. (IV.248), one can also arrive at the following expression for a system in which the solvent is randomly distributed and the equations for the energy terms for the solvent atoms are linear in form, i.e., the values of the parameters h_{AS}, β_{AS}, h_{AP}, β_{AP}, h_{PA}, β_{PA}, h_{PS}, β_{PS}, h_{SA}, β_{SA}, h_{SP} and β_{SP} in eq. (IV.248) are equal to zero.

$$\Delta\bar{G}^{ex,\infty}_{S(A+P+C)} = 2\ zRT\ [N_A^1\ \ln \frac{N_A^1}{N_A} + N_P^1\ \ln \frac{N_P^1}{N_P} + N_C^1\ \ln \frac{N_C^1}{N_C}]$$

$$+ N_A^1\ [\Delta\bar{G}^{ex,\infty}_{S(A)} - \Delta\bar{G}^{ex,}_{A(A+P+C)}]$$

$$+ N_P^1[\Delta\bar{G}^{ex,\infty}_{S(P)} - \Delta\bar{G}^{ex}_{P(A+P+C)}] + N_C^1[\Delta\bar{G}^{ex,\infty}_{S(C)} - \Delta\bar{G}^{ex}_{C(A+P+C)}]$$

$$+ \frac{N_A^1 . N_P^{1^2}}{N_A^1+N_P^1} . [\frac{k_P}{k_A} .RT\ \varepsilon^A_{S(P)} - \Delta\bar{G}^{ex,\infty}_{S(A)} + \Delta\bar{G}^{ex,\infty}_{S(P)} + \Delta\bar{G}^{ex,\infty}_{A(P)} - 2z\ RT$$

$$(\ln \frac{k_A}{k_P} + \frac{k_P-k_A}{k_A})]$$

$$+ \frac{N_A^{1^2} . N_P^1}{N_A^1+N_P^1} . [\frac{k_A}{k_P} .RT\ \varepsilon^P_{S(A)} - \Delta\bar{G}^{ex,\infty}_{S(P)} + \Delta\bar{G}^{ex,\infty}_{S(A)} + \Delta\bar{G}^{ex,\infty}_{P(A)} - 2z\ RT$$

$$(\ln \frac{k_P}{k_A} + \frac{k_A-k_P}{k_P})]$$

$$+\frac{N_P^1 N_C^{1^2}}{N_P^1+N_C^1}\cdot[\frac{k_C}{k_P}.RT\ \varepsilon^P_{S(C)}-\Delta\bar{G}^{ex,\infty}_{S(P)}+\Delta\bar{G}^{ex,\infty}_{S(C)}+\Delta\bar{G}^{ex,\infty}_{P(C)}-2\ z\ RT\cdot$$

$$[\ln\frac{k_P}{k_C}+\frac{k_C-k_P}{k_P})]$$

$$+\frac{N_P^{1^2}.N_C^1}{N_P^1+N_C^1}\cdot[\frac{k_P}{k_C}\cdot RT\ \varepsilon^C_{S(P)}-\Delta\bar{G}^{ex,\infty}_{S(C)}+\Delta\bar{G}^{-ex,\infty}_{S(P)}+\Delta\bar{G}^{ex,\infty}_{C(P)}-2z\ RT.$$

$$(\ln\frac{k_C}{k_P}+\frac{k_P-k_C}{k_C})]$$

$$+\frac{N_C^1\ N_A^{1^2}}{N_C^1+N_A^1}\cdot[\frac{k_A}{k_C}.RT\ \varepsilon^C_{S(A)}-\Delta\bar{G}^{ex,\infty}_{S(C)}+\Delta\bar{G}^{ex,\infty}_{S(A)}+\Delta\bar{G}^{ex,\infty}_{C(A)}-2z\ RT\cdot$$

$$(\ln\frac{k_C}{k_A}+\frac{k_A-k_C}{k_C})]$$

$$+\frac{N_C^{1^2}\ N_A^1}{N_C^1+N_A^1}\cdot[\frac{k_C}{k_A}.RT\ \varepsilon^A_{S(C)}-\Delta\bar{G}^{ex,\infty}_{S(A)}+\Delta\bar{G}^{ex,\infty}_{S(C)}+\Delta\bar{G}^{ex,\infty}_{A(C)}-2z\ RT\cdot$$

$$(\ln\frac{k_A}{k_C}+\frac{k_C-k_A}{k_A})] \qquad \ldots\ (IV.249)$$

From eq. (IV.249), one can arrive at the following expression for the excess partial molar free energy of solute component, S, at infinite dilution in a binary solvent containing components A and B only.

$$\bar{G}^{ex,\infty}_{S(A+B)}=2z\ RT[N_A^1\ \ln\frac{N_A^1}{N_A}+N_B^1\ \ln\frac{N_B^1}{N_B}]$$

$$+N_A^1\ [\Delta\bar{G}^{ex,\infty}_{S(A)}-\Delta\bar{G}^{ex}_{A(A+B)}]+N_B^1\ [\Delta\bar{G}^{ex,\infty}_{S(B)}-\Delta\bar{G}^{ex}_{B(A+B)}]$$

$$+\frac{N_A^1.N_B^{1^2}}{N_A^1+N_B^1}\cdot[\frac{k_B}{k_A}.RT\ \varepsilon^A_{S(B)}-\Delta\bar{G}^{ex,\infty}_{S(A)}+\Delta\bar{G}^{ex,\infty}_{S(B)}+\Delta\bar{G}^{ex,\infty}_{A(B)}-2z\ RT\ \cdot$$

$$(\ln\frac{k_A}{k_B}+\frac{k_B-k_A}{k_A})]$$

$$+\frac{{N_A^1}^2 \cdot N_B^1}{N_A^1+N_B^1}\left[\frac{k_A}{k_B} \cdot RT\varepsilon^B_{S(A)} - \Delta\bar{G}^{ex,\infty}_{S(B)} + \Delta\bar{G}^{ex,\infty}_{S(A)} - \Delta\bar{G}^{ex,\infty}_{B(A)} - 2z\ RT \left(\ln\frac{k_B}{k_A} + \frac{k_A-k_B}{k_B}\right)\right] \qquad \ldots (IV.250)$$

where, the parameters N_A^1, N_B^1 , k_A and k_B are defined by the expressions (IV.168) - (IV.171).

Generallizing eq. (IV.248) for a n-component solvent one can write the following expression for properties of the solute, S, at infinite dilution,

$$\Delta\bar{G}^{ex,\infty}_{S(1+2+\ldots+n)} = \sum_{i=1}^{n} 2z\ RT\ [N_i^1 \ln\frac{N_i^1}{N_i}]$$

$$+\sum_{i=1}^{n} [N_i\ (\Delta\bar{G}^{ex,\infty}_{S(i)} - \Delta\bar{G}^{ex}_{i(1+2+\ldots n)})]$$

$$+\sum_{\substack{i=1\\(i\neq j)}}^{n}\sum_{j=1}^{n} \frac{N_i^1{N_j^1}^2}{n_i^1+N_j^1}\left[\frac{k_j}{k_i} RT\ \varepsilon^i_{S(j)} - \Delta\bar{G}^{ex,\infty}_{S(i)} + \Delta\bar{G}^{ex,\infty}_{S(j)} + \Delta\bar{G}^{ex,\infty}_{i(j)} - 2z\ RT\ \left(\ln\frac{k_i}{k_j} + \frac{k_j-k_i}{k_i}\right)\right]$$

$$-\sum_{\substack{i=1\\(i\neq j)}}^{n}\sum_{j=1}^{n} \left(N_i^1\ N_j^2 - \frac{N_i^1\ {N_j^1}^2}{N_i^1+N_j^1}\right).\ \Delta\bar{G}^{ex,\infty}_{i(j)} \qquad \ldots (IV.251)$$

Similarly for a solution containing n-components solvent having linear forms of energy for their atomic species, one can write the following generalized expression for the partial molar free energy of solute component, S, at fnfinite dilution,

$$\begin{aligned}\Delta\bar{G}^{ex,\infty}_{S(1+2+3....+n)} = {} & \sum_{i=1}^{n} 2z\,RT[N_i^1 \ln \frac{N_i^1}{N_i}] \\ & +\sum_{i=1}^{n} [N_i(\Delta\bar{G}^{ex,\infty}_{S(i)} - \Delta\bar{G}^{ex}_{i(1+2+....+n)})] \\ & + \sum_{i=1}^{n} \sum_{\substack{j=1 \\ (i \neq j)}}^{n} \frac{N_i^1 N_j^{1^2}}{N_i+N_j} .[\frac{K_j}{K_i} .RT\, \varepsilon^i_{S(j)} - \Delta\bar{G}^{ex,\infty}_{S(i)} + \Delta\bar{G}^{ex,\infty}_{S(j)} + \Delta\bar{G}^{ex,\infty}_{i(j)} \\ & \qquad -2z\,RT(\ln \frac{K_i}{K_j} + \frac{K_j-K_i}{K_j})] \qquad \text{... (IV.252)}\end{aligned}$$

From the above expression, one can deduce for a binary solvent A - B, an expression for excess partial molar free energy of solute component, S, in the following form.

$$\begin{aligned}\Delta\bar{G}^{ex,\infty}_{S(A+B)} = {} & 2z\,RT[N_A^1 \ln \frac{N_A^1}{N_A} + N_B^1 \ln \frac{N_B^1}{N_B}] \\ & + N_A^1[\Delta\bar{G}^{ex,\infty}_{S(A)} - \Delta\bar{G}^{ex}_{A(A+B)}] + N_B^1[\Delta\bar{G}^{ex,\infty}_{S(B)} - \Delta\bar{G}^{ex}_{B(A+B)}] \\ & + N_A^1.N_B^{1^2}.[\frac{K_B}{K_A} RT\, \varepsilon^A_{S(B)} - \Delta\bar{G}^{ex,\infty}_{S(A)} + \Delta\bar{G}^{ex,\infty}_{S(B)} + \Delta\bar{G}^{ex,\infty}_{A(B)} \\ & \qquad -2z\,RT(\ln \frac{K_A}{K_B} + \frac{K_B-K_A}{K_A})] \\ & + N_A^{1^2}.N_B^1.[\frac{K_A}{K_B} .RT\, \varepsilon^B_{S(A)} - \Delta\bar{G}^{ex,\infty}_{S(B)} + \Delta\bar{G}^{ex,\infty}_{S(A)} + \Delta\bar{G}^{ex,\infty}_{B(A)} \\ & \qquad -2z\,RT(\ln \frac{K_B}{K_A} + \frac{K_A-K_B}{K_B})] \qquad \text{... (IV.253)}\end{aligned}$$

IV.2.2.3 All Components Distributed Preferentially

In this case, using eqs. (IV.175) - (IV. 180) , one can write the expression for partition function in the following form :

$$\ln\Omega = (n_A+n_P+n_C+n_S)\ln(n_A+n_P+n_C+n_S) + z\, n_A \ln n_A$$

$$- z\, n_A \ln(n_A+n_P+n_C+n_S) + z\, n_P \ln n_P - z n_P \ln(n_A+n_P+n_C+n_S)$$

$$+ z\, n_C \ln n_C - z n_C \ln(n_A+n_P+n_C+n_S) + z n_S \ln n_S$$

$$- z\, n_S \ln(n_A+n_P+n_C+n_S) - n_A^o \ln \alpha_A - n_A^1 \ln \alpha_A - n_P^o \ln \alpha_P$$

$$- n_P^1 \ln \alpha_P - n_C^o \ln \alpha_C - n_C^1 \ln \alpha_C - n_S \ln \alpha_S .$$

$$- \sum_{i=o} i(i-1) n_A^{ijo} \left(\frac{h_{AP} - kT\ \beta_{AP}}{2\ kT}\right) - \sum_{j=o} j(j-1) . n_A^{ijo} \left(\frac{h_{AC} - kT\ \beta_{AC}}{2\ kT}\right)$$

$$- \sum_{k=o} k(k-1) n_A^{kdl} \frac{(h_{AP} - kT\ \beta_{AP})}{2\ kT} - \sum_{d=o} d(d-1) . n_A^{kdl} \left(\frac{h_{AC} - kT\ \beta_{AC}}{2\ kT}\right)$$

$$- \sum_{x=o} x(x-1) n_P^{xyo} \left(\frac{h_{PC} - kT\ \beta_{PC}}{2kT}\right) - \sum_{y=o} y(y-1) . n_P^{xyo} \left(\frac{h_{PA} - kT\ \beta_{PA}}{2kT}\right)$$

$$- \sum_{p=o} p.(p-1) n_P^{pq1} . \left(\frac{h_{PC} - kT\ \beta_{PC}}{2kT}\right) - \sum_{q=o} q(q-1) . n_P^{pq1} . \left(\frac{h_{PA} - kT\ \beta_{PA}}{2kT}\right)$$

$$- \sum_{r=o} r(r-1) n_C^{rto} \left(\frac{h_{CA} - kT\ \beta_{CA}}{2kT}\right) - \sum_{t=o} t(t-1) n_C^{rto} . \left(\frac{h_{CP} - kT\ \beta_{CP}}{2kT}\right)$$

$$- \sum_{u=o} u.(u-1) n_C^{uvl} \left(\frac{h_{CA} - kT\ \beta_{CA}}{2kT}\right) - \sum_{v=o} v.(v-1) n_C^{uvl} . \left(\frac{h_{CP} - kT\ \beta_{CP}}{2kT}\right)$$

$$- \sum_{m=o} \sum_{w=o} m.w.\ n_S^{mw} \left(\frac{h_{S.AP} - kT\ \beta_{S.AP}}{2kT}\right) - \sum_{m=o} \sum_{w=o} w(z-m-w)\ n_S^{mw} .$$

$$\left(\frac{h_{S.PC} - kT\ \beta_{S.PC}}{2kT}\right) - \sum_{m=o} \sum_{w=o} m(z-m-w) \left(\frac{h_{S.CA} - kT\ \beta_{S.CA}}{2kT.}\right) . n_S^{m\omega}$$

...(IV.254)

For simplification, the parameters $h_{\Lambda P}$, $\beta_{\Lambda P}$, etc. for the solvent components are assumed to be negligible, and the eq. (IV.254), then takes the following form with the help of eqs. (IV. 181) - (IV.183b).

$$\ln \Omega = (n_\Lambda+n_P+n_C+n_S) \ln (n_\Lambda+n_P+n_C+n_S) + z\, n_\Lambda \ln n_\Lambda$$

$$- zn_\Lambda \ln(n_\Lambda+n_P+n_C+n_S) + zn_P \ln n_P - zn_P \ln(n_\Lambda+n_P+n_C+n_S)$$

$$+ zn_C \ln n_C - zn_C \ln (n_\Lambda+n_P+n_C+n_S)$$

$$- zn_S \ln (n_\Lambda+n_P+n_C+n_S) - n_\Lambda^0 \ln n_\Lambda^0$$

$$+ zn_\Lambda \ln[1+\exp(\pi_1 - \frac{\Delta W_\Lambda^{100} - kT \Delta \ln v_\Lambda^{100}}{kT}) +$$

$$\exp(-\pi_3 - \frac{\Delta W_\Lambda^{010} - kT \Delta \ln v_\Lambda^{010}}{kT})]$$

$$- 2n_\Lambda^1 \ln N_\Lambda^1 - n_\Lambda^1 (\frac{\Delta W_\Lambda^{001} - kT \Delta \ln v_\Lambda^{001}}{kT})$$

$$- n_\Lambda^1 \ln[1+\exp(\pi_1 - \frac{\Delta W_\Lambda^{100} - kT \Delta \ln v_\Lambda^{100}}{kT}) +$$

$$\exp(-\pi_3 - \frac{\Delta W_\Lambda^{010} - kT \Delta \ln v_\Lambda^{010}}{kT})]$$

$$- n_P^0 \ln n_P^0 + z\, n_P \ln[1+\exp(-\pi_1 - \frac{\Delta W_P^{010} - kT \Delta \ln v_P^{010}}{kT}) +$$

$$\exp(\pi_2 - \frac{\Delta W_P^{100} - kT \Delta \ln v_P^{100}}{kT})]$$

$$- 2\, n_P^1 \ln N_P^1 - n_P^1 (\frac{\Delta W_P^{001} - kT \Delta \ln v_P^{001}}{kT})$$

$$- n_P^1 \ln[1+\exp(-\pi_1 - \frac{\Delta W_P^{010} - kT\,\Delta \ln v_P^{010}}{kT}) + \exp(\pi_2 - \frac{\Delta W_P^{100} - kT\,\Delta \ln v_P^{100}}{kT})]$$

$$- n_C^0 \ln n_C^0 + z\, n_C \ln[1+\exp(\pi_3 - \frac{\Delta W_C^{100} - kT\,\Delta \ln v_C^{100}}{kT})$$

$$+\exp(-\pi_2 - \frac{\Delta W_C^{010} - kT\,\Delta \ln v_C^{010}}{kT})]$$

$$- 2\, n_C^1 \ln N_C^1 - n_C^1 \left(\frac{\Delta W_C^{001} - kT\,\Delta \ln v_C^{001}}{kT}\right)$$

$$- n_C^1 \ln[1+\exp(\pi_3 - \frac{\Delta W_C^{100} - kT\,\Delta \ln v_C^{100}}{kT}) + \exp(-\pi_2 - \frac{\Delta W_C^{010} - kT\,\Delta \ln v_C^{010}}{kT})]$$

$$- n_S \ln n_S - n_A^1 \left(\frac{\Delta W_S^{z0} - kT\,\Delta \ln v_S^{z0}}{zkT}\right) - n_P^1 \left(\frac{\Delta W_S^{0z} - kT\,\Delta \ln v_S^{0z}}{zkT}\right)$$

$$- n_C^1 \left(\frac{\Delta W_S^{00} - kT\,\Delta \ln v_S^{00}}{zkT}\right) - z(z-1)\, N_A^1 . N_P^1 . n_S . \left(\frac{h_{S,AP} - kT\,\beta_{S,AP}}{2\,kT}\right)$$

$$- z(z-1) N_P^1 . N_C^1 . n_S . \left(\frac{h_{S,PC} - kT\,\beta_{S,PC}}{2kT}\right) - z(z-1) N_C^1 . N_A^1 . n_S$$

$$\left(\frac{h_{S,CA} - kT\,\beta_{S,CA}}{2kT}\right) \qquad \ldots \text{(IV.255)}$$

From the above expression, one can arrive at the following expression for the partial molar free energy of component S at infinite dilution in the solvent containing components, A, P and C.

$$\Delta \bar{G}^{ex,\infty}_{S(A+P+C)} = 2z\, RT[N_A^1 \ln \frac{N_A^1}{N_A} + N_P^1 \ln \frac{N_P^1}{N_P} + N_C^1 \ln \frac{N_C^1}{N_C}] \,.$$

$$+ N_A^1 [\Delta \bar{G}^{ex,\infty}_{S(A)} - \Delta \bar{G}^{ex}_{A(A+P+C)}]$$

$$
\begin{aligned}
&+ N_P^1[\Delta\bar{G}^{ex,\infty}_{S(P)} - \Delta\bar{G}^{ex}_{P(A+P+C)}] + N_C^1[\Delta\bar{G}^{ex,\infty}_{S(C)} - \Delta\bar{G}^{ex}_{C(A+P+C)}] \\
&+ \frac{N_A^1 \cdot {N_P^1}^2}{N_A^1+N_P^1} \cdot [\frac{K_P}{K_A} \cdot RT\ \varepsilon^{A}_{S(P)} - \Delta\bar{G}^{ex,\infty}_{S(A)} + \Delta\bar{G}^{ex,\infty}_{S(P)} + \Delta\bar{G}^{ex,\infty}_{A(P)} \\
&\qquad -2z\ RT\ (\ln \frac{K_A}{K_P} + \frac{K_P-K_A}{K_A})] \\
&+ \frac{{N_A^1}^2 \cdot N_P^1}{N_A^1+N_P^1} \cdot [\frac{K_A}{K_P} \cdot RT\ \varepsilon^{P}_{S(A)} - \Delta\bar{G}^{ex,\infty}_{S(P)} + \Delta\bar{G}^{ex,\infty}_{S(A)} + \Delta\bar{G}^{ex,\infty}_{P(A)} \\
&\qquad -2z\ RT(\ln \frac{K_P}{K_A} + \frac{K_A-K_P}{K_P})] \\
&+ \frac{N_P^1 {N_C^1}^2}{N_P^1+N_C^1} \cdot [\frac{K_C}{K_P} \cdot RT\ \varepsilon^{P}_{S(C)} - \Delta\bar{G}^{ex,\infty}_{S(P)} + \Delta\bar{G}^{ex,\infty}_{S(C)} + \Delta\bar{G}^{ex,\infty}_{P(C)} -2z\ RT \\
&\qquad (\ln \frac{K_P}{K_C} + \frac{K_C-K_P}{K_P})] \\
&+ \frac{{N_P^1}^2 \cdot N_C^1}{N_P^1+N_C^1} \cdot [\frac{K_P}{K_C} \cdot RT\ \varepsilon^{C}_{S(P)} - \Delta\bar{G}^{ex,\infty}_{S(C)} + \Delta\bar{G}^{ex,\infty}_{S(P)} + \Delta\bar{G}^{ex,\infty}_{C(P)} -2z\ RT \\
&\qquad (\ln \frac{K_C}{K_P} + \frac{K_P-K_C}{K_C})] \\
&+ \frac{N_C^1 \cdot {N_A^1}^2}{N_C^1+N_A^1} \cdot [\frac{K_A}{K_C} \cdot RT\ \varepsilon^{C}_{S(A)} - \Delta\bar{G}^{ex,\infty}_{S(C)} + \Delta\bar{G}^{ex,\infty}_{S(A)} + \Delta\bar{G}^{ex,\infty}_{C(A)} -2z\ RT \\
&\qquad (\ln \frac{K_C}{K_A} + \frac{K_A-K_C}{K_C})] \\
&+ \frac{{N_C^1}^2 \cdot N_A^1}{N_C^1+N_A^1} \cdot [\frac{K_C}{K_A} \cdot RT\ \varepsilon^{A}_{S(C)} - \Delta\bar{G}^{ex,\infty}_{S(A)} + \Delta\bar{G}^{ex,\infty}_{S(C)} + \Delta\bar{G}^{ex,\infty}_{A(C)} -2z\ RT \\
&\qquad (\ln \frac{K_A}{K_C} + \frac{K_C-K_A}{K_A})] \qquad \ldots \text{(IV.256)}
\end{aligned}
$$

where, N_A^1, N_P^1, N_C^1, K_A, K_P and K_C are given by eqs. (IV.201a) - (IV.202c).

The above expression can be generalised for excess partial molar free energy of solute component , S, in a n-component solvent as given below.

$$\Delta \bar{G}^{ex,\infty}_{S(1+2+\dots+n)} = \sum_{i=1}^{n} 2z\ RT\ [N_i^1 \ln \frac{N_i^1}{N_i}]$$

$$+ \sum_{i=1}^{n} [N_i\ (\Delta \bar{G}^{ex,\infty}_{S(i)} - \Delta \bar{G}^{ex}_{i(1+2+\dots+n)})]$$

$$+ \sum_{\substack{i=1 \\ (i\neq j)}}^{n} \sum_{j=1}^{n} \frac{N_i^1 . N_j^{1^2}}{N_i+N_j} . [\frac{K_j}{K_i} .RT\ \varepsilon^i_{S(j)} - \Delta \bar{G}^{ex,\infty}_{S(i)} + \Delta \bar{G}^{ex,\infty}_{S(j)}$$

$$+ \Delta \bar{G}^{e,\infty}_{i(j)} - 2z\ RT(\ln \frac{K_i}{K_j} + \frac{K_j - K_i}{K_i})] \qquad \dots (IV.257)$$

where, the terms K_i , K_j, N_i^1 and N_j^1 have their usual meanings.

IV.3 Application and Discussion

In this section, applicability of the different expressions, derived in the previous section shall be listed to compute the thermodynamic properties of the different systems investigated in the present work. The different expressions derived for calculation of the thermodynamic properties show that for such computations, a knowledge of the partial molar properties of solvents is necessary.

IV.3.1 Partial Molar Properties of Solvents

Apart from pure lead, silver and copper, their binary and ternary solutions have also been used as solvents for sulphur

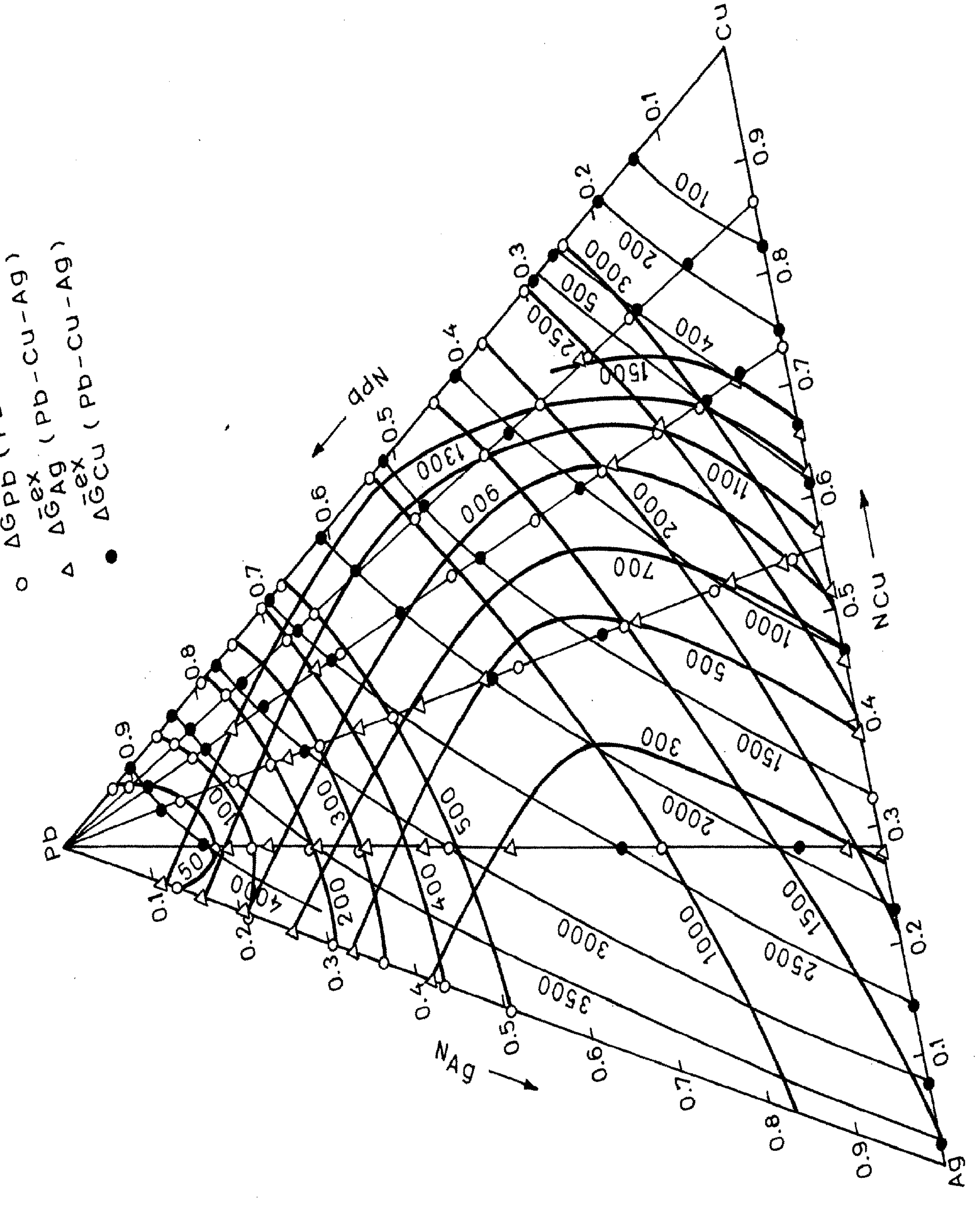

FIG. IV.1 ISO-FREE ENERGY CURVES FOR EXCESS PARTIAL MOLAR FREE ENERGY OF LEAD, COPPER AND SILVER IN TERNARY SOLUTIONS AT 1273°K. (in calories)

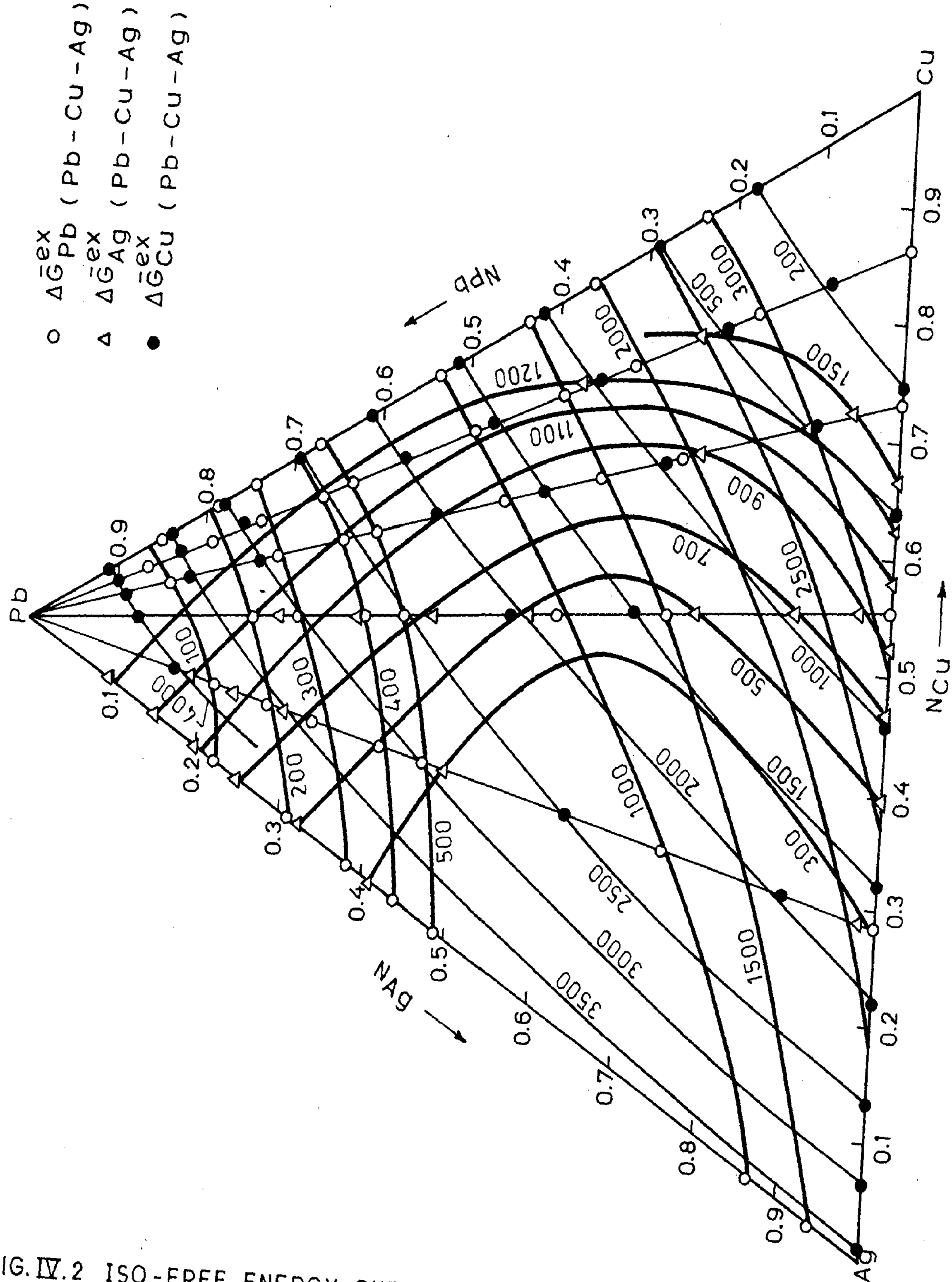

FIG. IV.2 ISO-FREE ENERGY CURVES FOR EXCESS PARTIAL MOLAR FREE ENERGY OF LEAD, COPPER AND SILVER IN TERNARY SOLUTIONS AT 1323°K. (in calories)

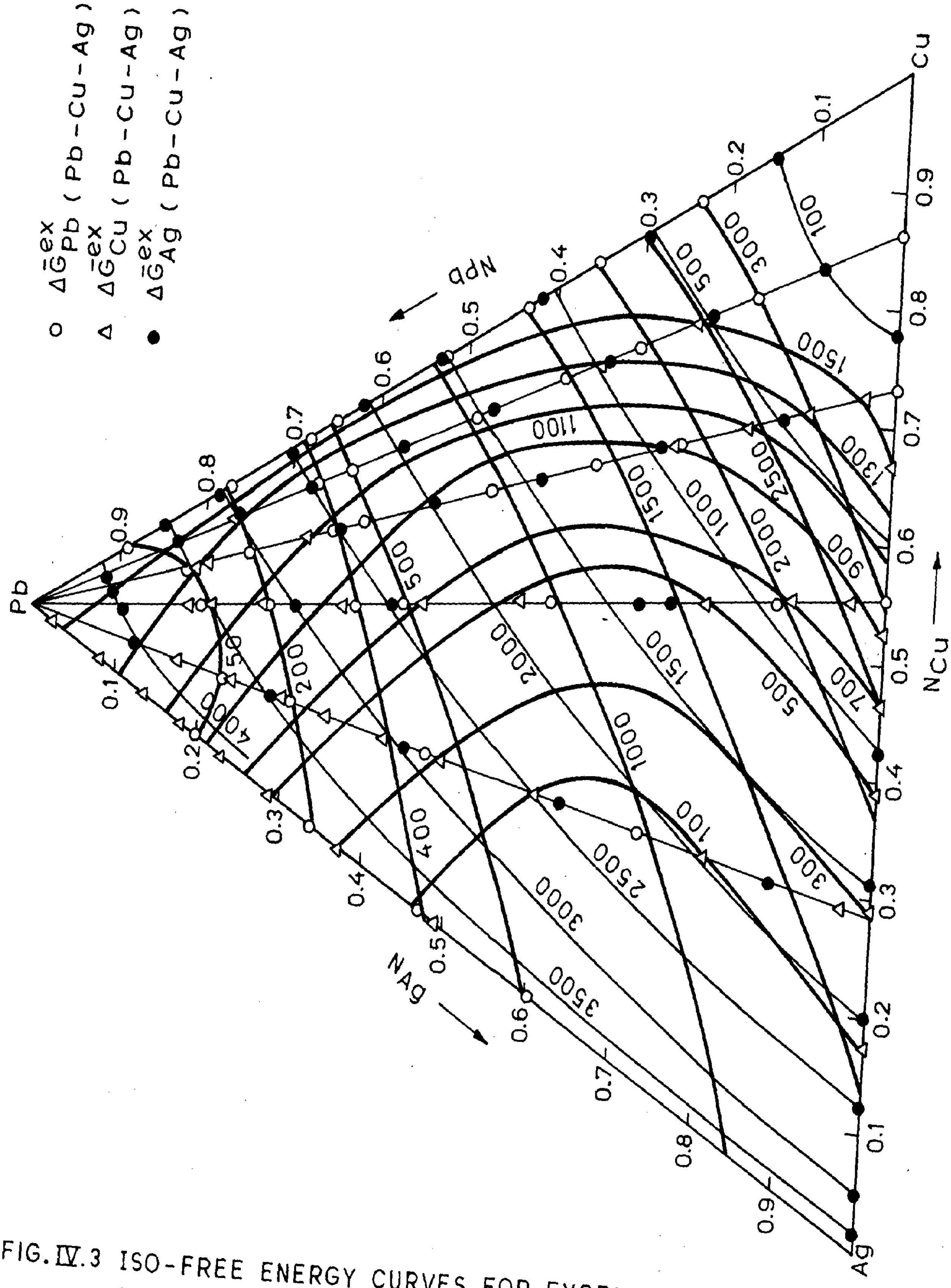

FIG. IV.3 ISO-FREE ENERGY CURVES FOR EXCESS PARTIAL MOLAR FREE ENERGY OF LEAD, COPPER AND SILVER IN TERNARY SOLUTIONS AT 1373° K. (in calories) composition and at temperatures of the present work. These have, therefore, to be calculated from the properties of terminal binary systems. A number of models, reviewed critically by Ansara [90], have been proposed for such calculations, among which the Kohler's equation [91] has been extensively applied to the ternary systems having component copper, lead, silver and many others. Hence for the calculation of thermodynamic properties of the system lead-copper-silver, in the present work, also, this model will be used. According to this model, the excess free energy, $\Delta G^{ex}_{(A+B+C)}$, of a ternary system containing components A, B and C, in terms of the properties of the binary systems A-B, B-C and C-A is given by the following expression,

$$G^{ex}_{(A+B+C)} = (N_A+N_B)^2 \cdot (\Delta G^{ex}_{AB})_{N_A/N_B} + (N_A+N_C)^2 \cdot (\Delta G^{ex}_{AC})_{N_A/N_C} + (N_B+N_C)^2 \cdot (\Delta G^{ex}_{BC})_{N_B/N_C} \qquad \text{... (IV. 259)}$$

where N_A, N_B and N_C are respectively the mole fractions of components A, B and C in the ternary system, the symbol $(\Delta G^{ex}_{AB})_{N_A/N_B}$ represents the excess free energy of mixing of components A and B in a binary solution having these components in the same ratio N_A/N_B as in the ternary system under study. $(\Delta G^{ex}_{BC})_{N_B/N_C}$ and $(\Delta G^{ex}_{CA})_{N_C/N_A}$ are also similarly defined.

From a knowledge of the properties of terminal binary systems, the excess partial molar properties of different components in the ternary lead-copper-silver system have been calculated using eq. (IV.259) for three different temperatures viz. 1273, 1323 and 1373°K. These values have been used to plot the iso-free energy curves in Figs.(IV.1)-(IV.3). Properties of the components of ternary solvent at infinite dilution are also calculated at different temperatures under study and are presented in Table (IV.1). With this, calculations for all properties of solvents needed for computation of properties involving solute are computed. Let us now proceed on to the calculation of properties of sulphur in binary and ternary systems, studied in the present work.

IV.3.2 Silver-Copper-Sulphur System

In Fig. (IV.4), the experimental and theoretical curves between free energy and composition corresponding to the different expressions derived for various models proposed in the preceding Section (IV.2) are plotted. For the calculation of theoretical curves, the data on binary systems as reported in Fig. (IV.1) and determined by the author has been used. As seen from Fig. (IV.4), the calculated curves form two different groups - one of these corresponding to the linear forms of energy and the other to non-linear forms. For both these sets, the curves for random and preferential distributions lie quite close to

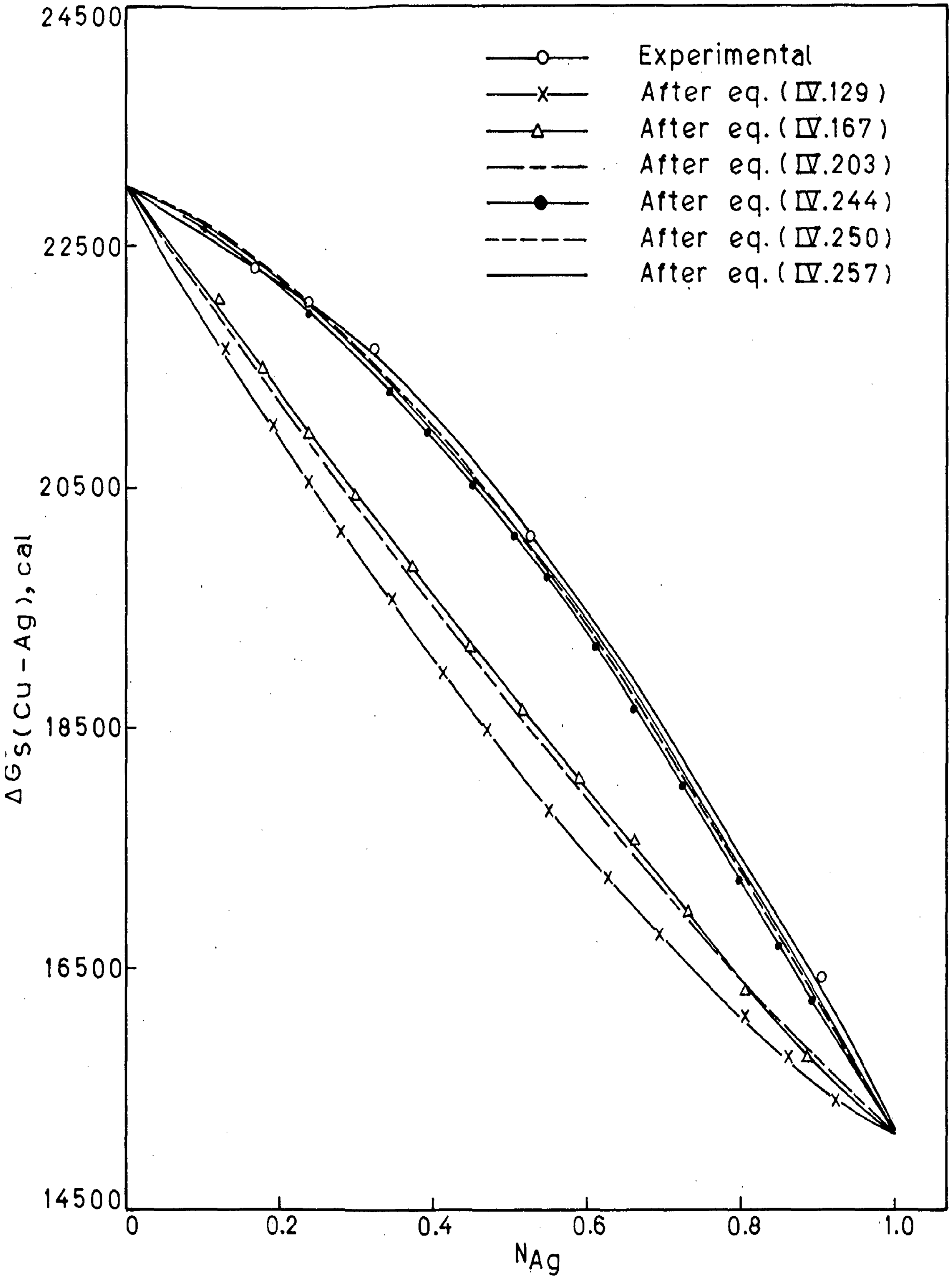

FIG. IV.4 COMPARISON OF EXPERIMENTAL AND CALCULATED VALUES OF FREE ENERGY OF EQUILIBRIA OF SULPHUR IN BINARY COPPER-SILVER ALLOYS AT 1273°K.

each other, showing thereby that in case of this system, (Ag-Cu-S), the free energy of solution of sulphur is only a weak function of distribution of different atoms present.

Fig. (IV.4), further shows that the expressions derived on the basis of linear forms of energies of the different atomic species deviate considerably from the experimentally determined data. Hence it can be concluded that models based on these assumptions are incapable of explaining the experimental data on this system. In order to extend the range of applicability of these models, Jacob and Alcock [92], incorporated in their derivations, a function, α, which is considered to be equal to the fraction of bonds broken. On this basis, these authors derived the following expression :

$$\begin{aligned}\Delta\bar{G}_{o(x+y)} &= N_x^o.[\Delta\bar{G}_{o(x)} - n.\alpha.\ \Delta\bar{G}^{ex}_{x(x+y)}] \\ &+ N_y^o.[\Delta\bar{G}_{o(y)} - n\alpha.\ \Delta\bar{G}^{ex}_{y(x+y)}] \\ &+ nRT.[N_x^o \ln \frac{N_x^o}{N_x} + N_y^o \ln \frac{N_y^o}{N_y}] \qquad \ldots \text{(IV.260)}\end{aligned}$$

Though this expression was able to explain the free energy of solution of oxygen in a number of binary alloys by making suitable adjustments in the value of α, it could not explain the behaviour of oxygen in iron-copper binary solvent. Further, there is no apparent justification as to why a substitutional or for that reason an interstitial solute component breaks more than the number of bonds it makes with neighbouring atoms. Therefore, the applicability

$$\Delta\bar{G}^{ex,oo}_{S(Ag+Cu)} = N_{Ag}\cdot[-15130 - \Delta\bar{G}^{ex}_{Ag(Ag+Cu)}]$$
$$+ N_{Cu}\cdot[-23265 - \Delta\bar{G}^{ex}_{Cu(Ag+Cu)}]$$
$$+ N_{Ag}.N_{Cu}\cdot[N_{Ag}\{3800 + 15130 - 23265 + 3490\}$$
$$+ N_{Cu}\{-11800 + 23265 - 15130 + 3680\}] \quad \ldots (IV.\ 261)$$

IV.3.3 Lead-Copper-Sulphur System

Values of free energy for the reaction expressed by eq. (III. 31) obtained experimentally as also computed, based on different models proposed in Sec. (IV.2), have been plotted against composition for the Pb-Cu-S system in Fig. (IV.5). Data on binary Pb-Cu system from Fig.(IV.1) for temperature 1273°K have been used for calculation of theoretical values of free energy. It will be noted from Fig. (IV.5), that the plots for the calculated values fall distinctly in two groups - one corresponding to the non-linear and the other to linear forms of energy. Further for both the sets, random or preferential distribution of atoms in the solution does not seem to affect the free energy values to an appreciable extent in this system, and the plots based on linear forms of energy appear farther away from the plot of empirical data, meaning thereby that assumption of linear forms of energy is not correct for explaining the behaviour of such solutions.

As discussed earlier, Sec (IV.3.2), the eqs.(IV.244),

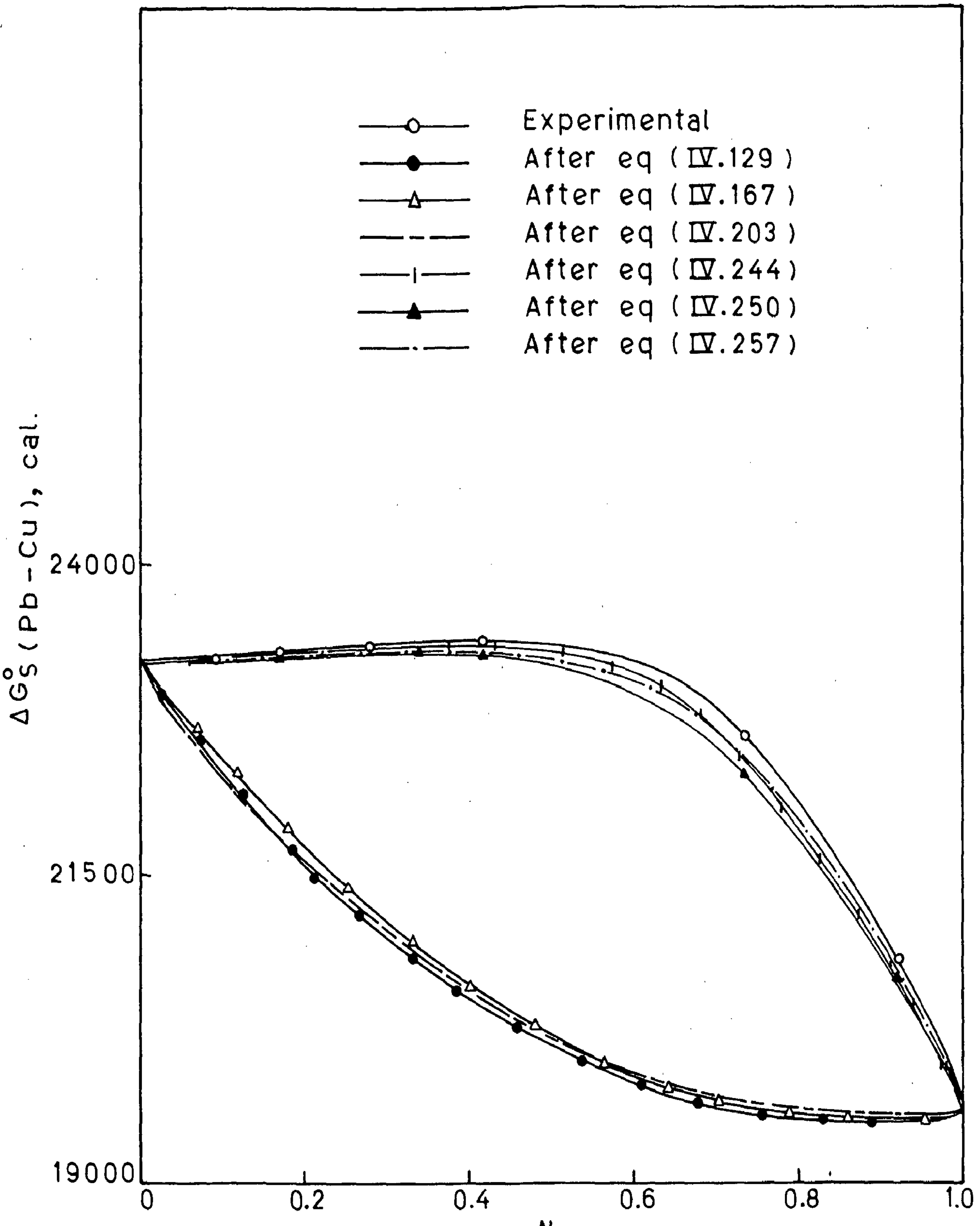

FIG. IV.5 COMPARISON OF EXPERIMENTAL AND CALCULATED VALUES OF FREE ENERGY OF EQUILIBRIA OF SULPHUR IN BINARY LEAD-COPPER ALLOYS AT 1273 °K.

(IV.250) and (IV.257) , developed based on non-linear forms of energy explain the behaviour of these solutions to a satisfactory degree of accuracy, Therefore, the following expression may be used satisfactorily for calculation of free energy for the reaction expressed by eq. (III. 31),

$$\begin{aligned}\Delta\bar{G}^{ex,\infty}_{S(Pb+Cu)} = {} & N_{Pb}\cdot[-19660 - \Delta\bar{G}^{ex}_{Pb(Pb+Cu)}] \\ & + N_{Cu}\cdot[-23265 - \Delta\bar{G}^{ex}_{Cu(Pb+Cu)}] \\ + N_{Pb}\cdot N_{Cu}\cdot[N_{Pb}\cdot & \{-127 + 19660 - 23265 + 5375\} \\ & + N_{Cu}\{-15100 + 23265 - 19660 + 4902\}] \qquad \ldots(IV.\ 262)\end{aligned}$$

IV.3.4 Lead-Silver-Sulphur System

Experimentally determined and theoretically calculated values of free energy, based on different models proposed in sec. (IV.2) have been plotted against composition for the Pb-Ag-S system in Fig. (IV.6). Theoretical calculations of free energy have been made using the data on binary Pb-Ag system from Fig. (IV.1) for temperature 1273°K. As is clearly observed, from Fig. (IV.6), the curves plotted for the calculated values of free energy fall in two distinct groups - one corresponding to the linear forms of energy and the other to the non-linear form. In both these sets, the curves for random and preferential distribution of the atomic species in the solution fall close by, which apparently shows that free energy of dissolution of sulphur in this

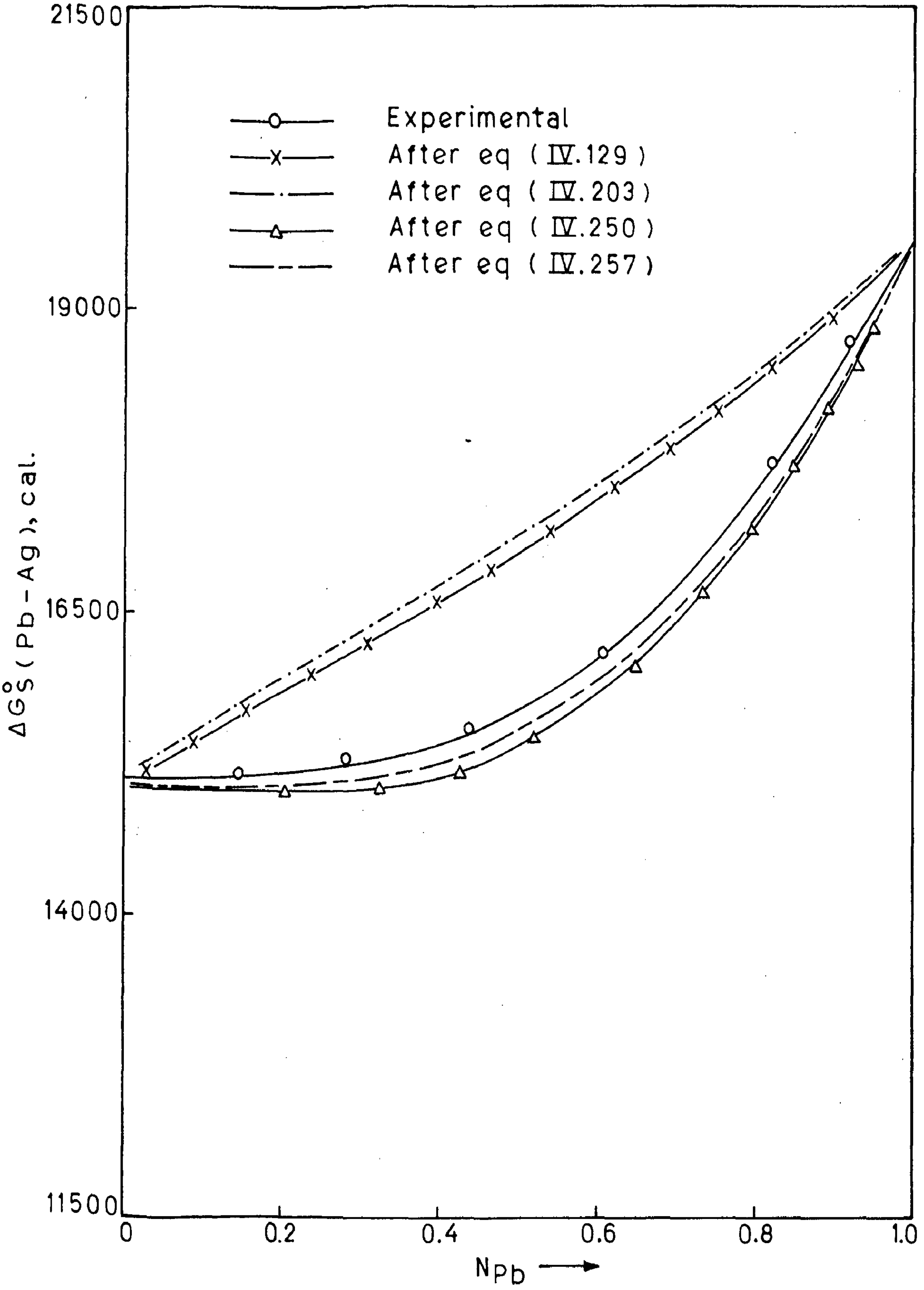

FIG. IV.6 COMPARISON OF EXPERIMENTAL AND CALCULATED VALUES OF FREE ENERGY OF EQUILIBRIA OF SULPHUR IN BINARY LEAD-SILVER ALLOYS AT 1273 °K.

system is not a strong function of the distribution pattern of the constituent atoms. It is further noted that curves plotted on the basis of linear forms of energy fall apart considerably from the experimental curves, suggesting thereby that solution models developed on the basis of linear relationships are incapable of explaining the behaviour of such systems.

As discussed in Sec. (IV.3.2), the approach of Jacob and Alcock [92], who tried to explain the behaviour of metallic solutions by introduction of an empirical function, α, denoting the fraction of **bonds** broken on dissolution of solute component in the binary solvent, has not been tested in the present work.

For the reasons described in Sec. (IV.3.2), in the present theoretical analysis of the empirical data also, it is observed that the plots corresponding to eqs.(IV.244), (IV.250) and (IV.257) based on equations derived by assuming quadratic forms of energy explain the behaviour of this system to an appreciably good degree of accuracy and the one corresponding to eq. (IV. 257) fits best in the empirical data. Since the other two plots also do not deviate much, the model corresponding to random distribution, eq. (IV.244), may be used for all practical purposes, as it is simple and easily calculable. In that case, the following expression may be used for calculation of the free energy of the reaction expressed by eq. (III. 30) at 1273°K,

$$\begin{aligned}\Delta \bar{G}^{ex,\infty}_{S(Pb+Ag)} &= N_{Pb}\cdot[-19660 - \Delta \bar{G}^{ex}_{Pb(Pb+Ag)}] \\ &+ N_{Ag}\cdot[-15130 - \Delta \bar{G}^{ex}_{Ag(Pb+Ag)}] \\ + N_{Pb}\cdot N_{Ag}\cdot[N_{Pb}\cdot\{&-833 + 19660 - 15130 - 200\} \\ &+ N_{Ag}\{14363 + 15130 - 19660 + 1792\}]\end{aligned}$$

... (IV. 263)

IV.3.5 Lead-Copper-Silver-Sulphur System

Experimental and computed values of free energy based on the different models proposed in the preceding Sec. (IV.2) for the reaction expressed by eq. (III. 34), have been plotted for the ternary alloy solvents having the same Cu/Ag ratio, at 1273°K in Fig. (IV.7).

Ternary solvent (Pb-Cu-Ag) data from Fig. (IV.1) has been used for the calculation of theoretical values of free energy.

As discussed in the earlier cases of binary solvents, the expressions developed on the basis of linear forms of energy do not explain the behaviour of such solutions to a satisfactory degree of accuracy nor the assumption of random or preferential distribution of atoms show a large variation in calculated values.

Hence the acceptable expressions for calculation of free energy of such solutions are based on the assumption of non-linear forms of energy to yield eqs. (IV. 243), (IV. 245), (IV. 248), (IV. 249) and (IV. 256).

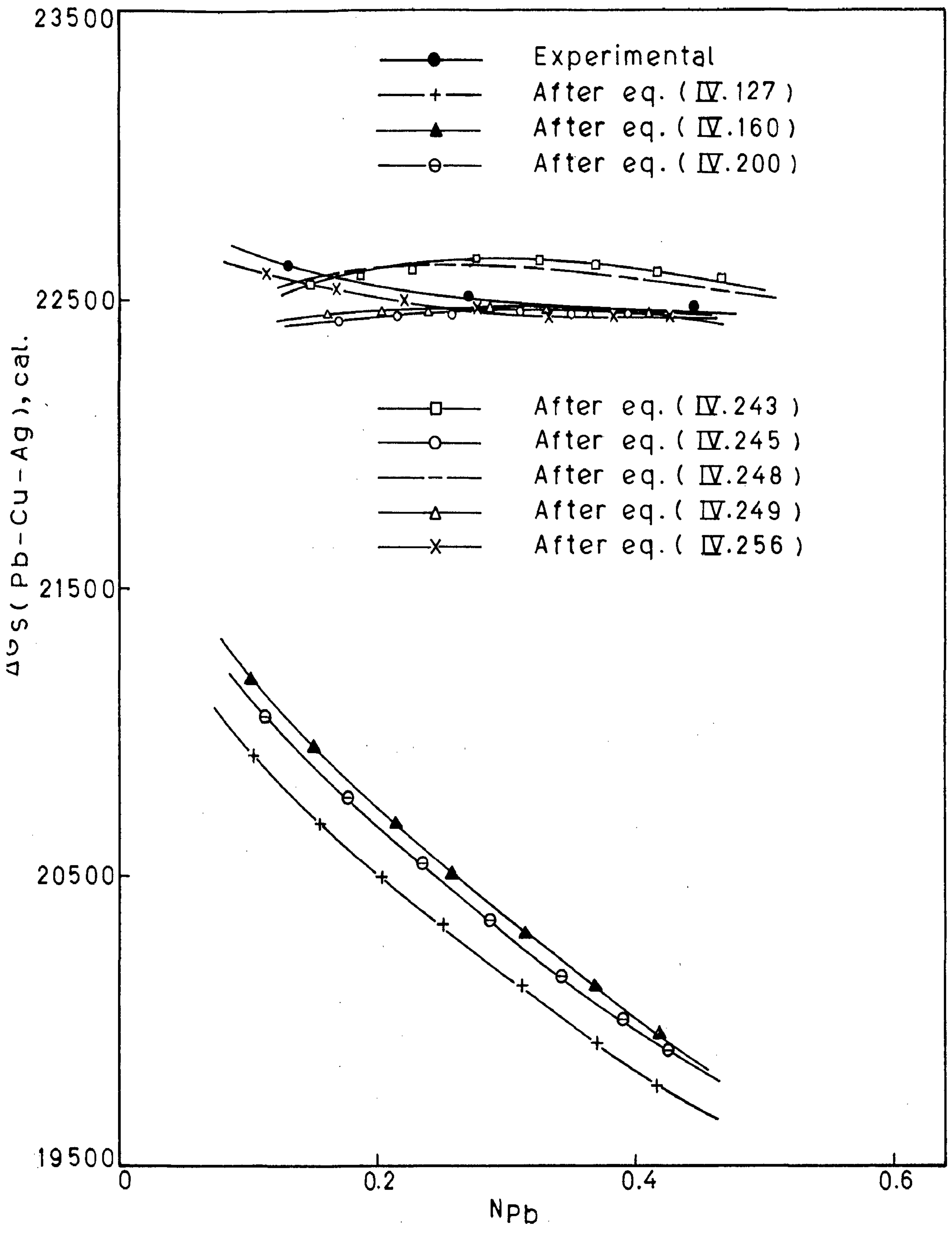

FIG. IV.7 COMPARISON OF EXPERIMENTAL AND CALCULATED VALUES OF FREE ENERGY OF EQUILIBRIA OF SULPHUR IN TERNARY Pb-Cu-Ag ALLOYS AT 1273 °K.

Out of these, the values obtained by eq.(IV.256) are best fit to the experimental values of free energy. But as the plots are quite close to each other corresponding to above five equations, for all practical purposes eq. (IV. 243) based on random distribution and non-linear forms of energy of both solvent and solute may be used for explaining the behaviour of such systems, to an acceptable degree of accuracy, for reasons of its simplicity and ease of application. Thus the expression, most suitable for this system at 1273°K is as follows:

$$
\begin{aligned}
\Delta \bar{G}^{ex,\infty}_{S(Pb+Cu+Ag)} = {} & N_{Pb} \cdot [-19660 - \Delta \bar{G}^{ex}_{Pb(Pb+Cu+Ag)}] \\
& + N_{Cu} \cdot [-23265 - \Delta \bar{G}^{ex}_{Cu(Pb+Cu+Ag)}] \\
& + N_{Ag} \cdot [-15130 - \Delta \bar{G}^{ex}_{Ag(Pb+Cu+Ag)}] \\
& + \frac{N_{Pb} \cdot N^2_{Cu}}{N_{Pb}+N_{Cu}} \cdot [-127 + 19660 - 23265 + 5375] \\
& + \frac{N^2_{Pb} \cdot N_{Cu}}{N_{Pb}+N_{Cu}} \cdot [-15107 + 23265 - 19660 + 4900] \\
& + \frac{N_{Cu} \cdot N^2_{Ag}}{N_{Cu}+N_{Ag}} \cdot [-11800 + 23265 - 15130 + 3680] \\
& + \frac{N^2_{Cu} \cdot N_{Ag}}{N_{Cu}+N_{Ag}} \cdot [3800 + 15130 - 23265 + 3490] \\
& + \frac{N_{Ag} \cdot N^2_{Pb}}{N_{Ag}+N_{Pb}} \cdot [14363 + 15130 - 19660 + 1792] \\
& + \frac{N^2_{Ag} \cdot N_{Pb}}{N_{Ag}+N_{Pb}} \cdot [-833 + 19660 - 15130 - 200] \qquad \ldots (IV.\ 264)
\end{aligned}
$$

...

CHAPTER - V

SUMMARY AND CONCLUSIONS

The different experimental results of the present study and the conclusions drawn are summarised below:

1) Empirical data on the free energy of different reaction equilibria and interaction parameters at different temperatures of study are presented in the Table-V.1.

2) In the different systems studied, effect of distribution of different atoms present-either random or preferential, is not appreciable on the computed results. Therefore for a theoretical quantitative analysis of these data, random distribution can be used with advantage of simplicity of treatment.

3) The linear forms of energies and free volumes of atoms do not explain the empirical data and only non-linear forms are to be used for their quantitative interpretation.

4) The different forms of expressions arrived at for theoretical interpretation of empirical data, based on random distribution and non-linear forms of energies and free volumes of atoms present in the equilibrated systems at 1273^{0}K are as follows:

TABLE-V.1 : Experimental values of different thermodynamic functions calculated for the solvent systems studied.

Temp ^{o}K	$\Delta G^{o}_{S(Pb)}$ cals.	$\Delta G^{o}_{S(Cu)}$ cals.	$\Delta G^{o}_{S(Ag)}$ cals.	$\varepsilon^{Pb}_{S(Cu)}$	$\varepsilon^{Cu}_{S(Pb)}$	$\varepsilon^{Pb}_{S(Ag)}$	$\varepsilon^{Ag}_{S(Pb)}$	$\varepsilon^{Cu}_{S(Ag)}$	$\varepsilon^{Ag}_{S(Cu)}$
1273	19660	23265	15130	-0.05	-5.97	-0.33	5.68	-4.665	1.503
1323	19240	22950	15080	-0.245	-7.82	-0.47	4.39	-5.33	1.033
1373	18810	22630	15030	-0.512	-8.70	-0.63	3.076	-6.11	0.437

i) Cu-Ag-S System

$$\Delta\bar{G}^{ex,\infty}_{S(Ag+Cu)} = N_{Ag}\cdot[-15130 - \Delta\bar{G}^{ex}_{Ag(Ag+Cu)}]$$

$$+ N_{Cu}\cdot[-23265 - \Delta\bar{G}^{ex}_{Cu(Ag+Cu)}]$$

$$+ N_{Ag}.N_{Cu}\cdot[15\ N_{Cu} - 845\ N_{Ag}] \qquad \ldots\ (V.1)$$

ii) Pb-Cu-S System

$$\Delta\bar{G}^{ex,\infty}_{S(Pb+Cu)} = N_{Pb}\cdot[-19660 - \Delta\bar{G}^{ex}_{Pb(Pb+Cu)}]$$

$$+ N_{Cu}\cdot[-23265 - \Delta\bar{G}^{ex}_{Cu(Pb+Cu)}]$$

$$+ N_{Pb}\cdot N_{Cu}\cdot[\ 1643\ N_{Pb} - 6593\ N_{Cu}] \qquad \ldots\ (V.2)$$

iii) Pb-Ag-S System

$$\Delta\bar{G}^{ex,\infty}_{S(Pb+Ag)} = N_{Pb}\cdot[-19660 - \Delta\bar{G}^{ex}_{Pb(Pb+Ag)}]$$

$$+ N_{Ag}\cdot[-15130 - \Delta\bar{G}^{ex}_{Ag(Pb+Ag)}$$

$$+ N_{Pb}\cdot N_{Ag}\cdot[\ 3497\ N_{Pb} + 11625\ N_{Ag}] \qquad \ldots\ (V.3)$$

iv) Pb-Cu-Ag-S System

$$\Delta\bar{G}_{S(Pb+Cu+Ag)} = N_{Pb}\cdot[-19660 - \Delta\bar{G}^{ex}_{Pb(Pb+Cu+Ag)}]$$

$$+ N_{Cu}\cdot[-23265 - \Delta\bar{G}^{ex}_{Cu(Pb+Cu+Ag)}]$$

$$+ N_{Ag}\cdot[-15130 - \Delta\bar{G}^{ex}_{Ag(Pb+Cu+Ag)}]$$

$$+ \frac{N_{Pb} \cdot N_{Cu}}{(N_{Pb}+N_{Cu})} \cdot [1643\ N_{Cu} - 6602\ N_{Pb}]$$

$$+ \frac{N_{Cu} \cdot N_{Ag}}{(N_{Cu}+N_{Ag})} \cdot [15\ N_{Ag} - 845\ N_{Cu}]$$

$$+ \frac{N_{Ag} \cdot N_{Pb}}{(N_{Ag}+N_{Pb})} \cdot [11625\ N_{Pb} + 3497\ N_{Ag}]$$

... (V.4)

5) At other temperatures of study the above equations have similar forms for the systems under reference, but the values of constants change with temperature.

6) The most important conclusion drawn is that the properties of the multicomponent solutions containing dilute solute, can not be computed using only partial molar properties of components and the composition of system but need essentially a knowledge of the interaction parameters for effect of additive elements on the solute, sulphur.

7) The entire composition range of different alloys containing sulphur need not be experimentally studied as the properties can be predicted at any composition using infinite dilution parameters of solvent and solute species of the system and the different expressions derived in this work.

SUGGESTIONS FOR FURTHER WORK

1) Behaviour of sulphur should be experimentally studied in other systems also for extensive determination of interaction parameters for the effect of other elements on sulphur in different solvents at different temperatures. For this purpose, systems consisting of Fe, Ni, Co, Zn, Sn, Sb, As etc. may be selected for experimental studies as these metals invariably occur in nature in the sulphide form.

2) Using the data obtained above, the universal applicability of the theoretical expressions derived in the present work can also be tested for their predictive value.

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