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TWO ASPECTS OF ALLOY THERMOCHEMISTRY: A. VARIATION OF PROPERTIES WITH COMPOSITION IN ORDERED PHASES B. SOLUTE INTERACTIONS IN DILUTE LIQUID ALLOYS

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September 17, 1965

PREFACE

Studies have been made of two different aspects of the problem of relating thermodynamic properties to atomic interactions or configurations in intermetallic alloys. Part A presents a general method of calculating the compositional variation of the configurational thermodynamic properties for ordered phases which disorder by means of substitutional defects. Part B reports the results of an experimental study of solute interactions in some dilute binary and ternary liquid tin-rich alloys.

Each part is preceded by an individual abstract, and the references for each part are also separately listed.

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Part A

VARIATION OF THERMODYNAMIC PROPERTIES WITH COMPOSITION IN ORDERED INTERMETALLIC PHASES

ABSTRACT

A method is presented for calculating the compositional variation of the configurational thermodynamic properties of ordered intermetallic phases which exist over a range of composition by means of the substitutional defect mechanism. The treatment, which is an extension of the one of Wagner and Schottky, is applied to the simple quasi-chemical model analogous to that employed in the Bragg and Williams treatment of the variation of degree of order with temperature.

The configurational thermodynamic properties are expressed as functions of the deviation from ideal stoichiometry and a composition dependent parameter which represents the atomic distribution. By minimizing the Gibbs energy with respect to the distribution parameter, an expression is obtained relating the equilibrium distribution with composition for given degrees of order at the stoichiometric composition. Solutions of this expression then permit the configurational properties to be evaluated as functions of composition for specified degrees of order at ideal stoichiometry.

The method of treatment is derived in detail for phases having the CsCl-type superlattice structure, and the results of corresponding treatments for AuCu-type and $AuCu_3$-type superlattice phases are

also given. Existing entropy of formation data for the AgMg, AuCd, and AuCu ordered phases are compared with values predicted by the treatments. Good correlations are obtained, leading to reasonable interpretations of the actual values in terms of the configurational and thermal contributions to the total entropies of formation.

It is proposed that the methods developed could provide the basis for more elaborate or extensive treatments, either which incorporate other defect mechanisms or which employ higher-order approximations of the quasi-chemical model.

I. INTRODUCTION

In binary intermetallic systems, there are many examples of intermediate phases which have highly ordered structures at a composition corresponding to some simple atomic ratio of the components, but which often exist over a considerable range of composition beyond the one at which perfect order is possible. Three of the most common types of ordered structures are: (1) the cubic, CsCl-type superlattice isotypic with β'-CuZn, in which Cu atoms occupy the corners and a Zn atom occupies the center of the unit cell, (2) the tetragonal superlattice isotypic with AuCu I, in which Au and Cu atoms form alternate layers on the (001) planes, and (3) the cubic superlattice isotypic with $AuCu_3$, in which Au atoms occupy the corners, and Cu atoms the face-centers of the unit cell. The three unit cells are illustrated in Fig. 1. Examples of intermetallic phases having these ordered structures, taken from the compilation of Laves,[1*] are listed in Table I.

Degree of Order and Its Variation with Temperature

The ordered arrangement of atoms in a superlattice extends for long distances throughout the crystal; hence the order is referred to as long-range order as distinguished from the short-range "order of neighbors" which frequently occurs in otherwise random solid-solutions.

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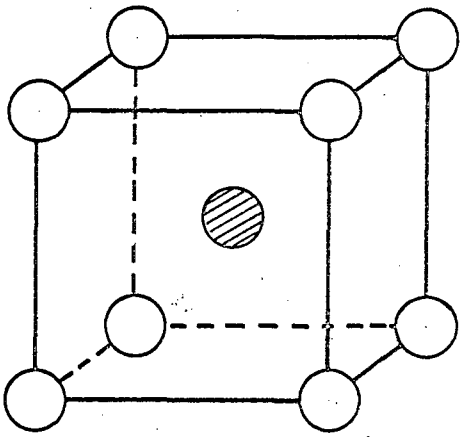
* References for Part A are listed separately, beginning on p. 52.

(a)

β' – CuZn

CsCl – type structure
(cubic)

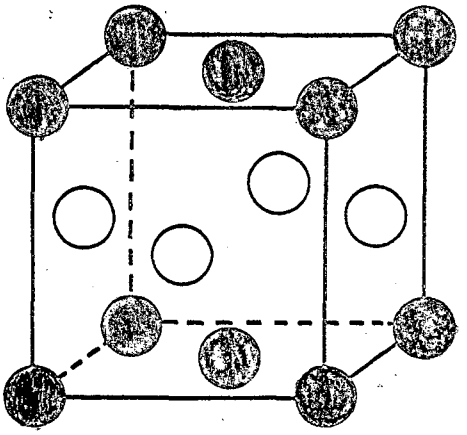


Cu atom Zn atom

(b)

AuCuI

prototype structure
(tetragonal)

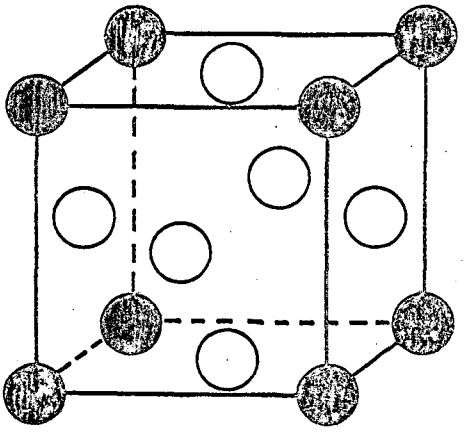


Au atom Cu atom

(c)

$AuCu_3$

prototype structure
(cubic)



Au atom Cu atom

FIG. 1 THREE COMMON SUPERLATTICE STRUCTURES.

TABLE I

Examples of Phases Having the Three Considered Types of Superlattice Structures*

CsCl-type			AuCu-type	AuCu$_3$-type	
AgCd	BiTl	HgPr	AgTi	Ag_3Pt	$GeNi_3$
AgCe	CaCd	HgSr	AlTi	$AgPt_3$	Ge_3U
AgLa	CaHg	InNi	AuCu	$AlNi_3$	$HgTi_3$
AgLi	CaTl	InPd	BiLi	Al_3Np	Hg_3Zr
AgMg	CdCe	LaMg	BiNa	Al_3U	In_3Pr
AgPr	CdLa	LaTl	CdPd	$AlZr_3$	In_3U
AgZn	CdPr	LaZn	CdPt	$AuCu_3$	$LaPb_3$
AlCo	CdSr	LiPb	CoPt	$CaPb_3$	$LaSn_3$
AlFe	CeHg	LiTl	FePd	$CaSn_3$	$MnNi_3$
AlNd	CeMg	MgPr	FePt	$CaTl_3$	$MnPt_3$
AlNi	CeTl	MgSr	HgPd	$CePb_3$	$MnZn_3$
AlPd	CeZn	MgTl	HgTi	$CeSn_3$	Ni_3Si
AuCd	CoFe	MnRh	HgZr	$CoPt_3$	$PbPd_3$
AuMg	CoTi	NiTi	InMg	Co_3V	Pb_3Pr
AuMn	CuPd	NiZn	IrMn	$CrIr_3$	Pb_3U
AuZn	CuZn	OsTi	MnNi	$CrPt_3$	Pd_3Sn
BaCd	FeTi	PrTl	MnPd	Cu_3Pd	$PrSn_3$
BaHg	FeV	PrZn	MnPt	Cu_3Pt	Pt_3Ti
BaZn	GaNi	RuSi	NiPt	$FeNi_3$	Pt_3Zn
BeCo	HgLa	RuTa	NiZn	$FePd_3$	Ru_3U
BeCu	HgLi	RuTi	PdZn	Fe_3Pt	Sn_3U
BeNi	HgMg	RuV	PtZn	$FePt_3$	Tl_3U
BePd	HgNd	SrTl		$GaNi_3$	$TiZn_3$
				Ga_3U	

*Taken from the compilation of Laves.[1]

The degree of long-range order for the stoichiometric compositions is usually designated by the well-known long-range order parameter, W, introduced by Bragg and Williams:[2]

$$W = \frac{r_A - x_A}{1 - x_A} \tag{1}$$

where r_A = fraction of A sites correctly occupied by A atoms

x_A = atomic fraction of A in the alloy

For the perfectly ordered configuration, $r_A = 1$ and thus $W = 1$; while for the completely random configuration, $r_A = x_A$ and $W = 0$.

Generally the degree of long-range order for the stoichiometric composition is nearly perfect, i.e. $W \approx 1$, at low temperatures, but decreases with increasing temperature due to the effect of increasing thermal agitation. The rate of disordering proceeds slowly at first but accelerates with increasing temperature due to the cooperative nature of the disordering process. An increasing amount of disorder reduces the distinction between the different kinds of sites, making it easier for further disorder to occur. The disordering process thus occurs over a range of temperature until finally at a certain critical temperature, T_c, the superlattice disappears more or less sharply resulting in an alloy generally having some degree of short-range order. The disordering process may be entirely a second-order process in which all the disordering energy is absorbed over a range of temperature with no latent heat effect at T_c, as is the case for CuZn;[3] or it may

be a combined second-order and first-order process with a catastrophic decrease in the degree of long-range order to zero accompanied by a latent heat absorption at T_c, as is shown by AuCu[4] and $AuCu_3$.[5,6] Many of the CsCl-type superlattices, to be discussed in detail later, retain large degrees of long-range order all the way to their melting temperatures, T_m, indicating that in those cases, $T_c > T_m$. There have been numerous treatments concerned with the variation of order with temperature for the stoichiometric ordered alloys, the best known of which is probably that of Bragg and Williams,[2] a good exposition of which is given by Cottrell.[7]

Variation of Degree of Order with Composition

In ordered phases of the types described which exist over a range of composition, departures from ideal stoichiometry can only be achieved by a defect mechanism which permits the addition of an excess of one of the components, decreasing the degree of order while retaining the basic long-range superlattice structure. As will be discussed in a later section, one of the primary mechanisms by which such deviations from ideal stoichiometry are achieved is by the substitution of excess atoms of one kind on lattice sites normally occupied by atoms of the other kind at the stoichiometric composition.

The problem to be considered in this paper is that of predicting the compositional variation of thermodynamic properties, especially the configurational entropy, for long-range-ordered phases which disorder by means of the substitutional mechanism. The general problem

of the effect of defect structure on thermodynamic properties was treated many years ago by Wagner and Schottky[8] (summarized more recently by Wagner[9]). Their solutions for specific cases, however, were restricted to approximations involving small concentrations of defects and thus were limited to only small deviations from stoichiometry. A general method of treating the problem of more extensive deviations from stoichiometry will be introduced. The proposed treatment will be described in considerable detail for the CsCl superlattice structure, and the results of similar analyses of the AuCu and $AuCu_3$ type structures will also be given. Available thermodynamic data will be compared with the results and interpreted in terms of the models developed.

II. ENTROPY OF ORDERED PHASES

The entropy of any alloy phase originates from two basic contributions: configurational and thermal.[10] The entropy of formation of an alloy may thus be considered as being the sum of two terms, such that:

$$\Delta S = \Delta S_c + \Delta S_{th} \tag{2}$$

ΔS_c, the configurational entropy of formation, is the contribution arising from the atomic configuration of the alloy. ΔS_{th}, the thermal entropy of formation, is used here to denote the sum of all other contributions, which will be enumerated later.

Configurational Entropy

Since the configurational entropy of the pure component metals is equal to zero, ΔS_c is merely equal to S_c, the configurational entropy of the alloy, which results from the uncertainty of position or distribution of the unlike atoms on the alloy lattice. It is related to the atomic distribution by the Boltzmann relationship:

$$\Delta S_c = S_c = k \ln \Omega \tag{3}$$

where k is Boltzmann's constant, and Ω is the total number of statistically possible distinguishable distributions of A and B atoms yielding the observed equilibrium energy state of the alloy.

For a perfectly ordered alloy, $\Omega = 1$ and $\Delta S_c = 0$. For a completely random alloy, the number of distinguishable distributions of N_A A atoms and N_B B atoms on N lattice sites, where $N = N_A + N_B$, is given by:[10]

$$\Omega_{random} = \frac{N!}{N_A!\, N_B!} = \frac{N!}{(x_A N)!\ (x_B N)!} \tag{4}$$

where x_A and x_B are the atomic fractions of the components. The configurational entropy calculated from Eqs. (3) and (4) is the ideal entropy of random mixing:[10]

$$\Delta S^{id} = -Nk\,(x_A \ln x_A + x_B \ln x_B) \tag{5}$$

Since $Nk = \frac{N}{N_o} R$, where N_o is Avogadro's number, the ideal entropy for n gram atoms of sites is given by:

$$\Delta S^{id} = -nR\,(x_A \ln x_A + x_B \ln x_B) \tag{6}$$

For any particular composition the configurational entropy of a binary alloy will have a value between zero and that calculated from Eq. (6) depending on the degree of order. For intermediate states of order between those of perfect order and complete disorder, the configurational entropy can be calculated from Eq. (3) if the average atomic distribution is known.

Thermal Entropy

There are three main possible contributions to the thermal entropy of formation of an alloy, vibrational, electronic, and magnetic, which

may be represented by:

$$\Delta S_{th} = \Delta S_{vib} + \Delta S_{el} + \Delta S_{mag} \tag{7}$$

The magnetic effect will contribute only in the case of alloys of one or more transition metals where there is a change in magnetic properties on alloying. Likewise, ΔS_{el}, the contribution due to the conduction electrons, may be expected to be small except in some cases involving transition metals.[11] The thermal entropy of a binary alloy originates primarily from the same source as that of a pure metal, namely the thermal vibration of the atoms.[10] Thus for many alloys, $\Delta S_{th} \approx \Delta S_{vib}$.

For temperatures well above the Debye temperatures of the alloy and its pure components, the vibrational contribution to the entropy of formation is given by the expression:[12]

$$\Delta S_{vib} = 3R \ln \frac{\theta_A^{x_A} \theta_B^{x_B}}{\theta} \approx -3R \frac{\Delta \theta}{\theta} \tag{8}$$

where θ is the mean Debye temperature of the alloy, and

$$\Delta\theta = \theta - (x_A \theta_A + x_B \theta_B) \tag{9}$$

Thus if the Debye temperature and consequently the vibrational spectrum for the alloy lattice are approximately linearly proportional to those of the pure components, $\Delta S_{vib} \approx 0$.

Direct calculation of the various contributions to ΔS_{th} is difficult. The terms may sometimes be deduced through analysis of experimentally determined values of the total entropy of formation.[11-13] In the

absence of changes in atomic configuration, integrated heat capacity data indicate the magnitude of ΔS_{th}, since, in this case:

$$\Delta S_{th} = \int_0^T \frac{\Delta Cp}{T} \, dT \tag{10}$$

where $$\Delta Cp = Cp_{alloy} - (x_A \, Cp_A + x_B \, Cp_B) \tag{11}$$

In the absence of the anomalous effects mentioned, Kopp's law of additivity of heat capacities is often approximately obeyed by ordered alloys, thus $\Delta Cp \approx 0$ and $\Delta S_{th} \approx 0$. For many phases of the types being considered, this result is often observed at temperatures below those at which disordering occurs. Thus for CuZn, $AuCu_3$, and AuCu at 298° K, the values of ΔCp are -0.03, 0.0, and 0.0, and those of ΔS are -0.16, 0.1, and -0.1, respectively.[14]

The treatment introduced in this paper is limited to evaluation of the configurational entropy contribution. However, since changes with composition are being considered, the significant assumption is that the thermal contribution does not change appreciably over small composition ranges, which should be reasonably valid. As will be discussed, comparisons of calculated values with actual data may sometimes be interpreted in terms of a thermal contribution to the entropy.

III. TREATMENT OF THE CsCl-TYPE STRUCTURE

Characteristics of the CsCl-Type Structure

The structure of the CsCl-type superlattice was described in Section I. From the examples listed in Table I, it is evident that this type of ordered phase occurs frequently in binary alloy systems.

Superlattices form only when there is a preference for unlike-atom bonds and thus are to be expected only in systems for which the A-B bond has a lower energy than the average energy of the A-A and B-B bonds. The CsCl-type structure is extremely efficient in maximizing the number of preferred bonds; for in the perfectly ordered superlattice (Fig. 1a), each atom is surrounded by eight unlike atoms as nearest neighbors and there are no like-atom nearest neighbor bonds. In the corresponding random body-centered-cubic structure, each atom will have, on the average, four like-atoms and four unlike-atoms as nearest neighbors. The CsCl-type structure is also well adapted to accommodate two components of considerably different atomic size while retaining cubic symmetry. Dwight[15] pointed out that CsCl-type phases have been found with atomic radius ratios of the components ranging as high as 1.416. Considerable lattice contractions generally accompany formation of CsCl-type phases.[1,15]

The bonding characteristics of the CsCl-type structure contribute to the relatively high stabilities of these phases, many of which have

heats of formation which are unusually large for intermetallic phases.[14] A few of the CsCl-type alloys, e.g. CuZn and CoFe, transform to disordered body-centered-cubic structures before they melt. The majority of the equiatomic alloys however, e.g. AlCo, AlNi, AgMg, AuCd, AuZn, and HgLi, remain highly ordered all the way to their melting temperatures, which in some cases (AlCo, AlNi, and HgLi) are higher than those of both of the pure component metals.

Defect Mechanisms for Departures from Stoichiometry

The CsCl-type structure is most conveniently treated by considering the superlattice to be divided into two interpenetrating simple-cubic sublattices, A and B, as shown in Fig. 2. For one gram atom of alloy there will be N_o total sites, $0.5N_o$ A sites and $0.5N_o$ B sites. In a perfectly ordered equiatomic alloy, AB, all A atoms will be on A sites and all B atoms will be on B sites. Departure from the ideal stoichiometric composition by increasing the atomic fraction of B, for example, could be accomplished by one or more of three possible mechanisms:[16]

(1) substitution of excess B atoms on A sites

(2) creation of vacancies on A sites, or

(3) formation of B atom interstitials

Mechanism (3) can be dismissed for the intermetallic phases being considered because of the large positive energies which would be required.[17] Interstitial solutions in metallic phases are only formed by relatively small atoms, such as C, H, O, and N, in the transition metals.[18]

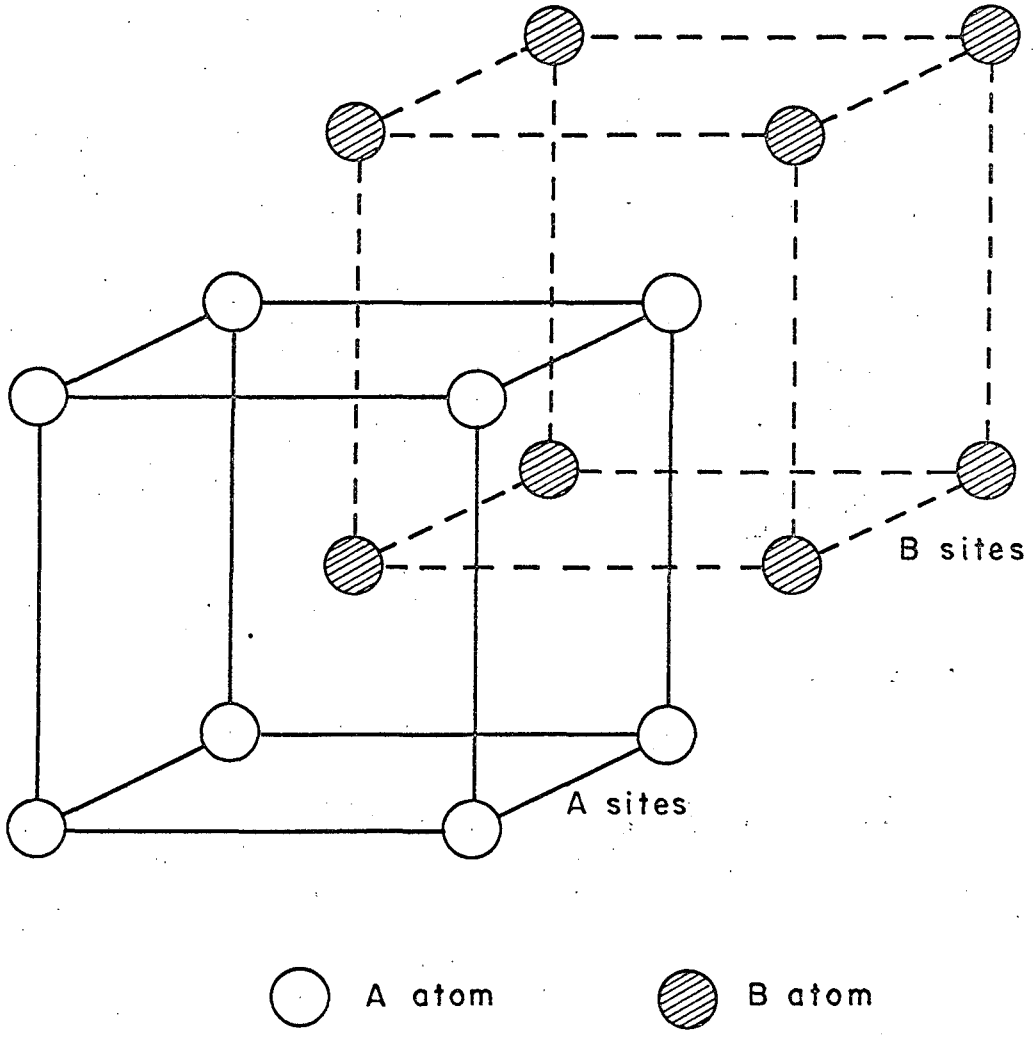


FIG. 2 DESIGNATION OF SUBLATTICES FOR CsCl - TYPE SUPERLATTICE STRUCTURE.

Differentiation between the substitutional and vacancy mechanisms can be obtained from a combination of lattice parameter and density measurements as a function of composition.[19] The vacancy mechanism (2) does occur in some CsCl-type phases. An example is afforded by the β'- AlNi phase which incorporates a different mechanism on either side of the equiatomic composition. On the Ni-rich side excess Ni atoms substitute onto the Al sublattice, but Al-rich compositions are achieved by the creation of vacancies on the Ni sublattice.[20]

The substitutional mechanism (1) is the more common process by which departures from stoichiometry are achieved by phases of the type being considered.[16] Calculations will be limited to cases of this type, although the proposed analysis would also be applicable to the vacancy mechanism.

Special Case with Perfect Order at the Stoichiometric Composition

The first case to be considered is the one for which the degree of order is perfect (W = 1) at the equiatomic composition. The atomic distribution on the sublattices for one gram atom of such an alloy is given in Table II(a). The configurational entropy will be equal to zero. If the atomic fraction of B is increased to a value $x_B = 0.5 + \chi$, and the (χN_o) excess B atoms are assumed to substitute on the A sublattice sites, the distribution will be that given in Table II(b). Throughout the derivation the symbol "χ" will be used to denote a departure from the stoichiometric composition on the B-rich side:

$$\chi = x_B - 0.5 \qquad (12)$$

TABLE II

Atomic Distributions on A and B Sublattices

for CsCl-type Structure with Perfect Order at $\chi = 0$

		Total Atoms	A Sites	B Sites
	No. of Sites	N_o	0.5 N_o	0.5 N_o
(a) $\chi = 0$	A Atoms	0.5 N_o	0.5 N_o	0
	B Atoms	0.5 N_o	0	0.5 N_o
(b) $\chi > 0$	A Atoms	$(0.5 - \chi)$ N_o	$(0.5 - \chi)$ N_o	0
	B Atoms	$(0.5 + \chi)$ N_o	χ N_o	0.5 N_o

In order to calculate the configurational entropy for the non-stoichiometric alloy as a function of χ, it will be assumed that the A and B atoms on the A sites are distributed randomly. The value of S_c for the entire alloy will be merely equal to the ideal entropy of mixing of $(0.5 - \chi)\, N_o$ A atoms and χN_o B atoms on the $0.5N_o$ A sites. Since the B sites are entirely occupied by B atoms, the configurational entropy on the B sublattice will be equal to zero. Application of Eq. (6) to the A sublattice thus gives the total configurational entropy for the phase:

$$S_c = \frac{R}{2} [2\chi \ln 2\chi + (1 - 2\chi) \ln (1 - 2\chi)] \qquad (13)$$

An identical relationship will be obtained for departures from the equiatomic composition on the A-rich side.

The configurational entropy for this case is shown plotted as a function of the deviation from stoichiometry in Fig. 3. At $\chi = 0$, the slopes of the symmetrical curves are infinite, since $\Delta\overline{S}_A \rightarrow \infty$ on the B sublattice and $\Delta\overline{S}_B \rightarrow \infty$ on the A sublattice as $\chi \rightarrow 0$. Thus, for the corresponding limiting values of the partial molar Gibbs energies: as $\chi \rightarrow 0$, $\Delta\overline{G}_A \rightarrow -\infty$ on the B sublattice and $\Delta\overline{G}_B \rightarrow -\infty$ on the A sublattice because of the contributions of the $(-T\Delta\overline{S}_i)$ terms, regardless of the energy required for the substitutions. From this it can be concluded that the perfectly ordered state at $\chi = 0$ can not possibly exist at any temperature other than 0°K. Consequently, the proper treatment, applicable to a finite temperature, must incorporate the existence of some degree of disorder at $\chi = 0$.

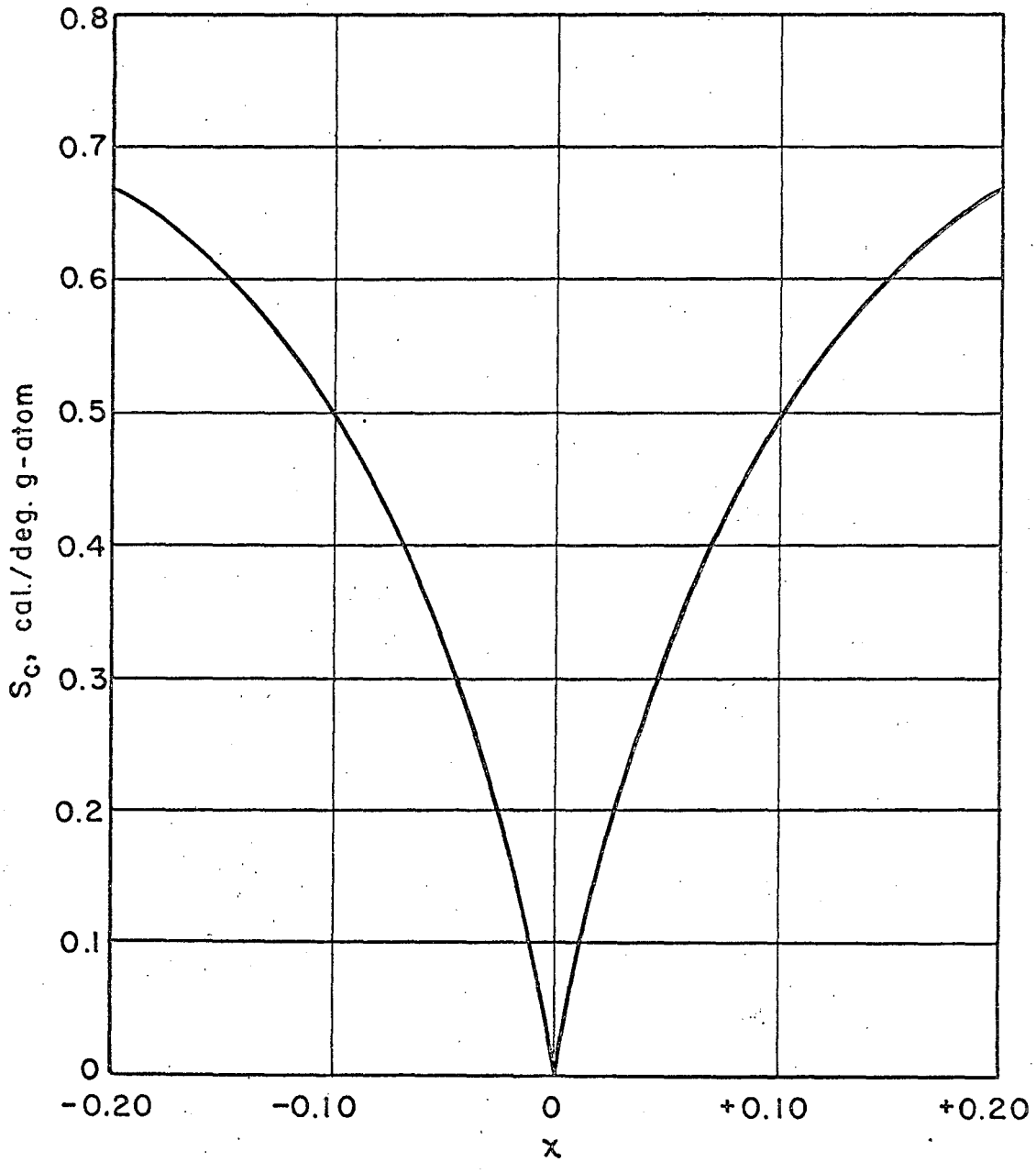


FIG. 3 CONFIGURATIONAL ENTROPY OF A CsCl-TYPE PHASE WITH PERFECT ORDER AT $x = 0$.

General Case with Some Disorder at the Stoichiometric Composition

The amount of disorder at $\chi = 0$ will be specified by the parameter α, as defined by Schottky and Wagner:[8]

$$\alpha = \left(\frac{N_{A(B)}}{N_o}\right)_{\chi=0} = \left(\frac{N_{B(A)}}{N_o}\right)_{\chi=0} \tag{14}$$

where $N_{i(j)}$ is the number of i atoms on j sites. The atomic distribution on the sublattices for one gram atom of alloy where $\chi = 0$ is given in Table III(a). It will be assumed that the atoms on each individual sublattice are randomly distributed on the sites of that sublattice. This assumption should be especially valid for this structure, since there are no nearest neighbor bonds between atoms on the same sublattice. The sum of the ideal entropies of mixing on the two separate sublattices, calculated using Eq. (6), is then the configurational entropy of the alloy:

$$S_c = -R[2\alpha \ln 2\alpha + (1 - 2\alpha) \ln (1 - 2\alpha)] \tag{15}$$

For $\chi > 0$ the equilibrium distributions will be specified in terms of a composition dependent variable, z, which is defined as the number of gram atoms of A atoms on B sites at any composition, i.e.:

$$z = \frac{N_{A(B)}}{N_o} \tag{16}$$

Comparison of Eqs. (14) and (16) reveals that α and z become identical at $\chi = 0$; thus:

$$\alpha = z_{(\chi = 0)} \tag{17}$$

TABLE III

Atomic Distributions on A and B Sublattices

for CsCl-type Structure with Some Disorder at $\chi = 0$

		Total Atoms	A Sites	B Sites
	No. of Sites	N_o	$0.5\ N_o$	$0.5\ N_o$
(a) $\chi = 0$	A Atoms	$0.5\ N_o$	$(0.5 - \alpha)\ N_o$	$\alpha\ N_o$
	B Atoms	$0.5\ N_o$	$\alpha\ N_o$	$(0.5 - \alpha)\ N_o$
(b) $\chi > 0$	A Atoms	$(0.5 - \chi)\ N_o$	$(0.5 - \chi - z)\ N_o$	$z\ N_o$
	B Atoms	$(0.5 + \chi)\ N_o$	$(\chi + z)\ N_o$	$(0.5 - z)\ N_o$

From the definition of z and the required balances of atoms and sites, the atomic distribution on the sublattices when $\chi > 0$ is expressed in terms of χ and z as shown in Table III(b). Again assuming a random distribution of atoms on each individual sublattice and using Eq. (6), the configurational entropy of the alloy where $\chi > 0$ is given by:

$$S_c = -\frac{R}{2}\left[2z \ln 2z + (1-2z) \ln (1-2z)\right.$$

$$\left. + 2(\chi+z) \ln 2(\chi+z) + (1-2\chi-2z) \ln (1-2\chi-2z)\right] \qquad (18)$$

Determination of the Equilibrium Distribution

In order to find S_c from Eq. (18) it is first necessary to find how z varies with χ. This will be done by minimizing the Gibb's energy of the alloy with respect to the distribution function, z, for any fixed value of χ. The Gibb's energy of the alloy is given by:

$$G = H - TS \qquad (19)$$

where H is the enthalpy and S is the absolute entropy of the alloy. From the relations $H = E + PV$ and $S = S_c + S_{th}$, G becomes:

$$G = E + PV - T(S_c + S_{th}) \qquad (20)$$

where E is the internal energy and V is the volume of the alloy. The equilibrium value of z at any composition is the one for which the Gibbs energy has the minimum value. Therefore, at equilibrium:

$$\left(\frac{\partial G}{\partial z}\right)_\chi = \left(\frac{\partial E}{\partial z}\right)_\chi + P\left(\frac{\partial V}{\partial z}\right)_\chi - T\left[\left(\frac{\partial S_c}{\partial z}\right)_\chi + \left(\frac{\partial S_{th}}{\partial z}\right)_\chi\right] = 0 \qquad (21)$$

where constancy of T and P, while not explicitly expressed in the subscripts, is of course implied. Ignoring the volume term, which is negligible, and assuming that $\left(\frac{\partial S_{th}}{\partial z}\right)_{\chi} = 0$; the condition for the equilibrium distribution becomes:

$$\left(\frac{\partial E}{\partial z}\right)_{\chi} = T\left(\frac{\partial S_c}{\partial z}\right)_{\chi} \tag{22}$$

Making the "zeroth-order" approximations of the quasi-chemical treatment, i.e., considering only the nearest neighbor bonds and assuming constancy of the interatomic bonding energies with composition, the energy of the alloy may be evaluated from the expression:

$$E = n_{AA}\,\epsilon_{AA} + n_{BB}\,\epsilon_{BB} + n_{AB}\,\epsilon_{AB} \tag{23}$$

where n_{AA} is the number of A-A bonds and ϵ_{AA} is the energy of an A-A bond, etc. The number of bonds of each type may be expressed in terms of the coordination between the sublattices, yielding:

$$E = 8\Big[N_{A(A)}x_{A(B)}\epsilon_{AA} + N_{B(A)}x_{B(B)}\epsilon_{BB} + (N_{A(A)}x_{B(B)} + N_{B(A)}x_{A(B)})\epsilon_{AB}\Big] \tag{24}$$

where again, $N_{i(j)}$ is the number of i atoms on j sites and $x_{i(j)}$ is the atomic fraction of i atoms on j sites. From the atomic distributions given in Table III(b), the values of $N_{i(j)}$ and $x_{i(j)}$ are substituted into Eq. (24), which gives, after simplification, for the energy of one gram atom of alloy:

$$E = 8\,N_o\left[(4z^2 + 4\chi z - 2z)V_{AB} - \chi(\epsilon_{AB} - \epsilon_{BB}) + \tfrac{1}{2}\epsilon_{AB}\right] \tag{25}$$

where V_{AB}, the nearest neighbor interaction parameter, is defined by the expression,

$$V_{AB} = \epsilon_{AB} - \frac{\epsilon_{AA} + \epsilon_{BB}}{2} \tag{26}$$

From Eq. (25), for any given fixed composition,

$$\left(\frac{\partial E}{\partial z}\right)_{\chi} = -16\, N_o V_{AB}(1 - 2\chi - 4z) \tag{27}$$

Similarly, from Eq. (18),

$$\left(\frac{\partial S_c}{\partial z}\right)_{\chi} = -R[\ln 2z - \ln(1 - 2z) + \ln 2(\chi + z) - \ln(1 - 2\chi - 2z)] \tag{28}$$

Application of the condition for equilibrium, Eq. (22), to Eqs. (27) and (28) yields the expression:

$$16N_o V_{AB}(1 - 2\chi - 4z) = RT \ln \frac{4z(\chi + z)}{(1 - 2z)(1 - 2\chi - 2z)} \tag{29}$$

The constant parameters in Eq. (29) may be related to α, the distribution function at $\chi = 0$ (Eq. 14). Solving Eq. (29) for the condition that when $\chi = 0$, $z = \alpha$ (Eq. 17), yields:

$$\frac{16N_o V_{AB}}{RT} = \frac{2}{1 - 4\alpha} \ln \frac{2\alpha}{1 - 2\alpha} \tag{30}$$

Substituting Eq. (30) into Eq. (29), and rearranging, yields the desired relationship between z and χ for discrete values of the equiatomic composition distribution parameter, α:

$$(1 - 2\chi - 4z)\frac{2}{1 - 4\alpha}\ln\frac{2\alpha}{1 - 2\alpha} = \ln\frac{4z(\chi + z)}{(1 - 2\chi - 4z) + 4z(\chi + z)} \qquad (31)$$

Eq. (31) cannot be solved explicitly for z, but graphical solutions can be obtained by plotting the left and right hand sides of the equation vs. z for given values of α and χ, as shown in Fig. 4. For χ below a critical limiting value, χ_ℓ, there will be two solutions for z. The lower-valued of the two is the desired solution for the ordered configuration; while the higher-valued solution for z, for which both sides of Eq. (31) are equal to zero, corresponds to the completely random configuration for which $1 - 2\chi - 4z = 0$. It will be shown later that the first solution corresponds to a minimum in the G vs. z curve, and the second, to a maximum value of G. For values of $\chi \geq \chi_\ell$, there is only one possible solution, given by $1 - 2\chi - 4z = 0$, which corresponds to random mixing. The Gibbs energy curve will have but one extremum when χ reaches its critical value; therefore at $\chi = \chi_\ell$:

$$\left(\frac{\partial^2 G}{\partial z^2}\right)_{\chi_\ell} = 0 \qquad (32)$$

From Eqs. (27, 28, 30 and 32), the critical value of χ is given by:

$$\chi_\ell = \left[.25 + \left(\frac{2}{1 - 4\alpha}\ln\frac{2\alpha}{1 - 2\alpha}\right)^{-1}\right]^{\frac{1}{2}} \qquad (33)$$

Solutions of Eq. (31) may readily be found by a computer using an iteration procedure. Solutions for three different values of α are given by the z vs. χ curves in Fig. 5. At $\chi = 0$, $z = \alpha$; following which the values of z first decrease with χ, reach a minimum, then increase

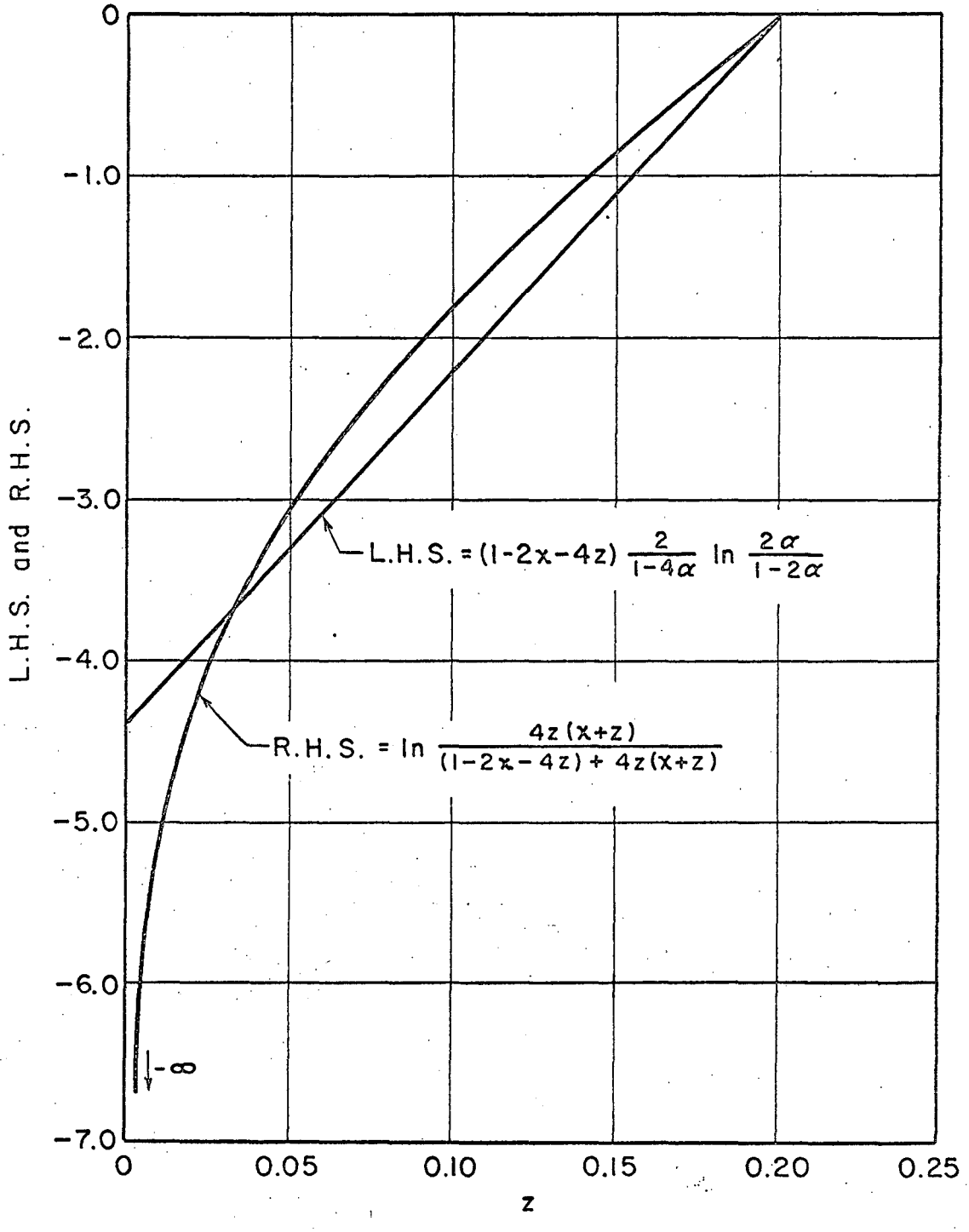


FIG. 4 GRAPHICAL SOLUTION OF DISTRIBUTION EQUATION FOR $\alpha = 0.05$, $x = 0.010$.

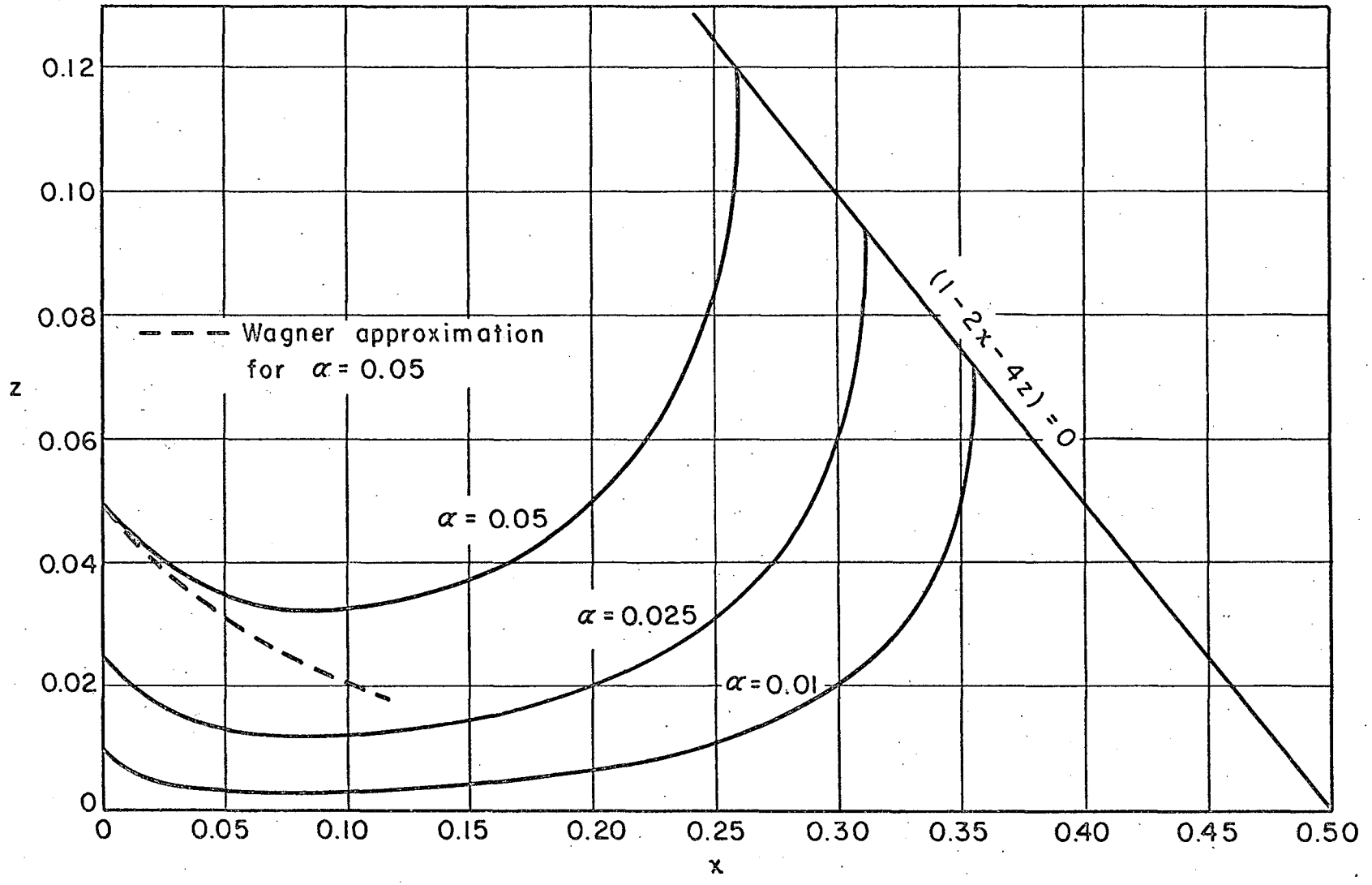


FIG. 5 VARIATION OF z WITH x FOR THREE DIFFERENT VALUES OF α.

more and more steeply until χ reaches the value χ_ℓ, at and above which the solution falls on the random solution line, $1 - 2\chi - 4z = 0$. The base line of Fig. 5, $z = 0$, corresponds to the hypothetical case where $\alpha = 0$.

Solution of the Entropy Equation

From solutions of Eq. (31), S_c vs. χ curves corresponding to specified values of α may be evaluated from Eq. (18). Symmetrically identical relationships will of course be obtained for departures from stoichiometry on the A-rich side. Calculated S_c curves for four different values of α are shown in Fig. 6. The slopes of the curves are continuous and equal to 0 at $\chi = 0$.

Relationship to the Bragg and Williams Parameter

As would be expected, α is related to the Bragg and Williams[2] order parameter, W, defined in Eq. (1). At the equiatomic composition, $W = \frac{r_A - 0.5}{0.5}$. From Table III(a), $r_A = 1 - 2\alpha$. Therefore, for the CsCl-type superlattice:

$$W = 1 - 4\alpha \tag{34}$$

Also, the Bragg and Williams treatment for this structure results in the following relationship between temperature and degree of order at $\chi = 0$:

$$2W \frac{T_c}{T} = \ln \frac{1 + W}{1 - W} \tag{35}$$

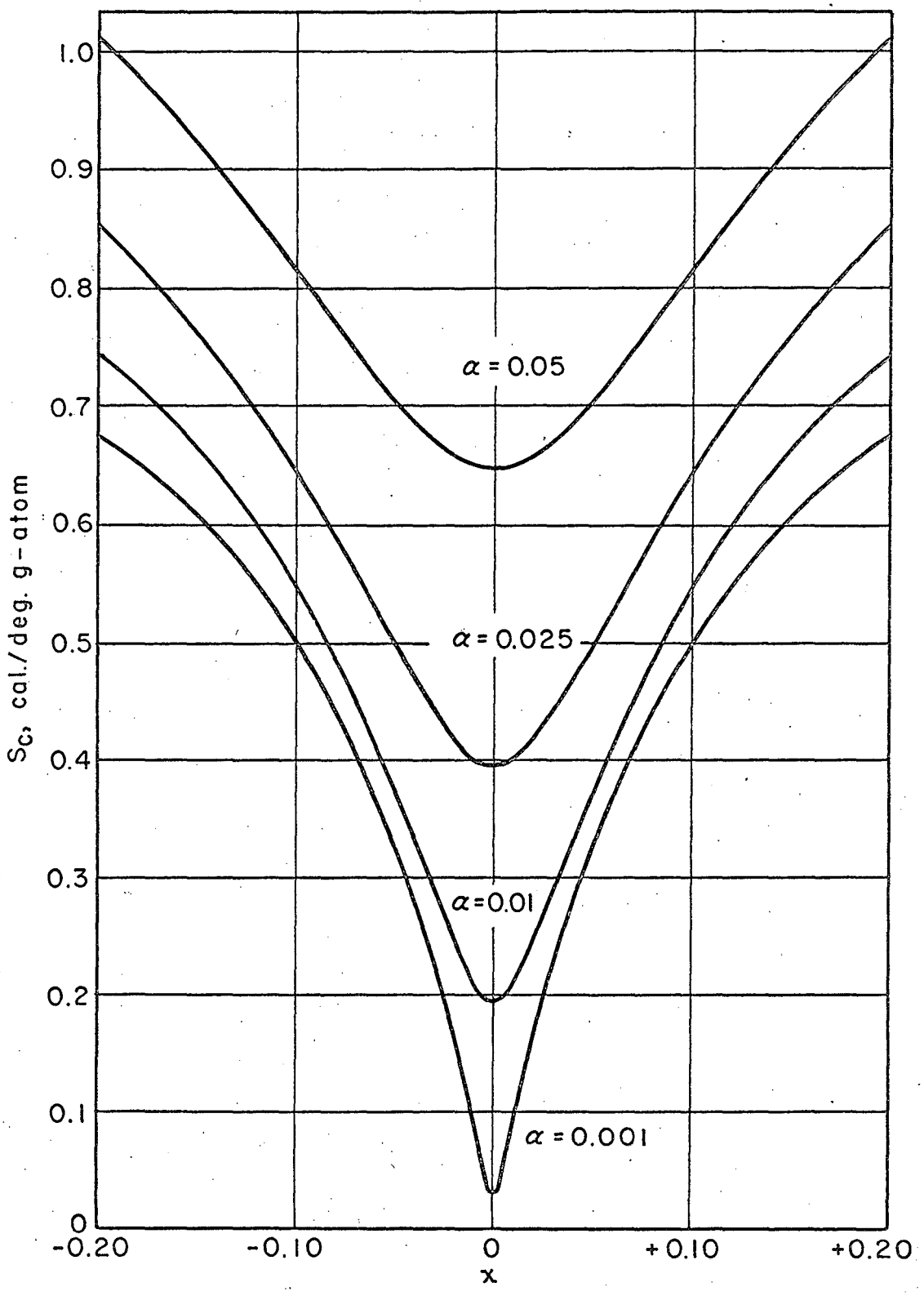


FIG. 6 CONFIGURATIONAL ENTROPY OF CsCl-TYPE PHASE FOR DIFFERENT VALUES OF α.

From Eqs. (34) and (35) is obtained:

$$\frac{2}{1 - 4\alpha} \ln \frac{2\alpha}{1 - 2\alpha} = -4\left(\frac{T}{T_c}\right)^{-1} \tag{36}$$

The left hand side of Eq. (36) is the constant factor appearing in Eq. (31). Table IV lists corresponding values of this factor, W, and $\frac{T}{T_c}$ for several values of α.

Relation to the Wagner Approximation

The solution of Wagner and Schottky[8] for the case of substitutional defects was limited to small concentrations of defects and thus to small departures from stoichiometry. Using the symbology employed in this paper, their distribution equation for the CsCl-type structure may be written as

$$z(\chi + z) = \alpha^2 \tag{37}$$

which is an approximation for the exact solution given by Eq. (31). A comparison of the two equations for $\alpha = 0.05$ is given in Fig. 5. The approximate solution appears to be reasonably valid for $\chi < 0.02$.

Solution of the Gibbs Energy Equation

The Gibbs energy of formation of the alloy is given by:

$$\Delta G = \Delta H - T\Delta S \approx \Delta E - TS_c \tag{38}$$

The energy of formation is given by:

$$\Delta E = E - x_A E_A - x_B E_B = E - (.5 - \chi)E_A - (.5 + \chi)E_B \tag{39}$$

TABLE IV

Distribution Parameters for CsCl-Type Structure

α	$\frac{2\alpha}{1-4\alpha} \ln \frac{2\alpha}{1-2\alpha}$	W	$\frac{T}{T_c}$
0	$-\infty$	1.000	0
0.001	-12.476	0.996	0.321
0.005	- 9.378	0.980	0.427
0.010	- 8.107	0.960	0.493
0.015	- 7.396	0.940	0.541
0.020	- 6.909	0.920	0.579
0.025	- 6.544	0.900	0.611
0.050	- 5.493	0.800	0.728
0.100	- 4.621	0.600	0.866
0.250	- 4.000	0	1.000

where E, the internal energy of the alloy, is given by Eq. (25), and E_A and E_B are the internal energies of the pure components. In order to obtain an expression for ΔE in terms of χ and z, it is necessary that E_A and E_B refer to the pure metals with the body-centered-cubic coordination number of eight, the same as that of the CsCl-type phase. For pure metals which exist only in some other structure, the difference in energy between the actual standard state and the hypothetical body-centered-cubic state must be estimated. Since only changes of ΔE with composition in the ordered phase are being considered, however, uncertainties in the reference state will not be too significant. Again considering only the nearest neighbor bonds, the energies of the pure components will be given by:

$$\left.\begin{aligned} E_A &= 4N_o\epsilon_{AA} \\ E_B &= 4N_o\epsilon_{BB} \end{aligned}\right\} \qquad (40)$$

Combining Eqs. (29, 39 and 40) gives the following expression for ΔE:

$$\Delta E = 4N_o V_{AB}(8z^2 + 8\chi z - 2\chi - 4z + 1) \qquad (41)$$

From Eqs. (30, 38 and 41), the equation for the Gibbs energy of formation then becomes:

$$\frac{\Delta G}{N_o V_{AB}} = 4(8z^2 + 8\chi z - 2\chi - 4z + 1) - \frac{16}{R}\left(\frac{2}{1-4\alpha}\ln\frac{2\alpha}{1-2\alpha}\right)^{-1} S_c \qquad (42)$$

where S_c is evaluated as already discussed.

For specific values of α and χ, Eq. (42) may be solved for arbitrary values of z to determine how the Gibbs energy varies with configuration for a fixed composition in the ordered phase. The results of such calculations for a series of compositions in the ordered phase in which $\alpha = 0.01$ are shown by the curves in Fig. 7. The minima and maxima on the curves correspond to the two possible solutions to Eq. (31) mentioned previously. As χ increases, the difference between the Gibbs energies of the equilibrium and random states decreases, until at χ_ℓ the random solution has the minimum value of ΔG.

Equation (42) may also be used to calculate the variation of ΔG with χ for the equilibrium values of z. The ΔG vs. χ curve for the ordered phase corresponding to $\alpha = 0.01$ is shown, plotted in units of $N_o V_{AB}$, in Fig. 8. Also shown is the ΔG vs. χ curve for the random regular solution for the same temperature; i.e. $T = 0.493\ T_c$, which is equivalent to $\alpha = 0.01$. The two curves become identical at $\chi_\ell = \pm 0.356$.

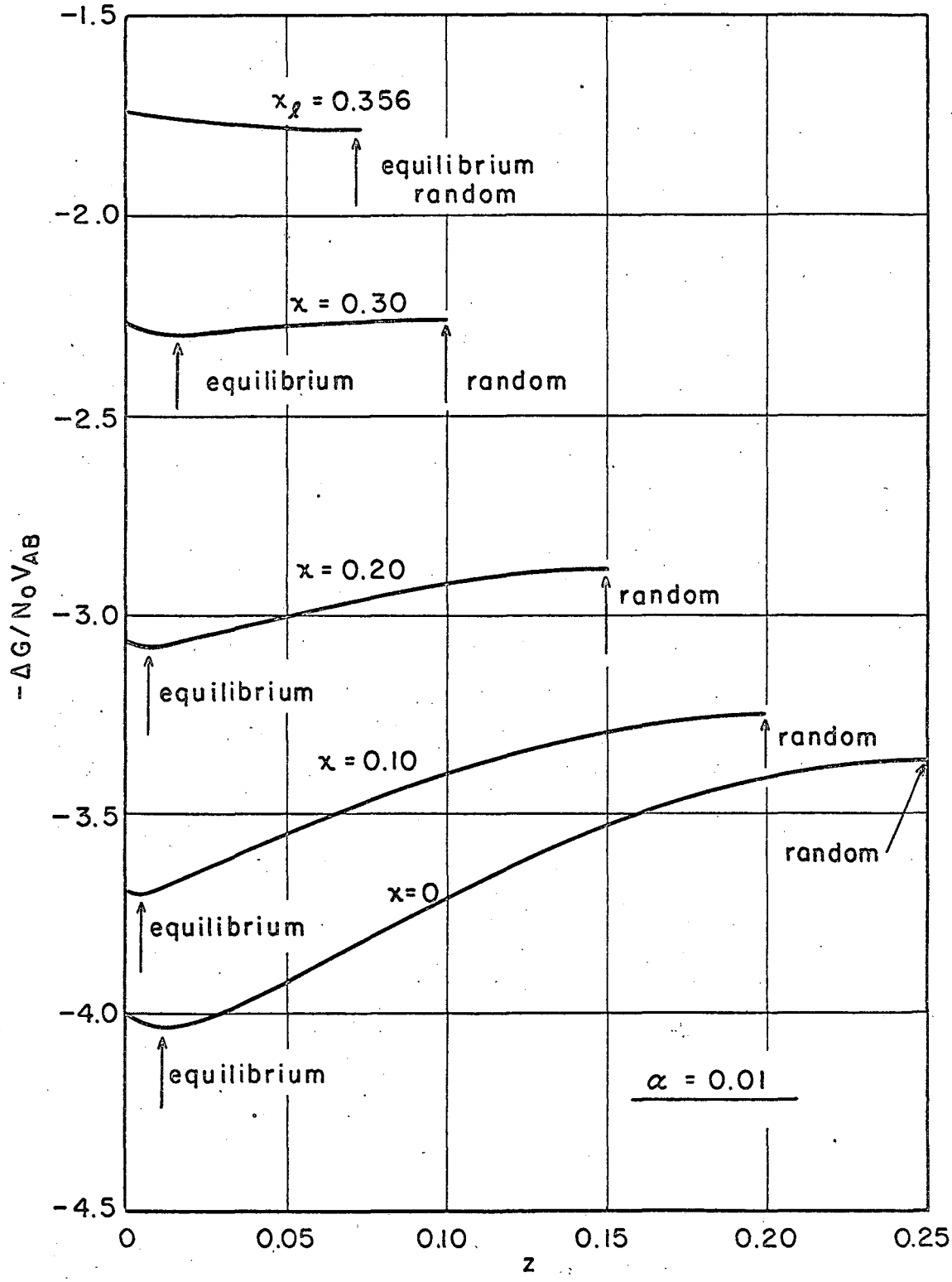


FIG. 7 VARIATION OF GIBBS ENERGY WITH CONFIGURATION IN CsCl-TYPE PHASE WITH $\alpha = 0.01$ FOR VARIOUS VALUES OF x.

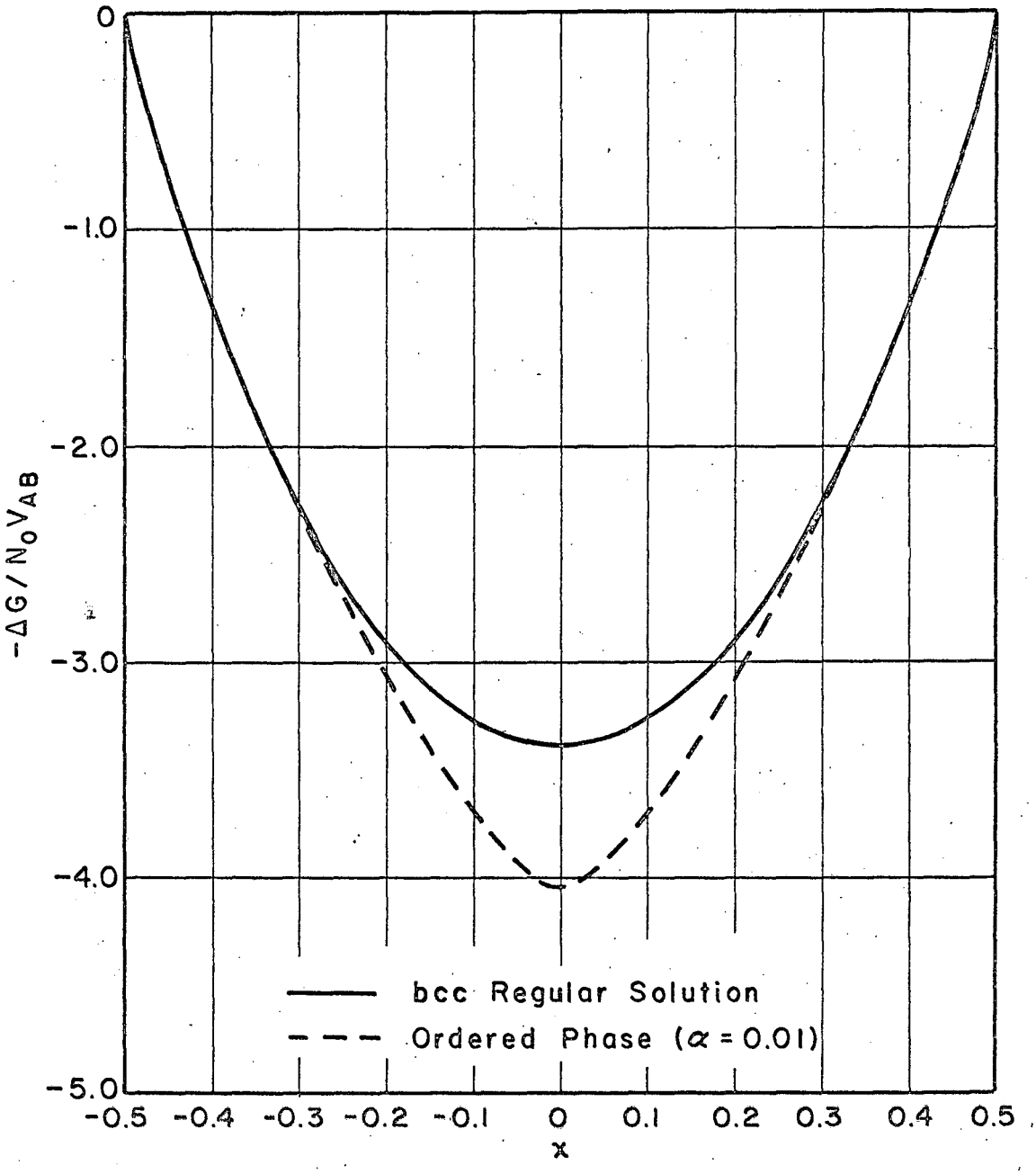


FIG. 8 GIBBS ENERGY CURVES FOR bcc REGULAR SOLUTION AND CsCl-TYPE ORDERED PHASE WITH $\alpha = 0.01$.

IV. TREATMENT OF THE AuCu-TYPE STRUCTURE

An AB phase alloy having the AuCu-type structure (Fig. 1b) may be divided into two interpenetrating simple tetragonal sublattices of A sites and B sites in a manner similar to that for the CsCl-type superlattice. The atomic distributions on the sublattices for $\chi = 0$ and and $\chi > 0$ will then be the same as those shown in Table III, and the entropy expressions will be identical with those of Eqs. (15) and (18).

There is, however, a significant difference in the bonding characteristics for this close-packed structure. In the previous case all nearest neighbor bonds are between atoms on different sublattices. In the AuCu-type structure, each A-site atom has four nearest neighbors on A sites and eight on B sites, and each B-site atom has four nearest neighbors on B sites and eight on A sites. This results in a difference in the energy, and consequently the Gibbs energy, relationships for this structure. The resulting equilibrium distribution equation, however, remains the same as that of Eq. (31), and the S_c vs. χ curves are identical to those of Fig. 6.

The pertinent equations resulting from the treatment of the AuCu-type structure are summarized below. Expressions which are identical to those obtained for the CsCl-type structure are merely indicated by reference to the applicable equations. Definitions and symbols are the same as in the preceeding section.

S_c ($\chi = 0$) : Given by Eq. (15)

S_c ($\chi > 0$) : Given by Eq. (18)

$\left(\frac{\partial S_c}{\partial z}\right)_\chi$: Given by Eq. (28)

$$E = N_o \left[8(2z^2 - \chi^2 + 2\chi z - z)V_{AB} + 4(1 - \chi)\epsilon_{AB} + (1 - 4\chi)\epsilon_{AA} + (1 + 8\chi)\epsilon_{BB}\right] \tag{43}$$

$$\left(\frac{\partial E}{\partial z}\right)_\chi = -8N_o V_{AB}(1 - 2\chi - 4z) \tag{44}$$

$$\frac{8N_o V_{AB}}{RT} = \frac{2}{1 - 4\alpha} \ln \frac{2\alpha}{1 - 2\alpha} = -4\left(\frac{T}{T_c}\right)^{-1} \tag{45}$$

Equilibrium distribution equation : Given by Eq. (31)

W : Given by Eq. (34)

$$\Delta E = 4N_o V_{AB}(4z^2 - 2\chi^2 + 4\chi z - \chi - 2z + 1) \tag{46}$$

$$\frac{\Delta G}{N_o V_{AB}} = 4(4z^2 - 2\chi^2 + 4\chi z - \chi - 2z + 1) - \frac{8}{R}\left(\frac{2}{1 - 4\alpha} \ln \frac{2\alpha}{1 - 2\alpha}\right)^{-1} S_c \tag{47}$$

The distribution parameters for various values of α will be same as those in Table IV.

V. TREATMENT OF THE $AuCu_3$-TYPE STRUCTURE

The $AuCu_3$-type superlattice structure (Fig. 1c) may be divided into four interpenetrating simple cubic sublattices, three of one type and one of the other. For one gram atom of alloy with the ideal stoichiometric composition A_3B, there will be $0.75\ N_o$ A sites and $0.25\ N_o$ B sites. The atomic distributions on the sublattices for $\chi = 0$ and $\chi > 0$, where now,

$$\chi = \chi_B - 0.25 \tag{48}$$

and α and z are defined as in the previous treatments, are given in Table V. Each A-site atom has eight nearest neighbors on A sites and four nearest neighbors on B sites, and each B-site atom has twelve nearest neighbors on A sites only.

The $AuCu_3$-type structure has been treated by the procedures described in Section III. The resulting pertinent expressions are summarized below, employing the same definitions and symbols already established.

For $\chi = 0$:

$$S_c = -R\left[\alpha \ln \frac{16}{3}\,\alpha^2 + (.75-\alpha)\ln\left(1-\frac{4}{3}\alpha\right) + (.25-\alpha)\ln(1-4\alpha)\right] \tag{49}$$

TABLE V

Atomic Distributions on Sublattices for A_3B Phase

Having the $AuCu_3$-type Structure with Some Disorder at $\chi = 0$

		Total Atoms	A Sites	B Sites
	No. of Sites	N_o	$0.75\ N_o$	$0.25\ N_o$
(a) $\chi = 0$	A Atoms	$0.75\ N_o$	$(0.75 - \alpha)\ N_o$	$\alpha\ N_o$
	B Atoms	$0.25\ N_o$	$\alpha\ N_o$	$(0.25 - \alpha)\ N_o$
(b) $\chi > 0$	A Atoms	$(0.75 - \chi)\ N_o$	$(0.75 - \chi - z)\ N_o$	$z\ N_o$
	B Atoms	$(0.25 + \chi)\ N_o$	$(x + z)\ N_o$	$(0.25 - z)\ N_o$

For $\chi > 0$:

$$S_c = -R\left[z \ln 4z + (.25-z) \ln (1-4z) + (\chi+z) \ln \frac{4}{3}(\chi+z) + (.75-\chi-z) \ln \frac{1}{3}(3-4\chi-4z)\right] \quad (50)$$

$$\left(\frac{\partial S_c}{\partial z}\right)_\chi = -R \ln \frac{16z(\chi+z)}{(1-4z)(3-4\chi-4z)} \quad (51)$$

$$E = N_o\left[\frac{32}{3}(2z^2-\chi^2+\chi z)V_{AB} + (4\chi-8z+3)V_{AB} + \frac{3}{2}(3-4\chi)\epsilon_{AA} + \frac{3}{2}(1+4\chi)\epsilon_{BB}\right] \quad (52)$$

$$\left(\frac{\partial E}{\partial z}\right)_\chi = -\frac{8}{3} N_o V_{AB} (3-4\chi-16z) \quad (53)$$

$$\frac{8N_oV_{AB}}{3RT} = \frac{1}{3-16\alpha} \ln \frac{16\alpha^2}{3-16\alpha+16\alpha^2} \quad (54)$$

$$(3-4\chi-16z)\frac{1}{3-16\alpha} \ln \frac{16\alpha^2}{3-16\alpha+16\alpha^2} = \ln \frac{16z(\chi+z)}{(3-4\chi-16z)+16z(\chi+z)} \quad (55)$$

$$W = 1 - \frac{16}{3}\alpha \quad (56)$$

$$\Delta E = N_oV_{AB}\left[\frac{32}{3}(2z-\chi)(\chi+z) + 4\chi-8z+3\right] \quad (57)$$

$$\frac{\Delta G}{N_oV_{AB}} = \left[\frac{32}{3}(2z-\chi)(\chi+z) + 4\chi-8z+3\right] - \frac{8}{3R}\left(\frac{1}{3-16\alpha} \ln \frac{16\alpha^2}{3-16\alpha+16\alpha^2}\right)^{-1} S_c \quad (58)$$

The distribution parameters for various values of α are given in Table VI. According to results of the Bragg and Williams' treatment

TABLE VI

Distribution Parameters for $AuCu_3$-Type Structure

α	$\frac{1}{3-16\alpha} \ln \frac{16\alpha^2}{3-16\alpha+16\alpha^2}$	W
0	$-\infty$	1.000
0.001	-4.067	0.995
0.005	-3.046	0.973
0.010	-2.635	0.947
0.015	-2.407	0.920
0.020	-2.254	0.893
0.025	-2.140	0.867
0.050	-1.830	0.733
0.1007	-1.625	0.463

for the stoichiometric alloy as a function of temperature,[21] the highest permissible value of W is 0.463, corresponding to $\alpha = 0.1007$. At the temperature yielding this degree of order, the stoichiometric alloy is predicted by that treatment to undergo a first-order transition to the disordered state. Corresponding discontinuities occur in the presently derived functions at limiting values of χ, depending on the value of α, beyond which the random configuration becomes the stable one. For $\alpha = 0.1007$ the discontinuity is at $\chi = 0$.

Because of the unsymmetrical nature of the $AuCu_3$-type structure, nonsymmetrical solutions for S_c result for $\chi < 0$ and $\chi > 0$. Calculated S_c vs. χ curves for three different values of α are shown in Fig. 9.

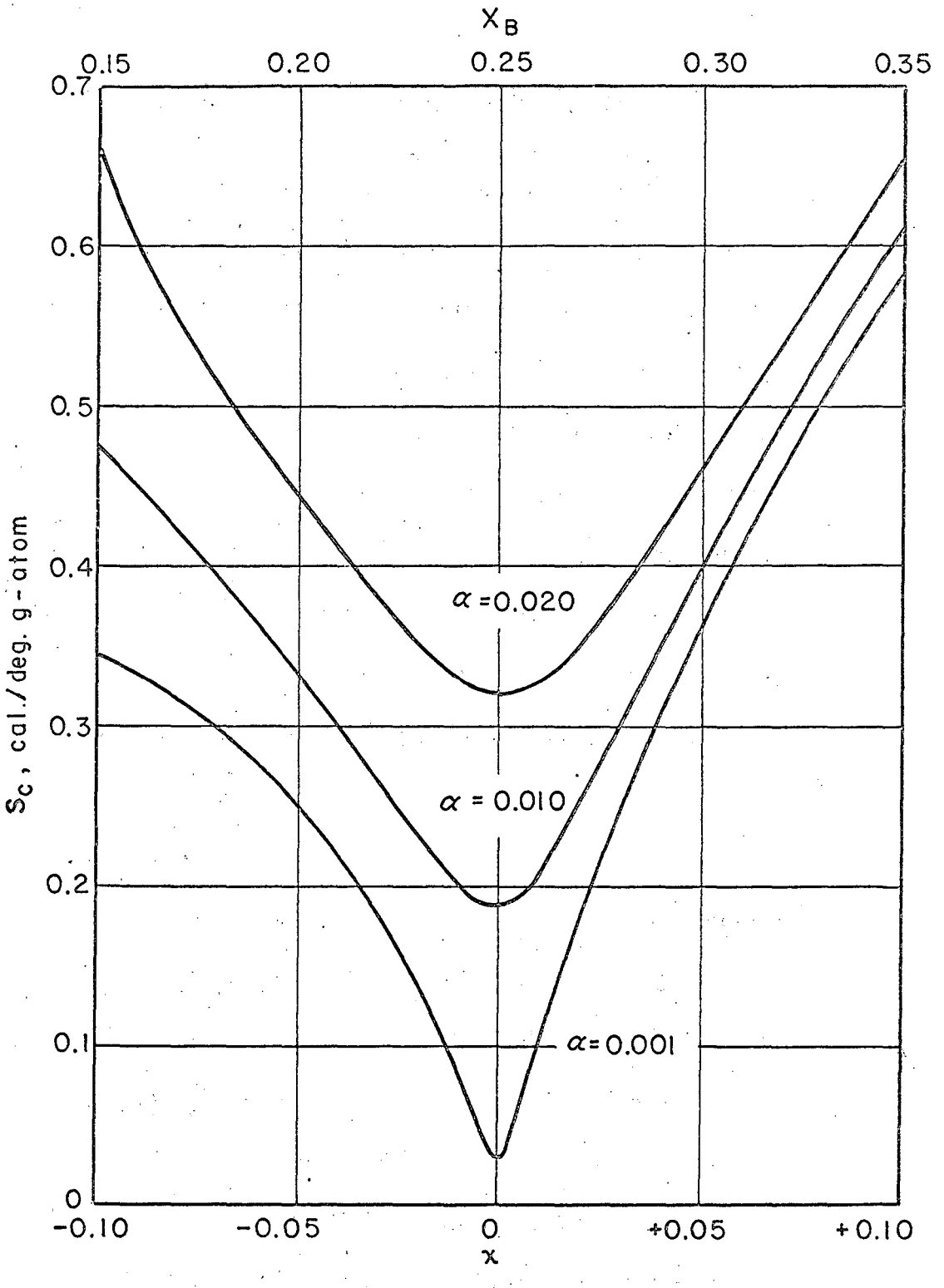


FIG. 9 CONFIGURATIONAL ENTROPY OF $AuCu_3$-TYPE A_3B PHASE FOR DIFFERENT VALUES OF α.

VI. COMPARISONS WITH MEASURED VALUES

Experimental data from which the variation of ΔS with composition in ordered phases may be evaluated are quite limited. Comparisons are possible, however, between the derived expressions for S_c and the ΔS values for the AgMg, AuCd, and AuCu phases taken from the evaluations of Hultgren, Orr, Anderson, and Kelley.[14] The most valid method of correlation would appear to be by means of the shapes of the ΔS vs. composition curves, differences between the absolute values of ΔS_{actual} and S_c then being interpreted in terms of a thermal contribution to the entropy of formation.

The values of ΔS for two CsCl-type phases, β' - AgMg at 773°K and β' - AuCd at 700°K, are plotted in Figs. 10 and 11, respectively. The terminal values apply to the boundaries of the phases at those temperatures.[14, 22] The data for the β' - AgMg phase[14] are seen to be represented reasonably well by the CsCl-type S_c curve for $\alpha = 0.015$, assuming $\Delta S_{th} \approx 0$. From Table IV it is seen that this value of α corresponds to $W = 0.94$ and $\frac{T}{T_c} = 0.541$. The resulting calculated critical temperature, $T_c = 1430°K$, is consistent with the fact that the equiatomic alloy retains a high degree of order to its melting point, 1090°K.[22] From lattice parameter and density measurements, Hagel and Westbrook[23] showed AgMg to disorder by means of the substitutional mechanism on both sides of stoichiometry.

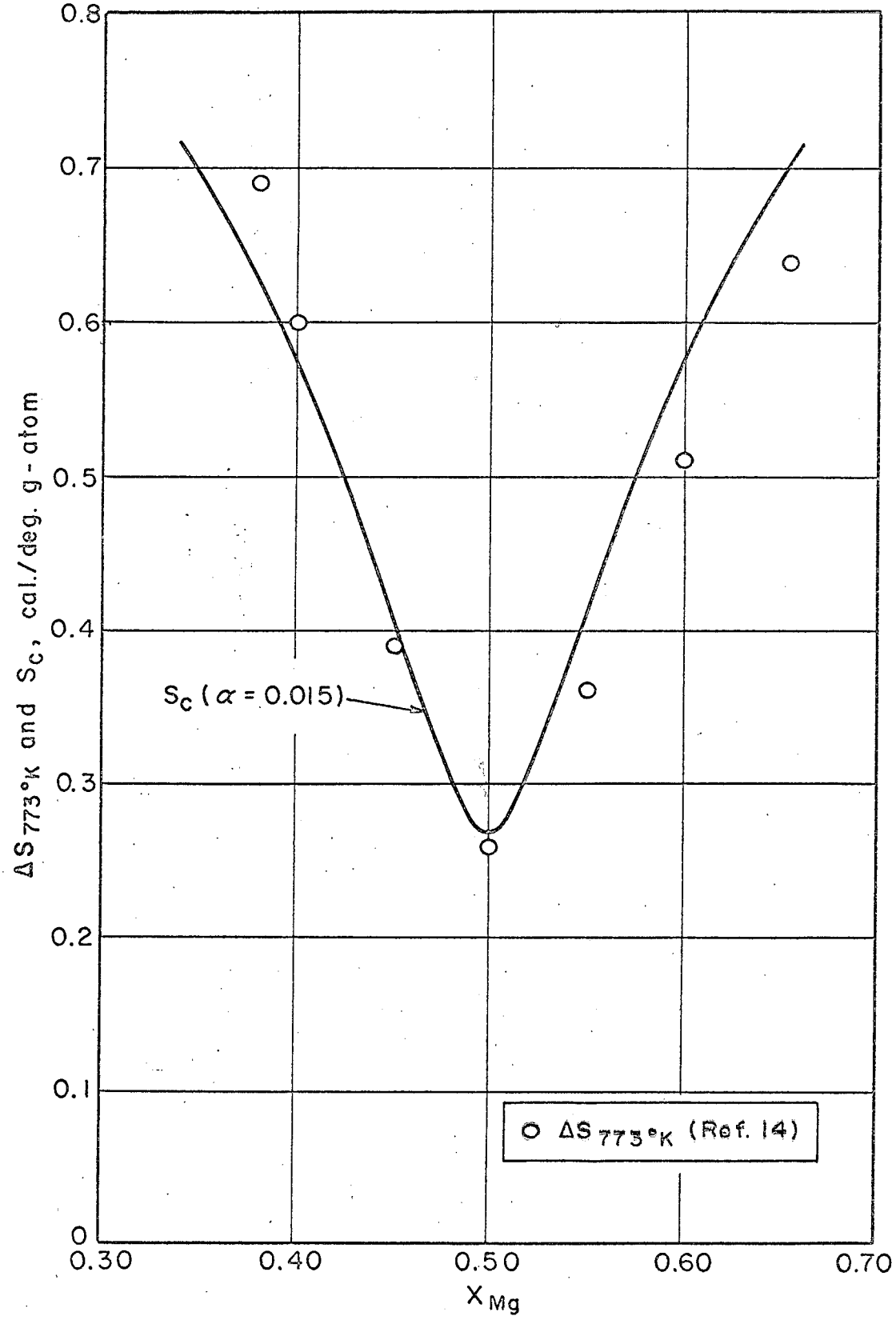


FIG. 10 CORRELATION OF ENTROPY DATA FOR THE β'-AgMg PHASE AT 773°K.

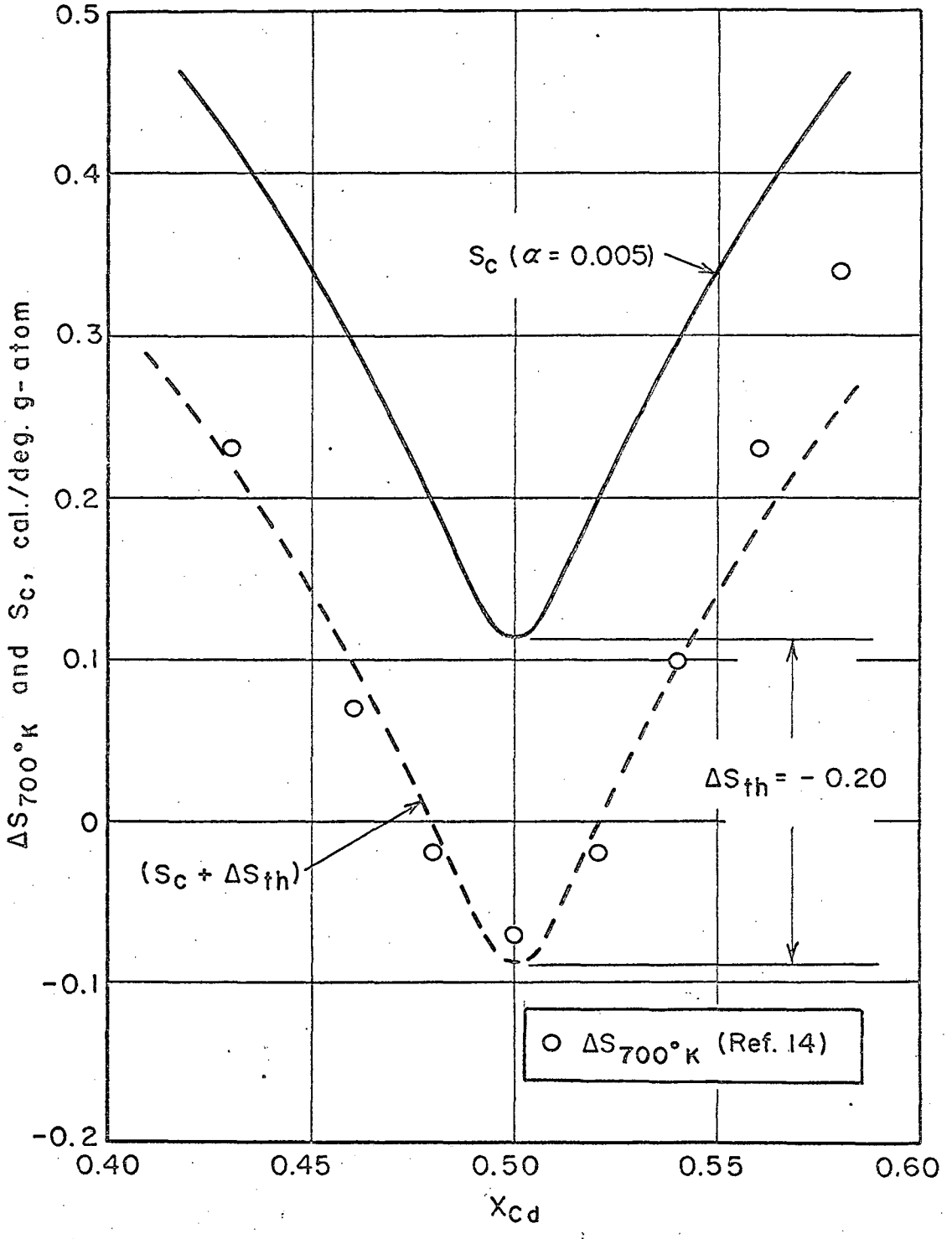


FIG. II CORRELATION OF ENTROPY DATA FOR THE β'-AuCd PHASE AT 700°K.

The data for the β' - AuCd phase[14] are fitted satisfactorily by the S_c curve for $\alpha = 0.005$, assuming $\Delta S_{th} = -0.20$ cal./deg. g-atom, as shown in Fig. 11. There are other indications of negative thermal contributions to the entropy of this system. For AuCd between 298° and 600°K, $\Delta Cp_{avg.} = -0.26$ cal./deg. g-atom,[14] presumably from thermal origin. For the liquid equiatomic alloy at 1000°K, $\Delta S^{xs} = \Delta S - \Delta S^{id} = -1.11$ cal./deg. g-atom,[14] which again indicates a negative thermal contribution to the entropy of formation, since it is unlikely for the liquid alloy to possess a significant degree of order. The value of α used to fit the data, 0.005, corresponds to $W = 0.98$ and $\frac{T}{T_c} = 0.427$, leading to a calculated value for T_c of 1640°K, far above the melting temperature of AuCd, 900°K.

The ΔS values[14] for the AuCu phase at 653°K are plotted in Fig. 12, where, again, the terminal values apply to the phase boundaries at that temperature.* Especially about the equiatomic composition and on the Cu - rich side, the data are represented extremely well by the S_c curve for $\alpha = 0.015$, assuming $\Delta S_{th} = +0.16$ cal./deg. g-atom. The suggested positive thermal entropy contribution is consistent with other data for this system. For the "disordered" equiatomic alloy at 720°K, 37° above T_c, $\Delta S = 1.36$ cal./deg. g-atom,[14] only 0.02 cal./deg. g-atom less than the ideal entropy of mixing. The high-temperature X-ray data

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* The high temperature orthorhombic modification of tetragonal AuCu I, the AuCu II phase stable between 658° and 683°K at $x_{Cu} = 0.5$, has been neglected. Calorimetric measurements have failed to show any change of properties between the two modifications.[4]

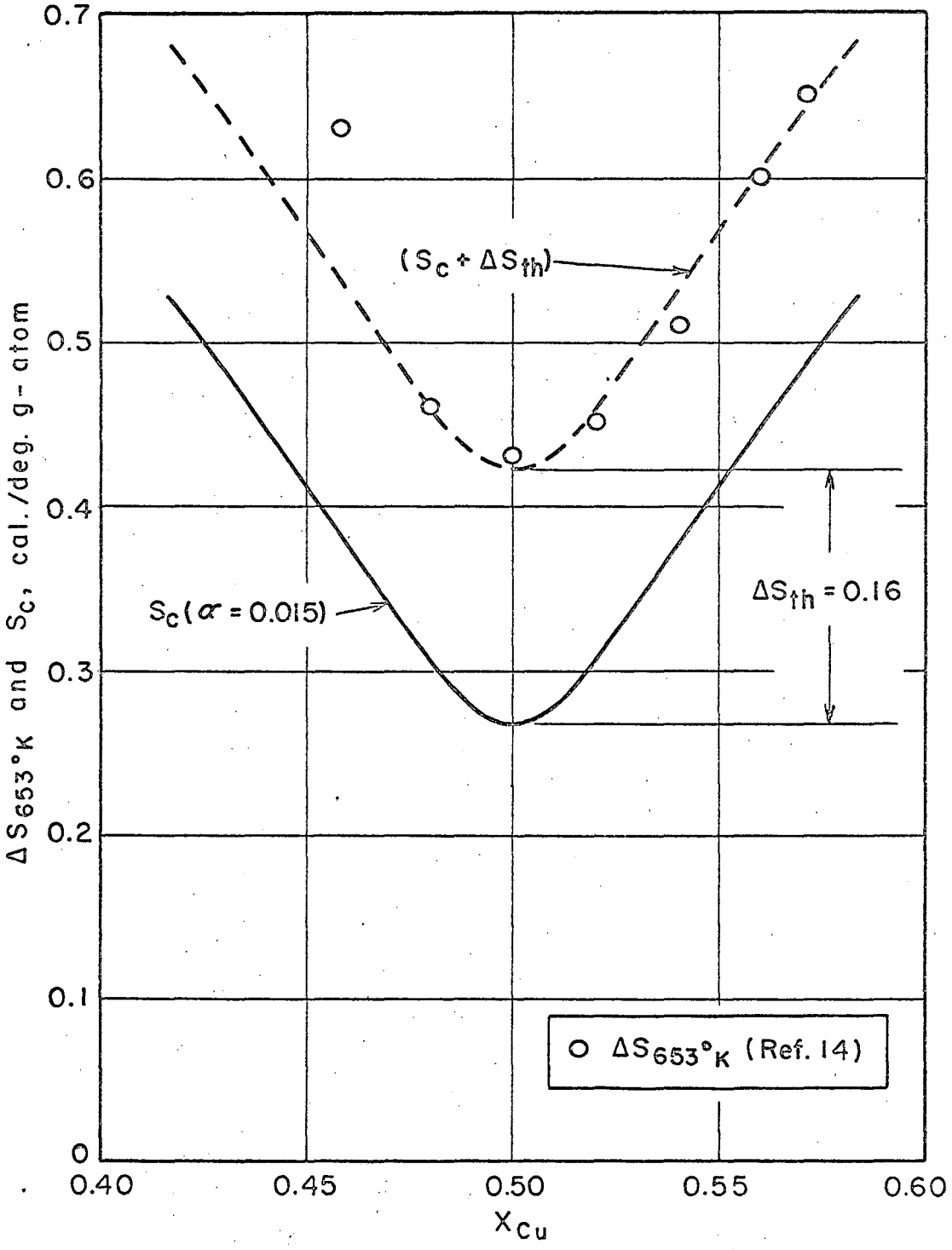

FIG. 12 CORRELATION OF ENTROPY DATA FOR THE AuCu ORDERED PHASE AT 653°K.

of Roberts,[24] however, indicate a high degree of short-range order for this alloy, with a number of excess Au-Cu bonds which is 36.5 per cent of the way between the completely random and perfectly ordered states. The configurational entropy of the short-range-ordered alloy must be significantly less than ideal; thus the thermal contribution to ΔS must be positive in order to yield the observed value of 1.36 cal./deg. g-atom.

The value of α used to fit the data at 653°K, 0.015, corresponds to W = 0.94, in fair agreement with the value determined by Roberts[24] for an alloy quenched from the same temperature, W = 0.97. It is possible that the degree of order increased somewhat during the quench, accounting for some of the difference. The calculated critical temperature, 1200°K, is much too high, as the degree of long-range order of the equiatomic alloy drops precipitously to zero at T_c = 683°K by a first order process involving a considerable latent heat effect.[4]

VII. DISCUSSION

Solutions for many of the expressions derived for the illustrative CsCl-type structure were extended to their mathematical limits. This was done with the object of exploring the behavior of the derived functions and not of suggesting that their validity should be expected to extend over such wide ranges of composition. The two primary assumptions involved in the treatment are those of (1) constancy of the nearest neighbor interaction parameter, V_{AB}, and of (2) random mixing of atoms on the individual sublattices. The validity of these two assumptions is likely to decrease with increasing departures from stoichiometry.

In actual alloy systems, the composition range of stability of a superlattice phase is often limited by the existence of other competing phases which become the stable ones on either side of the one considered. In the case of an ordered phase which transforms to a disordered alloy of the same or related lattice structure, the Gibbs energy curve for the "disordered" phase, e.g. in Fig. 8, will be lowered by the existence of short-range order, again reducing the range of stability of the ordered phase. Seldom does an ordered phase exist for departures from stoichiometry greater than $\chi = \pm 0.10$, for which range the assumptions made should remain reasonably valid.

It would also be expected that the basic assumptions should be more valid for the CsCl-type structure than for the close-packed superlattice structures considered, because of the difference in their bonding

characteristics. In the CsCl-type structure there are no nearest neighbor interactions between atoms on the same sublattice, which especially favors assumption (2). In the close-packed AuCu and $AuCu_3$-type structures, however, some of the nearest neighbor bonds are between atoms on the same sublattice, which, in the case of the tetragonal AuCu-type, have different bond lengths than those between atoms on different sublattices. In all cases the distinction between the sublattices will tend to break down with increasing amounts of disorder, resulting either from higher temperatures or greater departures from stoichiometry; but this may occur sooner for the close-packed structures.

Further assumptions are of course involved in ignoring interactions of longer range than the nearest neighbor ones and in considering the departures from stoichiometry to occur purely by substitutional defects. Even in cases where this is the predominant mechanism, there will always be thermal vacancies present which vary with composition and which may show a preference for one sublattice or the other. More extensive treatments would have to take these factors into account. It is believed that the methods presented here should provide the framework upon which more elaborate or sophisticated treatments may be based.

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Part B

SOLUTE INTERACTIONS IN DILUTE LIQUID ALLOYS

ABSTRACT

Calorimetric measurements are reported for the heats of solution of gold and indium in a number of liquid tin-rich alloys at a temperature of 705°K. From the data the partial molar enthalpies of gold are determined as a function of dilute solute concentrations in the binary Au-Sn system and in the ternary systems, Ag-Au-Sn, Au-Ni-Sn, and Au-In-Sn. Partial molar enthalpies of indium are determined for dilute solute concentrations in the In-Sn, Ag-In-Sn, and Au-In-Sn systems.

The data are expressed in terms of the interaction parameter concept introduced by Wagner and more recently extended by Lupis and Elliott. Values are obtained for the gold-gold, silver-gold, nickel-gold, gold-indium, and silver-indium enthalpy interaction parameters in liquid tin. Values of enthalpy interaction parameters are also evaluated from existing data for the temperature variation of the Gibbs energy interaction parameter in four liquid ternary alloy systems. The results are interpreted in terms of solute atom distributions through comparisons with values of the enthalpy interaction parameters predicted by the random solution and Henry's law models for the dilute solution.

I. INTRODUCTION

Interest in the thermodynamic behavior of dilute liquid alloys arises from two primary sources. From a practical viewpoint, it is often of importance to know or to be able to predict the effect that one solute will have on the thermodynamic properties of the other solutes in a multicomponent system. The leading example of this point of view is afforded by the extensive studies of Chipman[1] on the interactions of dilute solutes in liquid iron.[2] Studies of dilute solutions may also be rewarding from the theoretical point of view. Some of the complications and difficulties arising from the more complex interactions possible in concentrated solutions are avoided, leading to easier interpretations in terms of solution models and bonding energies. For example, in a binary alloy the limiting values of the partial molar properties of the solute represent the case for which each solute atom is completely surrounded by atoms of the solvent, and no other interactions are possible.

Interaction Parameters

Solute interactions in dilute solutions are conveniently treated by the interaction parameter concept of Wagner.[3] Using a Taylor series expansion for the logarithm of the activity coefficient, $\ln \gamma_i$, of a component, i, in a solution consisting of dilute solutes with atomic fractions x_i, x_j, x_k, etc., in a solvent, s, and neglecting the second- and higher-order terms, Wagner obtained the expression:

$$\ln \gamma_i = \ln \gamma_i^\circ + x_i \epsilon_i^i + x_j \epsilon_i^j + x_k \epsilon_i^k + \cdots \qquad (1)$$

where γ_i° is the limiting value of γ_i in the pure solvent, s. The coefficients, ϵ_i^i, ϵ_i^j, etc., are called the interaction parameters, defined by:

$$\epsilon_i^i = \left(\frac{\partial \ln \gamma_i}{\partial x_i} \right) x_s = 1 \quad , \qquad (2)$$

$$\epsilon_i^j = \left(\frac{\partial \ln \gamma_i}{\partial x_j} \right) x_s = 1 \quad , \text{ etc.} \qquad (3)$$

The self-interaction parameter, ϵ_i^i, represents the effect of interactions between atoms of component i; ϵ_i^j represents the effect of interactions between i and j atoms, etc. Since γ_i is related to the excess partial molar Gibbs energy of component i by $\Delta\overline{G}_i^{xs} = RT \ln \gamma_i$, ϵ_i^j will be referred to as the "Gibbs energy interaction parameter" to differentiate it from the other interaction parameters which will be employed.

Lupis and Elliott[4] proposed that Wagner's treatment be extended to the partial molar enthalpy, $\Delta\overline{H}_i$, and the excess partial molar entropy, $\Delta\overline{S}_i^{xs}$. They define the enthalpy interaction parameter as:

$$\eta_i^j = \left(\frac{\partial \Delta \overline{H}_i}{\partial x_j} \right) x_s = 1 \quad , \qquad (4)$$

and the entropy interaction parameter as:

$$\delta_i^j = \left(\frac{\partial \Delta \overline{S}_i^{xs}}{\partial x_j} \right) x_s = 1 \quad , \qquad (5)$$

leading to expressions similar to Eq. (1):

$$\Delta\overline{H}_i = \Delta\overline{H}_{i\,(x_s = 1)} + x_i\eta_i^i + x_j\eta_i^j + \cdots \tag{6}$$

$$\Delta\overline{S}_i^{xs} = \Delta\overline{S}_{i\,(x_s = 1)}^{xs} + x_i\delta_i^i + x_j\delta_i^j + \cdots \tag{7}$$

From the definitions in Eqs. (3-5) and since $\Delta\overline{G}_i^{xs} = \Delta\overline{H}_i - T\Delta\overline{S}_i^{xs}$, the three interactions parameters are related by:[4]

$$RT\,\epsilon_i^j = \eta_i^j - T\delta_i^j \tag{8}$$

From the usual Maxwell-type relationships between partial molar properties, Wagner[3] has shown that

$$\epsilon_i^j = \epsilon_j^i \tag{9}$$

Similar reciprocity relationships apply to the enthalpy and entropy interaction parameters[4], thus:

$$\eta_i^j = \eta_j^i \tag{10}$$

and

$$\delta_i^j = \delta_j^i \tag{11}$$

Relation between Gibbs Energy and Enthalpy Interaction Parameters

Dealy and Pehlke[5] derived the following relationship between the temperature dependence of ϵ_i^j and H, the total enthalpy per gram atom of alloy:

$$\frac{d\,\epsilon_i^j}{d\,\frac{1}{T}} = \frac{1}{R}\left(\frac{\partial^2 H}{\partial x_i\,\partial x_j}\right)_{x_s = 1} \tag{12}$$

The authors state that if the right hand side of Eq. (12) is not a strong function of temperature, then ϵ_i^j would be expected to vary linearly with $\frac{1}{T}$, permitting extrapolations of measured values to other temperatures of interest. Such a linear variation has indeed often been found in the measurements of Pehlke and his associates[6-9] on dilute ternary liquid alloys.

These authors neglected to point out, however, that a more useful relationship, subject to more meaningful interpretation, can be just as easily obtained. From the definition of ϵ_i^j (Eq. 3) and the fact that the order of differentiation in the mixed partial derivative is immaterial:

$$\frac{d\epsilon_i^j}{d\frac{1}{T}} = \frac{\partial}{\partial\frac{1}{T}}\left(\frac{\partial \ln \gamma_i}{\partial x_j}\right)_{x_s=1} = \frac{\partial}{\partial x_j}\left(\frac{\partial \ln \gamma_i}{\partial\frac{1}{T}}\right)_{x_s=1} \qquad (13)$$

Since, from the Gibbs-Helmholtz relation,

$$\frac{\partial \frac{\overline{\Delta G_i^{xs}}}{T}}{\partial\frac{1}{T}} = R\left(\frac{\partial \ln \gamma_i}{\partial\frac{1}{T}}\right) = \overline{\Delta H_i} \quad , \qquad (14)$$

one obtains:

$$\frac{d\epsilon_i^j}{d\frac{1}{T}} = \frac{1}{R}\left(\frac{\partial \overline{\Delta H_i}}{\partial x_j}\right)_{x_s=1} = \frac{\eta_i^j}{R} \qquad (15)$$

Eq. (15) thus relates, in the familiar way, data obtainable from equilibrium and calorimetric measurements. This relation could just as well be derived from Eq. (8) or Eq. (12). An observed linear variation of

ϵ_i^j with $\frac{1}{T}$ thus results from a temperature invariant value of η_i^j. Introducing here a further interaction parameter, σ_i^j, where:

$$\sigma_i^j = \left(\frac{\partial \Delta \overline{Cp}_i}{\partial x_j}\right)_{x_S=1} = \frac{d\eta_i^j}{dT} \quad , \tag{16}$$

η_i^j will be constant with temperature when $\sigma_i^j = 0$.

Experimental Measurement of Interaction Parameters

Experimental determination of the various interaction parameters requires extremely precise measurements of the appropriate properties as functions of solute concentrations in very dilute regions. Unfortunately, few such accurate data exist for intermetallic alloys, even for binary systems, because of the experimental difficulties involved. Examination of the evaluations of published data for binary alloys by Hultgren, Orr, Anderson, and Kelley[10] reveals that determination of the limiting values of γ_i° and $\Delta\overline{H}_{i\,(x_i=0)}$ often requires extrapolations to infinite dilution from $x_i \approx 0.05 - 0.10$. Similar difficulties were recently pointed out by Dealy and Pehlke[11] as having been encountered in their tabulations[5,12] of available values of γ_i° and ϵ_i^j in non-ferrous liquid alloys. Values of ϵ_i^j for several metallic and non-metallic solutes in liquid iron are tabulated by Elliott, Gleiser, and Ramakrishna.[2]

The use of high temperature galvanic cells for determining ϵ_i^j in dilute liquid alloys has been critically discussed by Dealy and Pehlke,[11] and such data for several ternary systems have recently been reported by Pehlke, et al.[6-9] Direct measurements of the enthalpy interaction

parameter, η_i^j, for multicomponent systems, however, are virtually nonexistent. This quantity is of course subject to calorimetric measurement, but its determination must be limited to cases where high experimental precision is possible.

The present paper will report the results of calorimetric measurements of the enthalpy interaction parameters for a few representative solute pairs in dilute solution in liquid tin. The data will be interpreted in terms of dilute solution models. Values of enthalpy interaction parameters will also be evaluated from existing data for the temperature variation of ϵ_i^j in liquid ternary alloys.

II. MODELS FOR DILUTE SOLUTION BEHAVIOR

Random Solution Behavior

In the quasi-chemical treatment of solutions, it is assumed that the energy of a solution may be expressed merely as the summation of all the nearest neighbor bond energies. Also, a composition independent value is assumed for the pairwise interaction energy term, V_{ij}, defined by:

$$V_{ij} = E_{ij} - \tfrac{1}{2}(E_{ii} + E_{jj}) \tag{17}$$

where E_{ij} is the energy of an i-j bond, etc. The so-called "zeroth" approximation[13] of this treatment, referred to throughout this paper as the "random solution model", further assumes random mixing of the component atoms. Based on this model, the integral heat of formation for one gram atom of a binary alloy is given by:[13]

$$\Delta H = \omega x_i x_j \tag{18}$$

where

$$\omega = N_o z V_{ij} \tag{19}$$

N_o being Avogadro's number and z the coordination number, assumed to be the same for the pure components and the alloy. Since, for this model, ω is constant for a given system, ΔH will be a parabolic function of composition. The corresponding values of the partial molar enthalpies for the two components are given by:

$$\Delta\overline{H}_i = \omega x_j^2 \tag{20}$$

and

$$\Delta\overline{H}_j = \omega x_i^2 \tag{21}$$

The limiting values for the partial molar enthalpies for the solutes in the terminal infinitely dilute solutions will thus be identical as shown by:

$$\Delta\overline{H}_{i\,(x_j=1)} = \Delta\overline{H}_{j\,(x_i=1)} = \omega = N_o z V_{ij} \tag{22}$$

The enthalpy self-interaction parameter for a solute showing random solution behavior in a dilute binary alloy may be calculated from Eqs. (4) and (20), yielding:

$$\eta_i^i = \left(\frac{\partial \Delta\overline{H}_i}{\partial x_i}\right)_{x_j=1} = -2\omega = -2\Delta\overline{H}_{i(x_j=1)} \tag{23}$$

The assumption that V_{ij} does not vary with composition is not generally valid for intermetallic systems. Failure of this assumption is shown by the fact that the limiting partial molar enthalpies in liquid binary alloy systems usually differ, sometimes by considerable amounts.[10] Nevertheless, over a small range of composition such as in the very dilute range for <u>one</u> of the components, the assumption that V_{ij} is constant should be reasonably valid. Therefore for component i in very dilute solution in j, a departure from the behavior predicted by Eq. (23) could be concluded to result primarily from a non-random distribution of the solute (i) atoms.

Applying the zeroth approximation assumptions to a liquid ternary alloy, Alcock and Richardson[14] derived the following equation for the enthalpy interaction parameter of dilute components i and j in solvent metal s:

$$\eta_i^j = \left(\frac{\partial \Delta\overline{H}_i}{\partial x_j}\right)_{x_s=1} = \Delta\overline{H}_i(\text{in j})_{x_j=1} - \Delta\overline{H}_i(\text{in s})_{x_s=1} - \Delta\overline{H}_j(\text{in s})_{x_s=1} \qquad (24)$$

where the three terms on the right hand side of the equation represent the limiting partial molar enthalpies in the three respective binary alloys. The last two terms are unambiguously evolved in the treatment, since metal s is the major component for the binary systems they represent as well as for the ternary alloy. The term, $\Delta\overline{H}_i(\text{in j})_{x_j=1}$, however evolves from the expression, $N_o z V_{ij}$, which according to the model employed could just as well be given by $\Delta\overline{H}_j(\text{in i})_{x_i=1}$. Thus in calculating the value of η_i^j predicted by this model in cases where the values of $\Delta\overline{H}_{i(x_j=1)}$ and $\Delta\overline{H}_{j(x_i=1)}$ for the binary i - j system are different, it would appear better to use an average of the two limiting values. From Eq. (24) the enthalpy self-interaction parameter for the ternary alloy is again given by:

$$\eta_i^i = -2\Delta\overline{H}_i(\text{in s})_{x_s=1} \qquad (25)$$

For the very dilute range of solutes i and j in solvent s, the assumption that the interaction energy terms, V_{is}, V_{js}, and V_{ij}, remain constant over the dilute range is not unreasonable. Thus, a departure in the behavior of an actual dilute ternary system from that predicted by

Eq. (24) is most likely to result from one or more of the following: (1) a non-random atomic distribution, (2) other than nearest neighbor interactions, or (3) a difference between the value of V_{ij} in the binary i-j and ternary i-j-s systems. Experimental departures from Eq. (24) must therefore be interpreted in terms of these possibilities, taking into account the nature of the systems involved and the direction and magnitude of the departures.

Henry's Law Behavior

Henry's law is merely the statement of the empirical observation sometimes made that for a component i in dilute solution:

$$a_i = k x_i \tag{26}$$

where a_i is the activity of component i and k is the Henry's law constant. Actually, Henry's law is a limiting law, which can be expressed as:

$$a_i \rightarrow k x_i \quad \text{as} \quad x_i \rightarrow 0 \tag{27}$$

In terms of the activity coefficient of component i, this becomes:

$$\gamma_i \rightarrow k \quad \text{as} \quad x_i \rightarrow 0 \tag{28}$$

from which it is obvious that $k = \gamma_i^\circ$, the limiting value of γ_i at $x_i = 0$.

For finite ranges of composition, Henry's law is best viewed as a hypothetical law which will be approached more or less closely by an actual solution, depending on the nature of the system and the limits of experimental precision available. Highly precise galvanic cell measurements of the activities of several metals in very dilute binary amalgams

have revealed departures from Henry's law at quite low solute concentrations, less than x = 0.0005 for K, Pb, and Sn, for example.[10] On the other hand, departures from Henry's law behavior are sometimes small or experimentally undetectable over finite ranges of composition. The solubilities of nitrogen[15] and hydrogen[16] in liquid iron at 1600°C, for example, have been found to obey Sievert's law (which assumes Henry's law for the dissolved species)[17] for pressures up to one atmosphere, at which $x_N = 0.00180$ and $x_H = 0.00137$.

The model deduced from Henry's law behavior for finite solute concentrations is one of a nonrandom atomic distribution for which there are no interactions between solute atoms. (An exception to this model is provided by the special case of an ideal solution, for which the solute obeys Raoult's law, a special case of Henry's law. In this case, $V_{ij} = 0$, and the solute atoms are randomly distributed.) Thus for a dilute binary solution, over the range that solute i is assumed to obey Henry's law, $\epsilon_i^i = 0$, $\eta_i^i = 0$, and $\delta_i^i = 0$; therefore $\Delta\overline{G}_i^{xs}$, $\Delta\overline{H}_i$, and $\Delta\overline{S}_i^{xs}$ will be constant and equal to their values at $x_i = 0$. Likewise, for a multicomponent solution in which each solute is assumed to obey Henry's law, all of the solute interaction parameters, ϵ_i^j, η_i^j, δ_i^j, etc., will have zero values.

The random solution and Henry's law models for the dilute solution represent limiting types of behavior as far as the nature of the distribution of the solute atoms is concerned. Thus, while both are idealized, they provide useful bases for the comparison and interpretation of the

properties of real dilute solutions. Comparisons of measured values of the enthalpy interaction parameter with those predicted by the two models should serve as most convenient criteria for making such interpretations.

III. CALCULATIONS FROM EXISTING ϵ_i^j TEMPERATURE COEFFICIENT DATA

Values of ϵ_i^j for dilute solute pairs in four intermetallic liquid ternary alloys have recently been determined from galvanic cell measurements by Pehlke, et al.[6-9] In each case ϵ_i^j was found to vary linearly with the reciprocal of the absolute temperature, yielding the values of $\frac{d\epsilon_i^j}{d\frac{1}{T}}$ listed in Table I. Values of η_i^j have been calculated from: (1) the reported temperature coefficients, using Eq. (15); and (2) the random solution model, using Eq. (24). The results are given in the last two columns of Table I.

Limiting values of the partial molar enthalpies in the appropriate binary systems, needed for the evaluation of Eq. (24), were taken from the selected values of Hultgren, et al.,[10] and are listed in Table II together with other binary data which will be referred to in this paper. For the reason discussed previously, the (i-j) binary term in Eq. (24) has been evaluated as the average of $\Delta\overline{H}_{i(x_j=1)}$ and $\Delta\overline{H}_{j(x_i=1)}$.

Values calculated from the temperature coefficient data and from the random solution model for η_{Zn}^{Ag} in bismuth and in lead and for η_{Zn}^{Pb} in tin agree surprisingly well, especially considering possible uncertainties in the limiting values for the binary systems. Also, it has been necessary to assume Kopp's law ($\Delta\overline{Cp}_i = 0$) for the binary systems, thus ignoring differences in the temperatures at which the enthalpies are known.

TABLE I

Enthalpy Interaction Parameters
Calculated from ϵ_i^j Temperature Coefficient Data
and from Random Solution Model

$$\eta_i^j = \left(\frac{\partial \Delta \overline{H}_i}{\partial x_j} \right)_{x_s = 1}, \text{ cal/(g-at)}^2$$

s	i	j	T, °K	$\frac{d\epsilon_i^j}{d\frac{1}{T}}$	Ref.	From $\frac{d\epsilon_i^j}{d\frac{1}{T}}$ Eq. (15)	Calculated from Random Sol'n Model Eq. (24)
Bi	Cd	Sn	673-683	4880	6	9700	1040
Bi	Zn	Ag	723-923	-4830	7	-9280	-10740
Pb	Zn	Ag	823-943	-5870*	8	-11660	-12770
Sn	Zn	Pb	723-923	2080	9	4130	5330

*Tentative value[8]

TABLE II

Limiting Values of Partial Molar Enthalpies in Liquid Binary Alloys

(taken from Hultgren, Orr, Anderson, and Kelley[10])

$$i_{(\ell)} = i\ (\text{in alloy})_{(\ell, x_i=0)}$$

Solvent	i	T, °K	$\Delta\overline{H}_{i(x_i=0)}$, cal/g-atom
Ag	Au	1350	- 4660
Ag‡	Zn	1050	- 5000*
Au	Ag	1350	- 3860
Au	Ni ‡	1369	2300
Bi	Ag‡	1000	2940
Bi	Cd	773	780
Bi	Sn	608	105
Bi	Zn	873	3680
Cd	Sn	773	2330
In	Ag‡	723	-1200
In	Au‡	723	-11200
Pb	Ag‡	723	2900
Pb	Zn	926	5750
Sn	Ag‡	723	870
Sn	Au‡	700	- 8030
Sn	Cd	773	1520
Sn	In	773	- 140
Sn	Ni ‡	910	-13900
Sn	Pb	773	1360
Sn	Zn	700	2220
Zn	Ag‡	1050	-3240*
Zn	Pb	926	12075

‡ Supercooled liquid

* Estimated assuming $\Delta\overline{S}_i^{xs}=0$

The values are certainly in sufficiently good agreement to suggest that these three systems closely approach random solution behavior in the dilute ranges studied.

The value of η_{Cd}^{Sn} in bismuth obtained from the temperature coefficient data disagrees strongly with the random solution value, in a direction opposite to that which would indicate an approach to Henry's law behavior. The discrepancy is much too large to result from uncertainties in the binary values used. The measured value appears to be several times more endothermic than can be explained by any reasonable interpretation other than possible uncertainties in the temperature coefficient data.

IV. EXPERIMENTAL

Systems Studied

Liquid tin was the major component for all of the systems studied. The heat of solution of gold was measured for several dilute solute compositions in the binary Au-Sn system and in the ternary systems: Ag-Au-Sn, Au-Ni-Sn, and Au-In-Sn. Similar measurements were made of the heat of solution of indium in the In-Sn, Ag-In-Sn, and Au-In-Sn systems. Measurements were made for all of the alloys at a temperature of 705 (±2)°K.

Materials

The materials used, together with the suppliers and reported purities, are listed below.

Material	Purity	Supplier
Sn	99.999 %	Vulcan Detinning Co., Sewaren, N. J.
Au	99.999+%	Cominco Products, Inc., Spokane, Wash.
In	99.999+%	American Smelting and Refining Co., South Plainfield, N. J.
Ag	99.999+%	Cominco Products, Inc., Spokane, Wash.
Ni	99.999 %	Chicago Development Corp., Riverdale, Md.

Experimental Procedure

The measurements were made using the liquid metal solution calorimeter and experimental methods described in detail in a previous publication.[18] The calorimeter basically consists of a stirred solvent-

metal bath contained in a molybdenum crucible which is supported within a heavy copper jacket. The jacket is heated by a surrounding resistance heating element and is maintained at a constant temperature, within ±0.001 °C, by means of a sensitive resistance thermometer temperature controller. The temperature difference between the crucible and jacket is measured by means of a copper-constantan differential thermocouple, and the jacket temperature is measured separately by a calibrated platinum-platinum +10% rhodium couple. The calorimeter is contained in the lower half of a chamber evacuated to a pressure of about 10^{-8} atmosphere. Located in the upper part of the chamber and separated from the calorimeter by several radiation shields is the dispenser unit which holds the solute specimens prior to dropping them into the solvent bath. Specimens are admitted to the dispenser unit through an external vacuum-lock device.

For each series of runs, approximately 250 g. of tin (~2.1 g-atoms) was melted under vacuum into the molybdenum crucible, which was then installed in the calorimeter and brought to the solution temperature, 705 (±2) °K. Small spherical specimens of gold and indium, consisting of about 0.003 g.-atoms of sample, were used for the measurements. The total heat effect accompanying the solution of a specimen dropped from the temperature of the dispenser unit (~321°K) was determined from the change in the crucible temperature, the measured heat capacity of the calorimeter, and a correction for heat transfer between jacket and crucible during the run, using calculation methods previously

described.[18] The heat capacity of the calorimeter was determined at the beginning of each series of runs by measuring the temperature change accompanying the addition of specimens of pure solid tin. Similar measurements were made during the runs by dropping specimens of tungsten into the bath. The known heat effects were obtained from tabulated heat content data for tin[10] and tungsten.[19] Solute additions for the purpose of changing the composition of the liquid alloy were also made through the dispenser unit.

Treatment of Data

The isothermal heats of solution at the temperature of the liquid alloy were determined from the measured heat effects and the enthalpy increments[10] of gold and indium between the initial specimen and final solution temperatures. The heat of solution per g-atom of solute added is the average partial molar enthalpy, $\Delta\overline{H}_i$, of that solute over the range of composition covered by the liquid alloy during the run. Since the change in composition of the solute was quite small, of the order of $\Delta x_i = 0.0012$, the values have been taken to represent the partial molar enthalpies at the average of the alloy compositions before and after each run.

During the course of six series of runs, the temperatures of the liquid alloys for individual runs differed by a maximum of only ±2°K from a mean value of 705°K. The measured partial molar enthalpies of gold have been corrected for these small differences from 705°K using the value of $\Delta\overline{Cp}_{Au(x_{Sn}=1),\ 700°K} = 3.0$ cal./deg. g-atom, tabulated

by Hultgren, et al.[10] The usual corrections were of the order of only 1 to 2 cal./g-atom; the maximum correction was 6 cal./g-atom. Reported heat capacity and heat of mixing data[10] indicate that liquid In-Sn alloys obey Kopp's law. It has thus been assumed that $\Delta\overline{Cp}_{In} = 0$, and the measured partial molar enthalpies of indium have been directly referred to 705°K.

Experimental Data

The experimentally determined partial molar enthalpies are given in Tables III - VIII. Since the temperature of measurement was above the melting temperature of indium, the data for indium were obtained directly with respect to liquid indium at 705°K; thus $\Delta\overline{H}_{In} = \overline{H}_{In} - H^{\circ}_{In_{(\ell)}}$. The data for gold, however, were obtained with respect to solid gold at 705°K. The values of $\Delta\overline{H}_{Au}$ have been referred to supercooled liquid gold at 705°K by assuming the heat of fusion of gold at 705°K to be 2955 cal./g-atom, the same as that at its melting temperature;[10] thus:

$$\Delta\overline{H}_{Au_{(\ell)}} = \overline{H}_{Au} - H^{\circ}_{Au_{(\ell)}} = \overline{H}_{Au} - H^{\circ}_{Au_{(s)}} - 2955 \qquad (29)$$

TABLE III

Measured Partial Molar Enthalpies of Gold*

in Liquid Au-Sn Alloys at 705°K

Run No.	$x_{Au}^{(avg.)}$	$\overline{H}_{Au} - H^{\circ}_{Au_{(\ell)}}$ cal./g-atom	Run No.	$x_{Au}^{(avg.)}$	$\overline{H}_{Au} - H^{\circ}_{Au_{(\ell)}}$ cal./g-atom
1-4	0.00035	-7964	1-14	0.0197	-7936
3-3	0.00070	-7971	1-15	0.0210	-7929
1-5	0.0011	-7955	1-16	0.0308	-7928
1-6	0.0018	-7951	1-17	0.0320	-7909
3-4	0.0021	-7942	1-18	0.0410	-7902
1-7	0.0028	-7963	1-19	0.0422	-7913
3-6	0.0035	-7962	1-20	0.0510	-7871
1-8	0.0042	-7945	1-21	0.0522	-7875
1-9	0.0056	-7940	1-22	0.0582	-7843
1-12	0.0069	-7946	1-23	0.0594	-7845
1-13	0.0083	-7944			

* Referred to supercooled $Au_{(\ell)}$ at 705°K

TABLE IV

Measured Partial Molar Enthalpies of Gold*

in Liquid Ag-Au-Sn Alloys at 705°K

Run No.	x_{Ag}(avg.)	x_{Au}(avg.)	$\overline{H}_{Au}-H^{\circ}_{Au_{(\ell)}}$ cal./g-atom
3-7	0.0199	0.0048	-8010
3-8	"	0.0062	-7985
4-8	0.0390	0.00069	-8016
4-9	"	0.0021	-8047
4-10	"	0.0034	-8026
4-11	"	0.0048	-8045
3-9	"	0.0074	-8012
3-10	"	0.0088	-7999
4-12	"	0.0116	-8018
4-13	"	0.0129	-8024
4-14	"	0.0236	-8006
4-15	"	0.0248	-7990
4-16	"	0.0339	-8013
4-17	"	0.0351	-7991
4-18	"	0.0452	-7977
4-19	"	0.0464	-7968
4-20	"	0.0556	-7929
4-21	"	0.0568	-7943
3-11	0.0579	0.0099	-8052
3-12	"	0.0112	-8015
3-13	"	0.0125	-8019

* Referred to supercooled $Au_{(\ell)}$ at 705°K

TABLE V

Measured Partial Molar Enthalpies of Gold*

in Liquid Au-Ni-Sn Alloys at 705°K

Run No.	x_{Ni}(avg.)	x_{Au}(avg.)	$\overline{H}_{Au}-H^{\circ}_{Au_{(\ell)}}$ cal./g-atom
4-3	0.0094	0.00074	-7965
4-4	"	0.0022	-7976
4-6	0.0111	0.0037	-7957
4-7	"	0.0051	-7975
4-8	"	0.0066	-7968

* Referred to supercooled $Au_{(\ell)}$ at 705°K

TABLE VI

Measured Partial Molar Enthalpies of Gold*

in Liquid Au-In-Sn Alloys at 705°K

Run No.	x_{In}(avg.)	x_{Au}(avg.)	$\overline{H}_{Au}-H^{\circ}_{Au_{(\ell)}}$ cal./g-atom
5-7	0.0045	0.0108	-7965
5-8	"	0.0122	-7970
5-13	0.0091	0.0283	-7992
5-14	"	0.0297	-7978
5-17	0.0115	0.0404	-7978

* Referred to supercooled $Au_{(\ell)}$ at 705°K

TABLE VII

Measured Partial Molar Enthalpies of Indium in Liquid In-Sn and Ag-In-Sn Alloys at 705°K

Run No.	x_{Ag}(avg.)	x_{In}(avg.)	$\overline{H}_{In} - H^{\circ}_{In_{(\ell)}}$ cal./g-atom
6-3	0	0.00047	-195
6-4	0.0100	0.0015	-238
6-5	"	0.0026	-226
6-6	0.0198	0.0037	-242
6-7	"	0.0048	-254
6-8	0.0295	0.0060	-248
6-9	"	0.0071	-274
6-10	0.0390	0.0082	-291
6-11	"	0.0094	-298
6-12	0.0484	0.0104	-327
6-13	"	0.0115	-308
6-14	0.0464	0.0503	-296
6-15	"	0.0515	-298

TABLE VIII

Measured Partial Molar Enthalpies of Indium in Liquid In-Sn and Au-In-Sn Alloys at 705°K

Run No.	x_{Au}(avg.)	x_{In}(avg.)	$\overline{H}_{In} - H^{\circ}_{In_{(\ell)}}$ cal./g-atom
5-3	0	0.00056	-205
5-4	0	0.0017	-210
5-5	0.0101	0.0028	-260
5-6	"	0.0039	-265
5-9	0.0193	0.0051	-283
5-10	"	0.0063	-296
5-11	0.0277	0.0074	-340
5-12	"	0.0085	-326
5-15	0.0398	0.0096	-379
5-16	"	0.0109	-384
5-18	0.0498	0.0120	-422
5-19	"	0.0133	-427

V. RESULTS AND DISCUSSION

The limiting values obtained for the partial molar enthalpies of gold and indium in liquid tin at 705°K are given in Table IX. The binary and ternary enthalpy interaction parameters calculated from the data are given in Table X, which also lists the corresponding values calculated from the random solution model using either Eq. (24) or Eq. (25). Details of the evaluations and interpretations of the values are given in the following sections.

Binary Au-Sn Alloys

The measured partial molar enthalpies of gold (Table III) are plotted as a function of x_{Au} in Fig. 1. The limiting value of $\overline{H}_{Au}-H^{\circ}_{Au_{(\ell)}}$ at $x_{Sn} = 1$ is obtained as -7955 cal./g-atom (-5000 cal./g-atom with respect to $Au_{(s)}$). The corresponding value obtained from the evaluations of Hultgren et al.[10] is -8010 cal./g-atom at 705°K, which is based primarily on earlier data from this laboratory. The present data were obtained using samples of both gold and tin of considerably higher purity than those used in any of the previous measurements, and this is believed to be responsible for at least part of the observed difference of 55 cal/g-atom.

Between $x_{Au} = 0$ and $x_{Au} \approx 0.038$ the data are well represented within a maximum scatter of about ±10 cal./g-atom by the linear relationship:

TABLE IX

Measured Limiting Partial Molar Enthalpies

in Liquid Tin at 705°K

Solute (i)	$\overline{H}_i - H^\circ_{i(\ell)}, x_{Sn}=1$ cal./g-atom	$\overline{H}_i - H^\circ_{i(s)}, x_{Sn}=1$ cal./g-atom
Au	-7955 (±15)	-5000 (±15)
In	- 205 (±10)	—

TABLE X

Enthalpy Interaction Parameters in Liquid Tin-Rich Alloys at 705°K

Interaction Parameter	η_i^j, cal./g-atom^2	
	Measured Value	Calculated from Random Sol'n Model
η_{Au}^{Au}	1125	15900
η_{In}^{In}	—	410
η_{Au}^{Ag}	- 2000	2820
η_{Au}^{Ni}	(-1800)	24200
η_{In}^{Ag}	-2200	-1860
η_{In}^{Au}	-4400	-3040

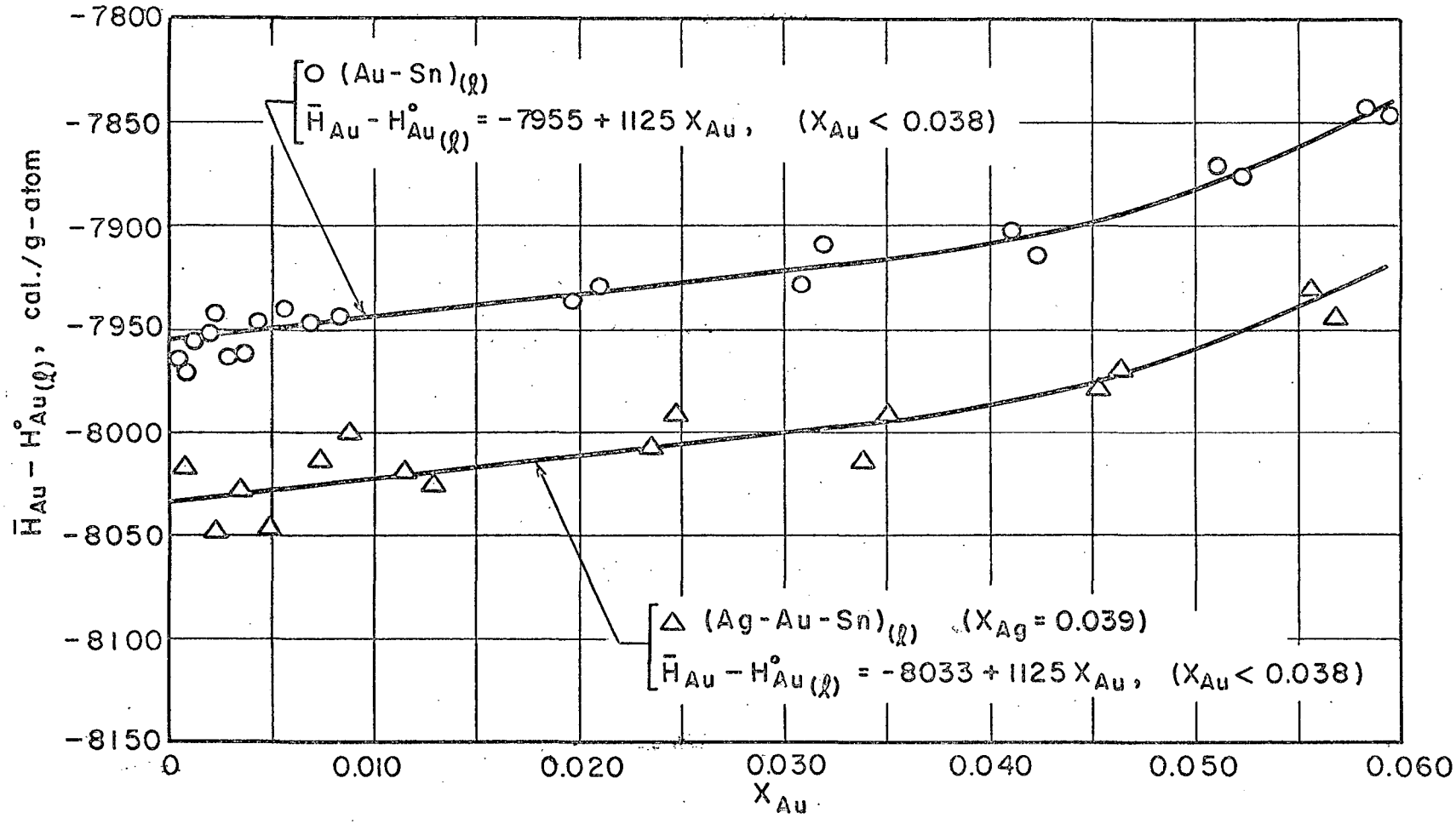

FIG. 1 PARTIAL MOLAR ENTHALPY OF Au IN LIQUID (Au-Sn) AND $(Ag-Au-Sn)_{(X_{Ag} = 0.039)}$ ALLOYS AT 705°K.

$$\Delta\overline{H}_{Au_{(\ell)}} = -7955 + 1125 x_{Au}, \quad (x_{Au} < 0.038) \tag{30}$$

where the slope at $x_{Au} = 0$ gives:

$$\eta_{Au}^{Au} = \left(\frac{\partial \Delta\overline{H}_{Au}}{\partial x_{Au}}\right)_{x_{Sn}=1} = 1125 \text{ cal./g-atom}^2.$$

Thus for $x_{Au} < 0.038$, the enthalpy self-interaction parameter of gold, η_{Au}^{Au}, remains constant at a value which is only about seven per cent of the random solution model value of 15900 cal./g-atom^2. In this composition range, therefore, gold shows only a small departure from Henry's law behavior. This undoubtedly results from the strongly exothermic character of the Au-Sn interaction energy which is indicated by the relatively large negative value of $\Delta\overline{H}_{Au_{(\ell)}}$ at $x_{Au} = 0$. For $x_{Au} > 0.038$ the departure from Henry's law behavior begins to increase more rapidly in a non-linear manner, suggesting that above that composition, the Au-Au interactions begin to become considerably more significant.

From Gibbs-Duhem integration of the values of $\Delta\overline{H}_{Au_{(\ell)}}$, partial molar enthalpies of tin at 705°K have been calculated, yielding the values:

x_{Au}	$\Delta\overline{H}_{Sn}$, cal./g-atom
0.04	-1.0
0.05	-2.3
0.06	-4.8

Thus, as would be expected, the departure of tin from Raoult's law behavior is also small within the measured composition range.

Ternary Ag-Au-Sn Alloys

The partial molar enthalpies of gold in ternary Ag-Au-Sn alloys in which $x_{Ag} = 0.039$ (Table IV) are also plotted as a function of x_{Au} in Fig. 1. The values are represented within the experimental precision by a curve parallel to that for the binary Au-Sn alloys. The linear range is given by:

$$\Delta\overline{H}_{Au_{(\ell)}} = -8033 + 1125\, x_{Au}, \quad (x_{Au} < 0.038) \tag{31}$$

where -8033 cal./g-atom is the limiting value at $x_{Au} = 0$ of $\Delta\overline{H}_{Au_{(\ell)}}$ in the ternary system for $x_{Ag} = 0.039$. The self-interaction parameter for gold, η_{Au}^{Au}, has the same value as in the binary Au-Sn system, 1125 cal./g-atom^2, and again remains constant to $x_{Au} \approx 0.038$.

Only a few runs were made for ternary alloys in which $x_{Ag} = 0.0199$ and $x_{Ag} = 0.0579$ (Table IV). From the data, values of $\Delta\overline{H}_{Au_{(\ell)}}$ at $x_{Au} = 0$ were calculated using the value of η_{Au}^{Au} established by the data in Fig. 1, from the relation:

$$\Delta\overline{H}_{Au,\, x_{Au}=0} = \Delta\overline{H}_{Au,\, x_{Au}} - 1125 x_{Au} \tag{32}$$

Since the maximum value of x_{Au} for these alloys was 0.0125, the linear relation should apply. The resulting values are plotted vs. x_{Ag} in Fig. 2 together with the values determined from Fig. 1 for $x_{Ag} = 0$ and $x_{Ag} = 0.039$. The curve drawn gives maximum weight to the value at $x_{Ag} = 0.039$, since that is the best established of the ternary values.

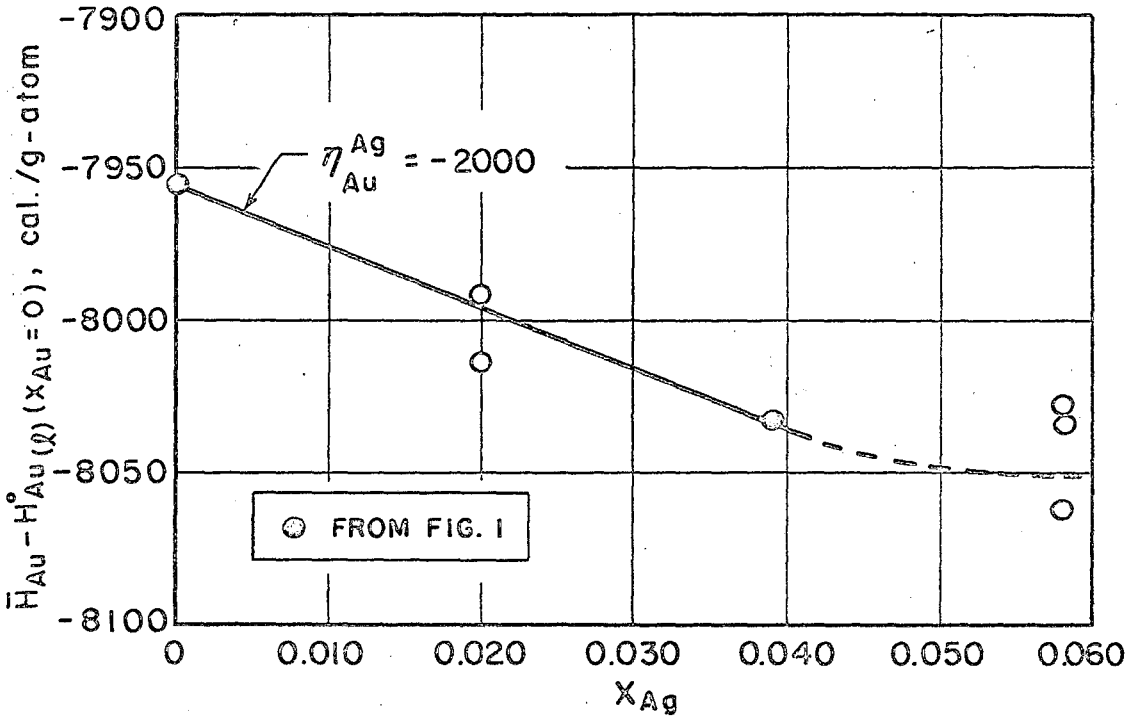

FIG. 2 DETERMINATION OF η^{Ag}_{Au} IN $Sn_{(\ell)}$ AT 705° K.

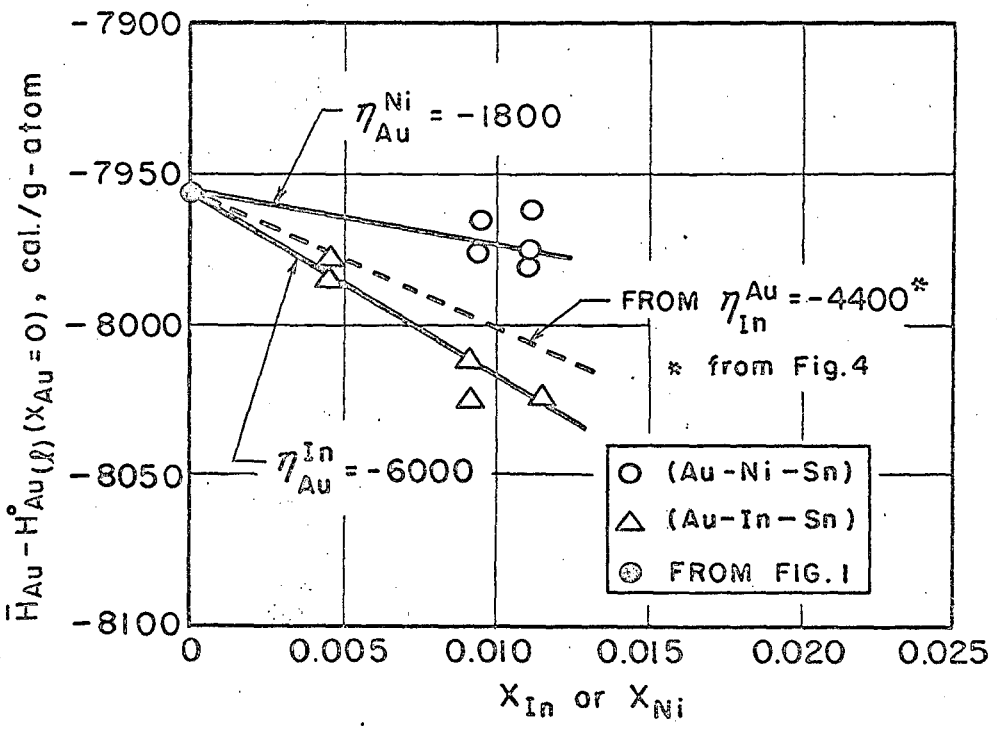

FIG. 3 DETERMINATION OF η^{Ni}_{Au} AND η^{In}_{Au} IN $Sn_{(\ell)}$ AT 705°K.

The slope of this curve at $x_{Ag} = 0$ gives

$$\eta_{Au}^{Ag} = \left(\frac{\partial \Delta\overline{H}_{Au}}{\partial x_{Ag}}\right)_{x_{Sn}=1} = -2000 \text{ cal./g-atom}^2$$

The curve has been drawn assuming η_{Au}^{Ag} to remain constant up to $x_{Ag} \approx 0.04$. A smooth curve could be drawn which would result in a slightly more negative value of η_{Au}^{Ag}, but this is not believed to be justified without more data at the lower compositions.

Because of the observed small departure of gold from Henry's law behavior in these alloys, it is not surprising that the value obtained for η_{Au}^{Ag} does not agree with the calculated random solution value of 2820 cal./g-atom^2. A negative value, which is well established by the data, does not appear amenable to simple interpretation, since the value of η_{Au}^{Au} is not affected by the presence of silver, and since the formation of a Ag-Au bond at the expense of a Au-Sn bond and a Ag-Sn bond should presumably be accompanied by a net endothermic effect. The negative value may result from longer range, i.e., other than nearest neighbor, interactions between Ag and Au atoms which would be expected to make an exothermic contribution.

Ternary Au-Ni-Sn Alloys

Only a few measurements were made in the ternary Au-Ni-Sn system because of the low solubility of nickel in liquid tin; at 705°K, $x_{Ni}(\text{max.}) \approx 0.015$.[20] From the data (Table V), values of $\Delta\overline{H}_{Au_{(\ell)}, x_{Au}=0}$

in alloys for which $x_{Ni} = 0.0094$ and $x_{Ni} = 0.0111$ were calculated using Eq. (32), assuming, as before, that $\eta^{Au}_{Au} = 1125$ cal./g-atom^2. The maximum value of x_{Au} was 0.0066, well within the range for which η^{Au}_{Au} was found to be constant for the Au-Sn and Ag-Au-Sn alloys.

The values are plotted in Fig. 3 together with the value of $\Delta\overline{H}_{Au_{(\ell)}, x_{Au}=0}$ for $x_{Ni} = 0$ taken from the data of Fig. 1. The line drawn indicates that $\eta^{Ni}_{Au} = -1800$ cal./g-atom^2. Actually, if an uncertainty of ±15 cal./g-atom is ascribed to the limiting value at $x_{Ni} = 0$, which is reasonable, since it was not determined independently for this series of runs, it would be concluded that $\eta^{Ni}_{Au} \approx 0$. The significant result is that the value calculated from the random solution model, 24200 cal./g-atom^2, is not at all approached. It would appear that both gold and nickel show only small departures from Henry's law and do not interact significantly in the ternary alloy. This might be expected from the highly exothermic character of the Au-Sn and Ni-Sn interaction energies coupled with the corresponding endothermic interaction of gold and nickel (see Table II).

Binary In-Sn Alloys

Measurements of $\Delta\overline{H}_{In}$ in the binary In-Sn system were made only at very dilute compositions ($x_{In} = 0.0005$-0.0017) at the beginning of the studies on the Ag-In-Sn and Au-In-Sn ternary systems (Tables VII and VIII). The average value found, -205(±10) cal./g-atom at 705°K, is more exothermic than the selected value of Hultgren, et al.,[10] -140

cal./g-atom at 773°K, which is based primarily on the data of Kleppa[21] and Cohen, et al.[22] at 723°K and 623°K, respectively. More recently, Pool and Lundin[23] reported $\Delta\overline{H}_{In}$ = -243(±30) cal./g-atom at 750°K, obtained from measurements of the heat of solution of solid indium, initially at 273°K, in liquid tin at 750°K, and the enthalpy increment of indium between 273° and 750°K taken from Kelley.[24] The present data were evaluated using enthalpy increment values for indium of Hultgren, et al.,[10] which incorporate the later Cp data (354°-801°K) of Kaznoff.[25] If the data of Pool and Lundin are recalculated using the latter values,[10] one obtains $\Delta\overline{H}_{In}$ = -210 (±30) cal./g-atom, in excellent agreement with the present value.

Ternary Ag-In-Sn Alloys

Data for $\Delta\overline{H}_{In}$ as a function of x_{Ag} in ternary Ag-In-Sn alloys (Table VII) are shown plotted in Fig. 4. It was assumed that for the small concentrations of indium present in the measurements (x_{In}=0.0015-0.0115), the effect of η_{In}^{In} would be undetectable within the experimental precision and could be neglected. (If η_{In}^{In} has the random solution value of 410 cal./g-atom^2, its effect on $\Delta\overline{H}_{In}$ at x_{In} = 0.01 would be +4 cal./g-atom.) To check this assumption two runs were made within the range of x_{Ag} studied with the low indium content alloys, but with a much higher indium content, $x_{In} \approx 0.05$. The results, shown plotted in Fig. 4, agree well within the experimental scatter with those obtained where $x_{In} < 0.012$.

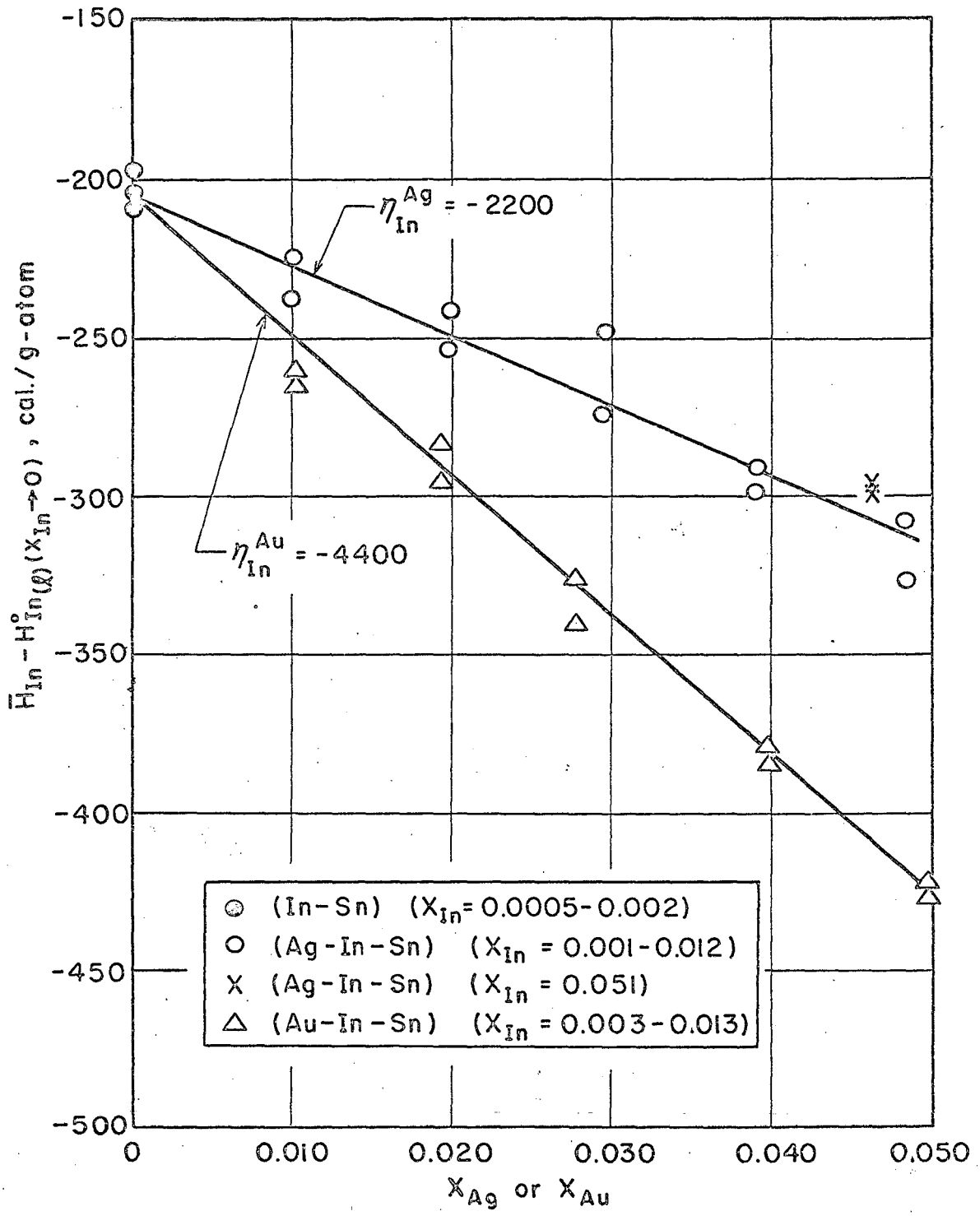

FIG. 4 DETERMINATION OF η^{Ag}_{In} AND η^{Au}_{In} IN $Sn_{(\ell)}$ AT 705°K.

The data yield the value, $\eta_{In}^{Ag} = -2200$ cal./g-atom^2, which appears to remain essentially constant over the measured range ($x_{Ag} < 0.05$) and which agrees reasonably well with the value calculated from the random solution model, -1860 cal./g-atom^2. For this dilute system the conditions may indeed be favorable for random solution behavior as the Ag-Sn and In-Sn interaction energies are small endothermic and exothermic quantities, respectively, and the Ag-In interaction energy is only moderately exothermic (see Table II).

Ternary Au-In-Sn Alloys

Data for $\Delta\overline{H}_{In}$ as a function of x_{Au} in ternary Au-In-Sn alloys (Table VIII) are also shown plotted in Fig. 4. Again the indium concentrations present in the measurements were small ($x_{In} = 0.0028$-0.0133), and the presumably small effect of η_{In}^{In} was neglected. The data yield the value, $\eta_{In}^{Au} = -4400$ cal./g-atom^2, which here also appears to remain constant over the measured range ($x_{Au} < 0.05$).

To check the reciprocity relation, Eq. (10), which for this system is expressed by:

$$\eta_{In}^{Au} = \eta_{Au}^{In} \tag{33}$$

a few determinations of $\Delta\overline{H}_{Au_{(\ell)}}$ were made in this same series of runs (Table VI). The results, corrected to $x_{Au} = 0$ assuming $\eta_{Au}^{Au} = 1125$ cal./g-atom^2 and using Eq. (32), are shown plotted vs. x_{In} in Fig. 3. Drawing a straight line through the points and the limiting value of $\Delta\overline{H}_{Au_{(\ell)}, x_{Au}=0}$ determined from the binary Au-Sn data, indicates

the value, η_{Au}^{In} = -6000 cal./g-atom^2. If, however, an uncertainty of ±15 cal./g-atom is ascribed to the absolute value of $\Delta\overline{H}_{Au_{(\ell)}, x_{Au}=0}$ at $x_{In} = 0$, which was not determined independently for this series of runs, a line with a slope of -4400 cal./g-atom^2 agrees quite satisfactorily with the data. In any event the value of η_{In}^{Au} obtained from the more extensive measurements of $\Delta\overline{H}_{In}$ as a function of x_{Au} is the better established.

The value obtained for η_{In}^{Au}, -4400 cal./g-atom^2, is about 50 per cent more exothermic than that calculated from the random solution model, -3040 cal./g-atom^2. In view of the demonstrated small departure of gold from Henry's law behavior in liquid tin, it at first seems surprising that the correspondence between the two values should be as close as it is. The interaction energy between gold and indium is also highly exothermic, however, as revealed by the limiting value of $\Delta\overline{H}_{Au_{(\ell)}, x_{Au}=0}$ in liquid indium, -11200 cal./g-atom (Table II), which is about 3000 cal./g-atom more negative than that in liquid tin. Thus in the ternary system, the indium atoms successfully compete with those of tin toward the formation of Au-In bonds.

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