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ACTIVITIES IN DILUTE MOLTEN ALLOYS

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TABLE OF CONTENTS

	<u>Page</u>
LIST OF TABLES.....	iv
INTRODUCTION.....	1
INTERACTION PARAMETER AND INFLUENCE OF TEMPERATURE.....	1
INTERACTION PARAMETERS IN NONFERROUS ALLOYS.....	5
EFFECT OF TEMPERATURE.....	8
APPLICATIONS OF SOLUTION MODELS.....	8
SUMMARY.....	11
ACKNOWLEDGEMENT.....	11
BIBLIOGRAPHY.....	12
REFERENCES FOR INTERACTION PARAMETERS.....	13

LIST OF TABLES

<u>Table</u>		<u>Page</u>
I	NONFERROUS INTERACTION PARAMETERS.....	15
II	ALLOY ENTHALPY DERIVATIVES CALCULATED FROM ϵ VS $1/T$ SLOPES.....	20
III	COMPARISON OF EXPERIMENTAL RESULTS WITH VALUES CAL- CULATED FROM WAGNER'S RELATIONSHIP.....	21
 <u>Figure</u>		
1	VARIATION OF ϵ WITH THE RECIPROCAL OF T.....	22

INTRODUCTION

A problem which has been of considerable interest in the field of metallurgy is the prediction of the effect of one alloying element present in dilute concentration on the thermodynamic properties of another dilute alloying element. Ultimately, the prediction may be accomplished entirely from statistical mechanical considerations. At the present, however, the problem remains unsolved since liquid solution models which are simple enough for analytical treatment are inadequate for such purposes. Thus, we desire some means of organizing the information on dilute systems which will serve as a guide for further study on interactions in dilute alloys, and also provide a basis for the utilization of thermodynamic data in the engineering design of alloys.

INTERACTION PARAMETER AND INFLUENCE OF TEMPERATURE

Probably the best basis for the organization of experimental data is the interaction parameter concept devised by Wagner⁽¹⁾. This parameter is the coefficient in a Taylor series expansion for the logarithm of the activity coefficient.

$$\ln \gamma_i = \ln \gamma_i^\circ + \left[x_i \left(\frac{\partial \ln \gamma_i}{\partial x_i} \right)_{x_i=0} + x_j \left(\frac{\partial \ln \gamma_i}{\partial x_j} \right)_{x_j=0} + \dots \right] \quad (1)$$

$$+ \left[\frac{1}{2} x_i^2 \left(\frac{\partial^2 \ln \gamma_i}{\partial x_i^2} \right)_{x_i=0, x_j=0} + x_i x_j \left(\frac{\partial^2 \ln \gamma_i}{\partial x_i \partial x_j} \right)_{x_i=0, x_j=0} + \dots \right] + \dots$$

If all except the first order terms are neglected, the expression for the logarithm of the activity coefficient becomes linear with respect to the mole fractions of the solutes present in the dilute alloy.

$$\ln \gamma_i = \ln \gamma_i^\circ + x_i \epsilon_i^i + x_j \epsilon_i^j + x_k \epsilon_i^k + \dots \quad (2)$$

The interaction parameter is thus expressed as:

$$\epsilon_i^i = \left(\frac{\partial \ln \gamma_i}{\partial x_i} \right)_{x_i} = 0 \quad (3)$$

$$\epsilon_i^j = \left(\frac{\partial \ln \gamma_i}{\partial x_j} \right)_{x_i = x_j = 0} \quad (4)$$

The experimental determination of the parameter ϵ_i^i , which represents the influence of alloying element i on its own activity coefficient in dilute solution, can be accomplished from thermodynamic studies of the dilute binary alloy. The parameter ϵ_i^j represents the effect of additions of component j on the activity coefficient of component i when both are very dilute. Thermodynamic data on the dilute ternary alloy are required to compute this parameter.

The inclusion of second order terms would seem to permit a better representation of the data since a binomial expression would be fitted to the activity data rather than a linear one. Indeed, for a ternary system such a representation can be extended somewhat further away from the infinitely dilute solution than the form suggested by Wagner. For a multi-component system, however, we must evaluate experimentally terms of the type:

$$\left[\frac{\partial^2 \ln \gamma_i}{\partial x_j \partial x_k} \right]_{x_i = x_j = x_k = 0}$$

This would require quaternary data and thus defeats the engineering advantage of the simpler expression.

It can be easily demonstrated from the Gibbs-Duhem equation that:

$$\epsilon_i^j = \epsilon_j^i \quad (5)$$

This reciprocity relationship is an important advantage of the Wagner representation.

A slight modification of this representation has been proposed⁽²⁾ which involves the use of weight percent as a concentration variable rather than mole fraction, and also common logarithms rather than natural ones:

$$\log f_i = \log f_i^\circ + e_i^1 (\% i) + e_i^j (\% j) + \dots \quad (6)$$

where:

$$f_i = \frac{a_i}{\% i}$$

$$e_i^j = \left(\frac{\partial \log F_i}{\partial \% j} \right)_{\% i = \% j = 0} \quad (7)$$

The reciprocal relationship for this parameter is:

$$e_i^j = \frac{M_i}{M_j} e_j^i \quad (M = \text{molecular weight}) \quad (8)$$

The relationship between the two parameters is:

$$e_i^j = \frac{M_{\text{solvent}}}{(2.303)(100)M_j} \epsilon_i^j \quad (9)$$

An important but previously undiscussed aspect of the use of interaction coefficients is their variation with temperature. It can easily be shown from thermodynamic relationships that this variation is given by:

$$\frac{\partial \epsilon_1^j}{\partial T} = - \frac{1}{RT^2} \left(\frac{\partial^2 H}{\partial x_i \partial x_j} \right)_{x_i = x_j = 0} \quad (10)$$

The derivative of the molar enthalpy is obtainable from heat of solution data.

When the derivative of enthalpy with respect to mole fractions of the two dilute solutes is not a strong function of temperature, an extrapolation to temperatures other than those in the experimental range can be accomplished directly. If Equation (10) is rewritten in the form:

$$\frac{d \epsilon_1^j}{d\left(\frac{1}{T}\right)} = \frac{1}{R} \left(\frac{\partial^2 H}{\partial x_i \partial x_j} \right)_{x_i = x_j = 0} \quad (11)$$

then a linear variation with the reciprocal of the absolute temperature is indicated.

For a binary, strictly regular solution, we have:

$$\ln \gamma_i = (1-x_i)^2 \frac{W}{RT} \quad (12)$$

where W is the solvent-solute molar interaction energy.

The interaction parameter predicted from this model is:

$$\left(\frac{\partial \ln \gamma_i}{\partial x_i} \right)_{T, x_i = 0} = \epsilon_i^i = - \frac{2W}{RT} \quad (13)$$

If W is a function of temperature, the effect of temperature on the parameter is:

$$\frac{d \epsilon_i^i}{dT} = - \frac{2}{R} \left[\frac{1}{T} \frac{dW}{dT} - \frac{W}{T^2} \right] \quad (14)$$

which can be rewritten as:

$$\frac{d \epsilon_i^1}{d\left(\frac{1}{T}\right)} = \frac{2}{R} \left[T \frac{dW}{dT} - W \right] \quad (15)$$

If, however, W is only a slight function of temperature, or if the extrapolation is over a small temperature interval, a proportionality with the reciprocal temperature is indicated. On the basis of these considerations, a linear $1/T$ relationship is recommended for interpolation or extrapolation to temperatures not directly measured by experiment. The application of this relationship to the tabulated parameters will be discussed later.

INTERACTION PARAMETERS IN NONFERROUS ALLOYS

In 1955, Chipman⁽²⁾ discussed the application of the Wagner representation to alloy steel thermochemistry and presented values for several interaction coefficients in liquid iron at 1600°C. A more complete list has recently been prepared for liquid iron alloys⁽³⁾. In Table I, interaction parameters are presented for dilute liquid nonferrous solvents as calculated from experimental data in the literature.

Several experimental methods have been used to measure the thermodynamic properties of liquid metallic solutions. Except for gas solubility measurements, very few of the data extended into the highly dilute region. For purposes of calculating an interaction parameter, the extrapolation to infinite dilution was attempted only where the experimental data included solutions at least as dilute as 10 mole percent. This is far from an ideal

situation, and indeed, the results represent only the authors' best estimate from available sources. Where data at more than one temperature were available, all values are given.

The interaction parameter was computed as the slope of a plot of $\ln \gamma_i$ versus x_i in the case of binary systems to determine ϵ_i^i , or versus x_j at $x_i = 0$ to determine ϵ_i^j in the case of ternary systems. The limiting slope of the free energy of mixing with respect to composition was also utilized to compute the parameter since data are often presented in this form. The partial molar free energy of mixing is:

$$\Delta \bar{G}_i = \bar{G}_i - \bar{G}_i^\circ = RT \ln a_i \quad (16)$$

In the case of a binary alloy:

$$\ln \gamma_i = \frac{1}{RT} \left[\Delta \bar{G}_i - RT \ln x_i \right] \quad (17)$$

where the bracketed term is recognized as the excess molar free energy of mixing:

$$\ln \gamma_i = \frac{1}{RT} \Delta \bar{G}_i^{xs} \quad (18)$$

The interaction parameter is then given by:

$$\epsilon_i^i = \left(\frac{\partial \ln \gamma_i}{\partial x_i} \right)_{T, x_i=0} = \frac{1}{RT} \lim_{x_i \rightarrow 0} \left[\frac{\partial \Delta \bar{G}_i^{xs}}{\partial x_i} \right] \quad (19)$$

Extending this development to the case of ternary data, and noting that x_i and x_j are independent:

$$\epsilon_i^j = \lim_{\substack{x_i \rightarrow 0 \\ x_j \rightarrow 0}} \left(\frac{\partial \Delta \bar{G}_i}{\partial x_j} \right) \quad (20)$$

Gas solubilities are usually given as cc of gas (STP) per 100 gms of alloy versus pressure at constant temperature. In all cases where gas solubility data were analysed, the gas was diatomic, and the data followed Sievert's law. This means that the gas dissolves atomically and that the dissolved gas follows Henry's law. Of course the self interaction of any material which follows Henry's law is zero. Consequently, to get ϵ_i^j , one need not take the limit as $x_i \rightarrow 0$ but can use $\left(\frac{\partial \ln \gamma_i}{\partial x_j}\right)_{T, x_i, x_j = 0}$ at any constant value of x_i within the Henry's Law region. In the case of hydrogen, for example, if the gas phase is ideal, one has

$$P_{H_2} = f_{H_2} \quad (= \text{fugacity}) \quad (21)$$

thus:

$$\epsilon_H^j = \frac{1}{2} \left(\frac{\partial \ln P_{H_2}}{\partial x_j}\right)_{T, x_j = 0, x_H} \quad (22)$$

where "H" represents atomic hydrogen in solution. If the data are given at constant pressure we can use:

$$\epsilon_H^j = - \left(\frac{\partial \ln x_H}{\partial x_j}\right)_{T, P, x_j = 0} \quad (23)$$

or:

$$e_H^j = - \left[\frac{\partial \log (\text{wt. \% H})}{\partial (\text{wt. \% j})} \right]_{T, P, (\% j) = 0} \quad (24)$$

EFFECT OF TEMPERATURE

In several instances, data at three or more temperatures were available. Several examples are presented in Figure 1 showing the relationship between ϵ and $1/T$. Straight lines were drawn through the points in accordance with the conclusions above. The slopes of these lines were used to compute an approximate value for the second derivative of the alloy enthalpy with respect to the mole fractions of the dilute components. These values, calculated by means of Equation (11), are given in Table II.

APPLICATIONS OF SOLUTION MODELS

Although many solution models have been proposed, none of these has been found satisfactory for quantitative predictions of interaction parameters because of conceptual or mathematical limitations⁽⁴⁾. Actually, our demands are reasonably simple; we do not wish to predict absolute values of the ordinary thermodynamic functions but only the effect of added components on the partial molar free energy of the others. Only two theories have as yet been applied to this specific problem. One is the free electron theory and the other is based on a nearest neighbor lattice model.

Studies of gas solubilities in metal alloys led Wagner to the formulation of a free electron theory⁽⁵⁾. The basis of the theory is that when an added element dissolves as protons and electrons, if the ion-electron interactions are much stronger than the ion-ion interactions, then the primary variable of importance is the free energy of the electrons and the effect of added elements thereon. Based on this idea Wagner has derived a relationship between ϵ_1^j and the self-interaction parameters, ϵ_1^i and ϵ_j^j . This

relationship is:

$$\epsilon_i^j = \pm \sqrt{\epsilon_i^i \epsilon_j^j} \quad (25)$$

A corollary of this result is that for a given solvent, all self-interaction parameters should have the same sign. This has been found to be true only when deviations from ideality are large. Wagner verified his equation for the case of several alkali amalgams⁽⁶⁾. His comparisons are included in Table III. In general, we can hope to make a reasonable prediction by means of Wagner's equation whenever the self-interaction parameters are very large and have the same sign. Comparisons between values predicted from this theory and experimental values are made in Table III.

A reasonably simple model for solutions and one which is especially attractive both because of our quasi-crystalline picture of a liquid and because of the simplicity of the basic concepts involved is the chemical bond theory based on the neighbor lattice model first devised by Ising. The model was applied by Hildebrand who hypothesized the "regular solution". This development proved to be somewhat too general for accurate analysis and a later simplification, the "strictly regular solution" was discussed by Fowler and Guggenheim⁽⁷⁾. The only case examined in the literature for such models is that of a binary non-electrolyte.

The problem is somewhat more complicated when we deal with a multicomponent system. Let us consider for the moment a dilute solution of A and B in a solvent C. Possible types of pairs are: A-A, A-B, B-B, A-C, B-C, and C-C. We are first tempted to assume that the latter three types of pairs would predominate and that there would be few of the first three types of

bond. This means that nearly all solute molecules A and B are surrounded by C and that there is no direct A-B interaction. Thus, under the assumptions of the regular solution we would have no effect of A on B or of B on A.

Alcock and Richardson^(8,9), however, have applied a similar model to the case of a ternary alloy in which one solute is somewhat more dilute than the other. Strictly speaking, their problem is somewhat different from the one at hand, for we are interested in the interactions at infinite dilution of all of the solutes. In the development of a lattice model for this problem, all types of bonds must be taken into account. In the case of a ternary this would be 6 different ones whose relative magnitudes would be expected to determine the extent and type of clustering in the model lattice. In view of this complexity, and the assumptions implicit in the model, the obtaining of dependable quantitative results with this approach is precluded at present. Several difficulties which arise immediately and are not easily treated theoretically include the variation of the interaction energies with composition, the non-normality of the solution, the influence of composition on more than one degree of freedom, and the case where the coordination numbers of the solutes are different from that of the solvent. Hence, no attempt is being made at present to derive a suitable model on this basis.

Finally, the attempt of Gokcen and Ohtani⁽¹⁰⁾ to establish an empirical correlation for interaction parameters in iron on the basis of atomic number should be mentioned. The results are interesting, but without a definite theoretical base. The general utility of this approach appears to be quite limited.

SUMMARY

Wagner's expression for predicting activities of dilute solutes in multicomponent systems is a simple and promising quantification of a complex metallurgical problem. The data available for its use are presently limited. Table I of this paper has summarized these parameters for nonferrous metallic solutions.

The interaction parameter can be extrapolated or interpolated to temperatures other than those measured by experiment if a linear $1/T$ relationship is assumed. Such a procedure is indicated by theoretical considerations.

The direct prediction of parameters from statistical mechanics appears to exist somewhere in the distant future. Wagner, however, has attempted to predict interaction coefficients from the self interaction parameters, for the case of certain types of solutes. A comparison of data on several systems indicates that this is a reasonable estimate whenever the values of the self interactions are large and of the same sign.

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TABLE I
NONFERROUS INTERACTION PARAMETERS

Solvent	i	j	ϵ_i^j	Temperature, °C	Ref.
Aluminum	Ag	Ag	-3.1	1000	8
	Cu	H	see ϵ_H^{Cu}	700-1000	*
	H	Cu	39.0	700	22
	H	Cu	16.6	800	22
	H	Cu	20.1	900	22
	H	Cu	4.3	1000	22
	H	H	0	700-1000	22
	H	Si	11.5	700	22
	H	Si	6.2	800	22
	H	Si	4.2	900	22
	H	Si	1.8	1000	22
	Si	H	see ϵ_H^{Si}	700-1000	*
	Antimony	Cd	Cd	1.5	500
Cd		Pb	2.8	500	11
Pb		Cd	2.8	500	*
Pb		Pb	0.59	500	11
Sn		Sn	2.2	905	20
Bismuth	Au	Au	2.1	700	18
	Cd	Cd	-1.22	500	11
	Cd	Pb	1.62	500	11
	Hg	Hg	-0.33	321	20
	Mg	Mg	0.85	700	10
	Pb	Cd	1.62	500	*
	Pb	Pb	1.44	500	11
	Pb	Pb	0.75	665	25
	Pb	Pb	0.91	475	25
	Sn	Sn	-0.056	330	25
	Tl	Tl	3.22	270	27
	Tl	Tl	2.14	480	25
	Zn	Zn	-3.3	600	19

TABLE I (CONT'D)

Solvent	i	j	ϵ_{ij}^j	Temperature, °C	Ref.
Cadmium	Bi	Bi	-6.5	500	11
	Bi	Pb	-3.2	500	11
	Hg	Hg	3.36	327	20
	Hg	Hg	2.5	350	23
	Hg	Na	-6	350	12
	Na	Hg	-6	350	*
	Na	Na	17.8	350	12
	Na	Na	15.8	395	20
	Pb	Bi	-3.2	500	*
	Pb	Pb	-4.56	500	11
	Pb	Sb	0	500	11
	Pb	Sn	2.86	500	11
	Sb	Pb	0	500	*
	Sb	Sb	-6.5	500	11
	Sn	Pb	2.86	500	*
	Sn	Sn	-1.5	500	11
	Zn	Zn	-1.78	682	6
	Cobalt	Cr	N	-19.5	1600
Fe		H	.53	1600	*
H		Fe	.53	1600	7
H		Ni	.09	1600	7
N		Cr	-19.5	1600	5
N		Si	80	1600	5
N		V	-72	1600	5
Ni		H	.09	1600	*
Si		N	80	1600	*
S		Cu	-4(+2)	1500	**
V		N	-72	1600	*
Copper	H	Sn	5+ <u>.3</u>	1100-1300	4
	S	Au	6.9(+ <u>1</u>)	1115	**
	S	Co	-4.8(+ <u>.8</u>)	1300	**
	S	Fe	-7.4(+ <u>.5</u>)	1300	**
	S	Ni	-6.6(+ <u>1</u>)	1300	**
	S	Pt	9.2(+ <u>0.2</u>)	1200	**
	S	Si	6.9(+ <u>2</u>)	1200	**
	Sn	H	5+ <u>.3</u>	1100-1300	*

TABLE I (CONT'D)

Solvent	i	j	ϵ_i^j	Temperature, °C	Ref.
Copper (cont'd)	Zn	Zn	0.38	802	15
	Zn	Zn	0.72	727	15
	Zn	Zn	1.185	653	15
	Zn	Zn	1.40	604	15
Gold	Bi	Bi	0.1	700	18
	Pb	Pb	5	600	16
	Sn	Sn	38.9	600	17
	Tl	Tl	0.1	700	18
Lead	Ag	Ag	-0.6	1085	20
	Ag	Ag	-0.92	1000	8
	Au	Au	3.2	600	16
	Bi	Bi	2.6	500	11
	Bi	Cd	-0.86	500	11
	Cd	Bi	-0.86	500	*
	Cd	Cd	-2.6	500	11
	Cd	Sb	-1.6	500	11
	Cd	Sn	1.35	500	11
	Hg	Na	-5.25	400	*
	Mg	Mg	0.6	833	20
	Mn	Mn	0	750-1000	27
	Na	Hg	-5.25	400	13
	Na	Na	3.6	400	13
	Sb	Cd	-1.6	500	*
	Sb	Sb	0.16	500	11
	Sn	Cd	1.35	500	*
	Sn	Sn	-1.17	500	11
	Tl	Tl	0.1	450	20
	Zn	Zn	-5.3	653	19
Mercury	Ba	Ba	127	298	3
	Cd	Na	6.0	350	*
	Ce	Ce	126.9	25	3
			66.0	281	3
			61.0	301	3
			57.0	327	3
			51.0	378	3
	K	K	73	0	2

TABLE I (CONT'D)

Solvent	i	j	ϵ_i^j	Temperature, °C	Ref.	
Mercury (cont'd)			65.3	25	2	
			61.6	50	2	
			67	?	26	
			54.4	200	3	
			50.3	250	3	
			47.0	310	3	
			43.8	390	3	
		K	Na	46.5	?	*
		K	Tl	30.8	?	26
		Li	Li	26.5	25	24
		Li	Tl	17.5	?	26
		Na	Cd	6.0	350	12
		Na	K	46.5	?	26
		Na	Na	46.1	25	3
				30.7	335.5	3
				29.6	375	3
				23.4	350	12
				36.0	?	26
				43.0	400	13
		Na	Pb	6	400	13
		Na	Tl	22.1	?	26
		Pb	Na	6	400	*
		Tl	K	30.8	?	*
		Tl	Li	17.5	?	*
		Tl	Na	22.1	?	*
		Tl	Tl	6.0	325	21
		Tl	Tl	13.1	?	26
Nickel	Co	H	2.58	1600	*	
	Cr	N	-23.6	1600	*	
	Fe	H	.009	1600	*	
	Fe	N	-3.25	1600	*	
	Fe	O	132	1594	*	
	H	Co	2.58	1600	7	
	H	Fe	.009	1600	7	
	N	Cr	-23.6	1600	14	
	N	Fe	-3.25	1600	14	
	O	Fe	132	1594	29	
	S	Cu	0(+1)	1600	**	

TABLE I (CONT'D)

Solvent	i	j	ϵ_{ij}^j	Temperature, °C	Ref.
Silver	Al	Al	6.4	700	28
			5.6	800	28
			4.6	900	28
			4.22	1000	8
	Cd	Cd	1.47	827	20
	Pb	Pb	-0.4	1000	8
Sodium	Cd	Hg	4.2	350	*
	Hg	Cd	4.2	350	9
	Hg	Hg	2.0	350	9
Thallium	Au	Au	2.6	700	18
	Hg	Hg	0.091	325	21
	Sn	Sn	-1.7	325	8
	Sn	Sn	-0.8	414	8
	Sn	Sn	0	478	8
Tin	Au	Au	5.8	600	17
	Cd	Cd	-1.05	500	11
	Cd	Cd	-2.36	700	20
	Cd	Pb	0	500	11
	Cd	Zn	-1.65	700	*
	Cu	H	see ϵ_{H}^{Cu}	1000-1300	*
	H	Cu	-9.65	1000	4
	H	Cu	-8.05	1100	4
	H	Cu	-5.64	1200	4
	H	Cu	-4.45	1300	4
	Pb	Cd	0	500	*
	Pb	Pb	0.65	500	11
	Tl	Tl	-3.2	352	8
	Tl	Tl	-1.78	414	8
	Tl	Tl	-0.475	478	8
	Zn	Cd	-1.65	700	20
	Zn	Zn	-1.0	437	20
Zn	Zn	-0.6	684	6	
Zinc	Cd	Cd	-3.33	682	6

* Calculated from reciprocity relationship.

** Values taken from (2) where x_s not zero.

TABLE II

ALLOY ENTHALPY DERIVATIVES CALCULATED
FROM ϵ VS $1/T$ SLOPES

Solvent	Element i	Element j	$\left(\frac{\partial^2 H}{\partial x_i \partial x_j}\right)_{x_i=0, x_j=0}$
Ag	Al	Al	1.9×10^4
Al	H	Co	8×10^4
Al	H	Si	1.8×10^4
Bi	Pb	Pb	4.0×10^3
Cu	Zn	Zn	1.0×10^4
Hg	Ce	Ce	1.1×10^5
Hg	K	K	3.8×10^4
Hg	Na	Na	2.3×10^4
Sn	H	Cu	-3.9×10^3
Sn	Tl	Tl	-1.2×10^4
Tl	Sn	Sn	-7.5×10^3

TABLE III

COMPARISON OF EXPERIMENTAL RESULTS WITH VALUES
CALCULATED FROM WAGNER'S RELATIONSHIP*

Solvent Metal	Metal i	Metal j	ϵ_i^i (Experimental)	ϵ_j^j	ϵ_i^j (Exp)	ϵ_i^j (Calc)
Sb	Cd	Pb	1.5	0.59	2.8	0.8
Cd	Sb	Pb	-6.5	-4.56	0	-5
Cd	Bi	Pb	-6.5	-4.56	-3.2	-5
Pb	Sn	Cd	-1.17	-2.6	1.35	1.7
Hg	Na	Tl	35	13	22	21
Hg	Na	K	35	55	46.5	44
Hg	K	Tl	55	13	30.8	27
Hg	Li	Tl	26.5	13	17.5	18.6
Sn	Zn	Cd	-2.4	-1	-1.6	-1.6

* Experimental data from Table I.

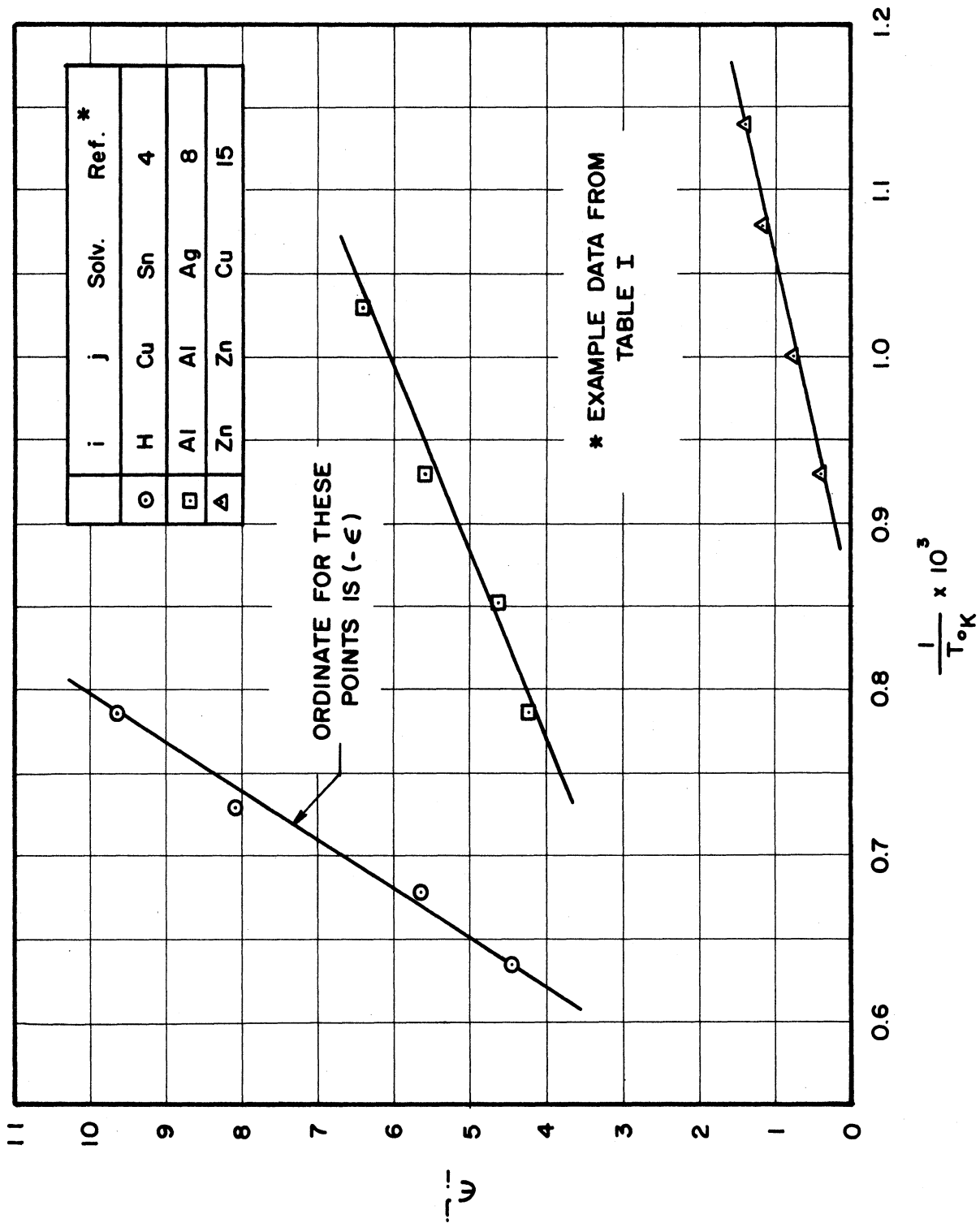


FIGURE 1 , VARIATION OF ε WITH THE RECIPROCAL OF T

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