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Thermodynamics of Rare-Metal Bearing Binary Substitutional Alloy Systems

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CONTENTS

ABSTRACT

A novel statistical thermodynamic approach, based on free volume theory, has recently been applied to the binary alloy systems of some important rare metals. The theoretically calculated values of properties of such solutions, obtained by making use of experimentally determined infinite dilution properties of both the components and expressions developed in this new approach, show excellent correspondence to selected empirical data of these systems over their entire range of composition. Asymmetric behaviour of several of these systems is also successfully explained. However, the general behaviour of solutes based on their fundamental characteristics cannot be predicted quantitatively in such solutions.

1. INTRODUCTION

Metallic solutions are commonly encountered in the extraction of metals from their primary and secondary sources; in refining of commercial metals to a state of high-purity; in combating corrosion; in alloy design and development to meet challenging specific service requirements and in the processing of metals and alloys. Thermodynamic properties of such solutions naturally play a significant role in all these fields and hence have been extensively studied experimentally. However, due to several inherent limitations and problems of such experimental studies, especially in the dilute solution range of solutes and in multi-component solvents, a number of theoretical attempts were also made simultaneously. Several solution models /1-8/ viz quasi-chemical theory, regular solution model, sub-regular solution model, central (surrounded) atom models, etc., have been developed and used to theoretically calculate, interpret and predict the properties of such solutions, with varying degrees of success, because, essentially, they are limited due to their basic assumptions. Kapoor /9/ has critically reviewed these and has also developed a novel statistical thermodynamic approach /10/ based on free volume theory and, by making use of non-linear quadratic forms after Wagner /8/, of energies and free volumes of different atoms present in such binary substitutional metallic solutions. This approach has previously been very successfully applied to the binary alloy systems of a number of common metals such as silver /9/, iron /11/, zinc /12/, copper /13/, aluminium /14/, chromium /15/, lead /16/, antimony /17/, manganese /18/, gold /19/, nickel /20/, cadmium /21/, tin /22/ and bismuth /23/. With development of science and technology, especially for nuclear, high temperature and space applications, several rare-metals have now become strategically important and are being used increasingly for specific and demanding applications in scientific research and industry. In the present work, therefore, the same novel approach is applied and tested for its predictive value, to the binary substitutional alloy systems of some of these rare-metals.

2. THEORY

The basic assumptions of the new approach /10/ are:

1. A metallic solution of substitutional components, liquid or solid, is assumed to form a quasi-crystalline lattice with each atom having an average coordination number, z.
2. Each atom moves around its lattice site within a cell, which is determined by nearest neighbour interactions of the atom.
3. The energy and also the free volume of any atom is a non-linear quadratic function of the type and number of atoms in its first coordination shell.

For a binary substitutional solution containing n_A atoms of component A and n_B of component B, the configurational partition function, Ω_c according to the free-volume theory /4,10/ can be expressed as

$$\Omega_c = \Sigma\Pi(V_{Ai})\cdot\Pi(V_{Bj})\cdot\exp(-W_o/kT) \qquad (1)$$

and, with all atoms fixed at their respective mean-sites, the energy of the system, W_0, being equal to the sum of the energies of all the atoms present in the system as

$$W_o = \sum_{i=0}^{z} n_{Ai}\cdot W_{Ai} + \sum_{j=0}^{z} n_{Bj}, W_{Bj} \qquad (2)$$

Therefore, the free energy of mixing, ΔG_{mix} of the system can be expressed as

$$\begin{aligned}(n_A+n_B)\cdot\Delta G_{mix} = \\ -kT\ln\Omega - n_A\cdot W_{Ao} - n_B\cdot W_{Bo} \\ -kT(n_A\cdot\ln V_{Ao} + n_B\cdot\ln V_{Bo})\end{aligned} \qquad (3)$$

where the partition function, Ω, of the system is

$$\Omega = \Omega_c / n_{A!}\ n_{B!} \tag{4}$$

In the above expressions, symbols k and T represent, respectively, Boltzmann's constant and absolute temperature: n_{Ai} and n_{Bj}, the number of A and B atoms respectively, having 'i' atoms of B and 'j' atoms of A in their first coordination shells; W_{Ai} and W_{Bj} their respective energies and V_{Ai} and V_{Bj} their respective free volumes. Symbols W_{Ao}, W_{Bo}, V_{Ao} and V_{Bo} represent, respectively, the corresponding energies and free volumes of pure A and pure B atoms.

In general, the atoms of A and B differ in their basic characteristics such as atomic number, atomic mass, atomic radius, electronegativity, crystal structure, etc. Therefore consecutive replacement of one type of atom from the surroundings of any central atom of A or B, consequent to their mixing on formation of binary solution, results in changes in energies and also in free volumes, of central atoms of A and B, that are not constant for successive substitutions. Mathematically, following Wagner's approach /8/, one can write

$$\Delta W_{A1} \neq \Delta W_{A2} \neq \Delta W_{A3} \neq \ldots \neq \Delta W_{Az} \tag{5}$$

where

$$\Delta W_{Ai} = W_{Ai} - W_{A(i=1)} \tag{6}$$

However, because of substitution by the same type of atoms, one can assume with sufficient accuracy that

$$\Delta W_{A(i+1)} - \Delta W_{Ai} = \delta_A \quad (\textit{a constant}) \tag{7}$$

and, similarly,

$$\Delta W_{B(j+1)} - \Delta W_{Bj} = \delta_B \ (\textit{another constant}) \tag{8}$$

Using Eqs. (7) and (8), one can, by again following Wagner's approach /8/, arrive at the following general non-linear quadratic form of expressions for the energies of central A and B atoms,

$$W_{Ai} = W_{Ao} + i \cdot \Delta W_A + \delta_A \cdot i(i-1)/2 \tag{9}$$

and

$$W_{Bj} = W_{Bo} + j \cdot \Delta W_{B1} + \delta_B \cdot j(j-1)/2 \tag{10}$$

Evidently, an assumption of δ_A and δ_B equal to zero leads to the linear forms of energies postulated in the quasi-chemical theory or regular solution model /2,4,9/.

Following similar analysis, the natural logarithms of free-volumes of these types of atoms will also be expressed by the following quadratic expressions:

$$\ln V_{Ai} = \ln V_{Ao} + i \Delta \ln V_{A1} + \eta_A \cdot i(i-1)/2 \tag{11}$$

and

$$\ln V_{Bj} = \ln V_{Bo} + J \cdot \Delta \ln V_{B1} + \eta_B \cdot j(j-1)/2 \tag{12}$$

where η_A and η_B are also system-dependent constants, defined in an identical manner as δ_A and δ_B, which correspond to changes in the natural logarithms of free volumes of atoms on substitution of atoms, as explained above.

Using these values of energies, free volumes and partition function, one can arrive at the following expression for the excess molar free energy of mixing of the binary solution,

$$\begin{aligned}\Delta G^{xs}_{mix} = Z \cdot N_A N_B\ [N(\Delta\rho_{A1} + \Delta\rho_{B1}) + \\ (Z-1)N(\delta_A - kT\eta_A) \cdot \frac{N_B}{2}(Z-1) \cdot \\ N(\delta_B - kT\eta_B) \cdot \frac{N_A}{2} - \frac{[N \cdot (\Delta\rho_{A1} + \Delta\rho_{B1})]^2}{RT} \cdot \\ Z N_A^2 N_B^2 + Z(Z-1)[(\delta_B - kT\eta_B) \cdot N_B + (\delta_A - kt\eta_A 0 \cdot N_A] \cdot \\ \frac{N \cdot (\Delta\rho_{A1} + \Delta\rho_{B1})}{RT} \cdot N_A^2 N_B^2\end{aligned} \tag{13}$$

where N_A and N_B are, respectively, the atom-fractions of components A and B of the binary substitutional solution (A+B) and where

$$\Delta\zeta_{AI} = \Delta W_{A1} - kT \cdot \Delta(\ln V_{A1}) \tag{14}$$

and

$$\Delta\zeta_{BI} = \Delta W_{Bi} - kT \cdot \Delta(\ln V_{B1}) \tag{15}$$

From Eq. (13), expressions for ΔH_{mix} and ΔS^{xs}_{mix} for the solution can be obtained using relevant differential functions.

In general, values of the different theoretical parameters in the above expressions are not known for different binary substitutional alloy systems. Therefore, for making practical use of these expressions, the various theoretical parameters viz ΔW, $\Delta \ln V$, δ and η terms, should be substituted by experimentally determinable parameters, i.e. the excess partial molar properties at infinite dilution and the self-interaction parameters of the components of the binary solution. Making these substitutions, the different expressions for excess thermodynamic properties of the binary solution under study can be rewritten as follows:

$$\Delta G^{xs}_{mix} = (\Delta \overline{G}^{xs,\infty}_{B(A)} \cdot N_A + \Delta G^{xs,\infty}_{A(B)} \cdot N_B) \cdot N_A N_B + [(\epsilon^{A}_{A(B)}/2 - \Delta \overline{G}^{xs,\infty}_{B(A)} + 2 \cdot \Delta \overline{G}^{xs,\infty}_{A(B)}) \cdot N_B] + (\epsilon^{B}_{B(A)}/2 - \Delta \overline{G}^{xs,\infty}_{A(B)} + 2 \cdot \Delta \overline{G}^{xs,\infty}_{B(A)}) N_A] \cdot N_A^2 N_B^2 \tag{16}$$

$$\Delta H_{mix} = (\Delta \overline{H}^{\infty}_{A(B)} \cdot N_B + \Delta \overline{H}^{\infty}_{B(A)} \cdot N_A) \cdot N_A N_B + [(\rho^{A}_{A(B)}/2 - \Delta \overline{H}^{\infty}_{B(A)} + 2\Delta \overline{H}^{\infty}_{A(B)}) \cdot N_b + (\rho^{B}_{B(A)}/ - \Delta \overline{H}^{\infty}_{A(B)} + 2\Delta \overline{H}^{\infty}_{B(A)}) n_A] \cdot N_A^2 N_B^2 \tag{17}$$

and

$$\Delta S^{xs}_{mix} = (\Delta \overline{S}^{xs,\infty}_{A(B)} \cdot N_B + \Delta \overline{S}^{xs,\infty}_{B(A)} \cdot N_A) \cdot N_A N_B + [(\sigma^{A}_{A(B)}/2 - \Delta S^{xs,\infty}_{B(A)} + 2\Delta S^{xs,\infty}_{A(B)}) N_B + (\sigma^{B}_{B(A)}/2 - \Delta S^{xs,\infty}_{A(B)} + 2\Delta \overline{S}^{xs,\infty}_{B(A)}) \cdot N_A] \cdot N_A^2 N_B^2 \tag{18}$$

where

$$\Delta \overline{G}^{xs,\infty}_{i(j)} = \Delta \overline{H}^{\infty}_{i(j)} - T \cdot \Delta \overline{S}^{xs,\infty}_{i(j)} \tag{19}$$

and also

$$\epsilon^{i}_{i(j)} = \rho^{i}_{i(j)} - RT \cdot \sigma^{i}_{i(j)} \tag{20}$$

In these expressions, symbols $\Delta \overline{G}^{xs,\infty}_{i(j)}$, $\Delta \overline{H}^{\infty}_{i(j)}$ and $\Delta \overline{S}^{xs,\infty}_{i(j)}$ represent respectively the partial molar excess free energy, enthalpy and excess entropy at infinite dilution of the component i (either A or B) and symbols $\epsilon^{i}_{(j)}$, $\rho^{i}_{i(j)}$ and $\sigma^{i}_{i(j)}$ respectively, the free energy, enthalpy and entropy of self-interaction of the component 'i' in the binary (i+j) solution.

As can be observed, the above expressions for ΔG^{xs}_{mix}, ΔH_{mix} and ΔS^{xs}_{mix} are made up of two components: one for the random distribution of atoms in the solution represented by the first term in all expressions; the other for their preferential distribution, represented by all the remaining terms, resulting from appreciable differences in their basic characteristics and, therefore, energies and free volumes of the different atoms of the components of the binary solution. Therefore, functions $\Delta G^{xs}_{mix}/N_A N_B$, $\Delta H_{mix}/N_A N_B$ and $\Delta S^{xs}_{mix}/N_A N_B$ will be linear functions of the composition N_B of the binary randomly distributed alloy systems. Any deviation from this linear behaviour is an indication of preferential distribution of atoms in such systems, which in turn is also an inverse function of temperature of the system.

Kapoor /10/ also arrived at the following relationships for randomly distributed substitutional binary (A+B) metallic solutions

$$\Delta G^{xs}_{mix} = (\Delta \overline{G}^{xs,\infty}_{A(B)} \cdot N_B + \Delta \overline{G}^{xs,\infty}_{B(A)} \cdot N_A) \cdot N_A N_B \tag{21}$$

$$\Delta H_{mix} = (\Delta \overline{H}^{\infty}_{A(B)} \cdot N_B + \Delta \overline{H}^{\infty}_{B(A)} \cdot N_A) \cdot N_A N_B \tag{22}$$

$$\Delta S^{xs}_{mix} = (\Delta \overline{S}^{xs,\infty}_{A(B)} \cdot N_B + \Delta \overline{S}^{xs,\infty}_{B(A)} \cdot N_A) \cdot N_A N_B \tag{23}$$

$$\rho^{A}_{A(B)} = R \cdot \left(\frac{\partial^2 \ln \gamma_{A(B)}}{\partial T \cdot \partial N_A} \right)_{N_B \to 1} = 2.\Delta \overline{H}^{\infty}_{B(A)} - 4.\Delta \overline{H}^{\infty}_{A(B)} \tag{24}$$

$$\rho^{B}_{B(A)} = R \left(\frac{\partial^2 \ln \gamma_{A(B)}}{\partial T \cdot \partial N_A} \right)_{N_B \to 1)} = 2.\Delta \overline{H}^{\infty}_{B(A)} - 4.\Delta \overline{H}^{\infty}_{A(B)} \tag{25}$$

$$\sigma^{A}_{A(B)} = \frac{\partial}{\partial T} \left[RT \left(\frac{\partial \ln \gamma_{A(B)}}{\partial N_A} \right) \right]_{N_B \to 1} = 2.\Delta \overline{S}^{xs,\infty}_{A(B)} - 4.\Delta \overline{S}^{xs,\infty}_{B(A)} \tag{26}$$

and

$$\sigma^{B}_{B(A)} = \frac{\partial}{\partial T} \left[RT \left(\frac{\partial \ln \gamma_{B(A)}}{\partial N_B} \right) \right]_{N_A \to 1} = 2\Delta \overline{S}^{xs,\infty}_{B(A)} - 4\Delta \overline{S}^{xs,\infty}_{A(B)} \tag{27}$$

and consequently,

$$e^{A}_{A(B)} = RT\left(\frac{\partial \ln \gamma_{A(B)}}{\partial N_A}\right)_{N_B \to 1} = P^{A}_{A(B)} - \qquad (28)$$

$$RT \cdot \sigma^{A}_{A(B)} = 2.\Delta \overline{G}^{xs,\infty}_{A(B)} - 4.\Delta \overline{G}^{xs,\infty}_{B(A)}$$

and

$$e^{B}_{B(A)} = RT\left(\frac{\partial \ln \gamma_{B(A)}}{\partial N_B}\right)_{N_A \to 1} = P^{B}_{B(A)} - \qquad (29)$$

$$RT \cdot \sigma^{B}_{B(A)} = 2.\Delta \overline{G}^{xs,\infty}_{A(B)} - 4.\Delta \overline{G}^{xs,\infty}_{B(A)}$$

where $\gamma_{A(B)}$ and $\gamma_{B(A)}$ are, respectively, the activity coefficients of components A and B of the binary (A+B) substitutional solution.

3. APPLICATION OF THE THEORY

3.1. Thermodynamic Properties of 61 Rare-Metal Binary Metallic Systems

Selected values of empirical thermodynamic properties of 61 binary metallic systems of rare-metals, In, Tl, Pd, Pt, Ga, Ge, V, Si, Nb, Th, Ti, Be, Ir, Mo, Li, Ce, Zr and Pr, tabulated by Hultgren et al. /24/, have been used to calculate functions $\Delta G^{xs}_{mix}/N_A N_B$, $\Delta H_{mix}/N_A N_B$ and $\Delta S^{xs}_{mix}/N_A N_B$ for various compositions, N_B, of such solutions, and the liquid and solid binary alloy systems of these rare-metals are illustrated (by points) in Figs. 1 to 6.

From these plots of empirical data, values of infinite dilution partial molar properties, $\Delta \overline{G}^{xs,\infty}_{i(j)}$, $\Delta \overline{H}^{\infty}_{i(j)}$, and $\Delta \overline{S}^{xs,\infty}_{i(j)}$ and self-interaction parameters, $\epsilon^{i}_{i(j)}$, $\rho^{i}_{i(j)}$ and $\sigma^{i}_{i(j)}$ are calculated for both components of these binary solutions, using the procedure developed by Kapoor /10/. These are presented in Table 1 and Table 2, respectively. Some important characteristics of the solvents and solutes of these binary systems, utilised for qualitative analysis of these infinite dilution parameters, are presented in Table 3.

Making use of these calculated values of the empirical infinite dilution parameters of both the components of such solutions, the same parameters $\Delta G^{xs}_{mix}/N_A N_B$, $\Delta H_{mix}/N_A N_B$ and $\Delta S^{xs}_{mix}/N_A N_B$ are recalculated using Eqs. (16)-(18), at selected compositions $N_B = 0.1, 0.2, 0.3, = 0.9$, and also plotted (by smooth curves) in the same figures for the binary metallic systems under study.

An excellent correspondence between these two calculated values of the plotted parameters–one using expressions derived in this new approach and the empirical infinite dilution parameters of both components, the other using only the tabulated selected empirical data on these binary systems, both in the liquid and solid states–points to a very successful applicability of the new approach to these rare-metal bearing binary substitutional solutions. It is further to be noted that (1) the asymmetric behaviour of some of these systems and (2) all the three parameters–excess free energy, enthalpy and excess entropy–are also simultaneously explained by the new approach. The theoretical models mentioned earlier, including Miedema's formalism for enthalpy of mixing /25/, are not capable of explaining either all these functions simultaneously for the entire range of compositions of solutions or the asymmetric behaviour, to the same degree of accuracy as the new approach.

From the data tabulated and plotted, therefore, it is possible to theoretically calculate and predict the thermodynamic properties of binary substitutional metallic systems at any desired composition, but this requires a knowledge of the infinite dilution properties of both components of such systems at the temperature of interest.

A qualitative analysis of the data presented in Tables 1-3 also reveals that although characteristics of solute, viz. position in periodic table, atomic number, atomic radius, crystal structure and electronegativity, have observable and occasionally appreciable effects on thermodynamic properties of both the solute and the solvent components, yet in many cases no regularity in their variation (either increase or decrease) can be predicted with a regular variation of the solute characteristics. Similarly, although appreciable differences in thermodynamic properties of the components have been observed in alloys of the same binary system in the liquid and solid states, no measurable differences are observed in the case of several others.

One could only note the following typical examples of regular behaviour in the different systems studied in the present work.

3.2. Binary Alloys of Indium

1. With an increase in atomic number and also atomic radius of the solute in liquid alloys from copper to

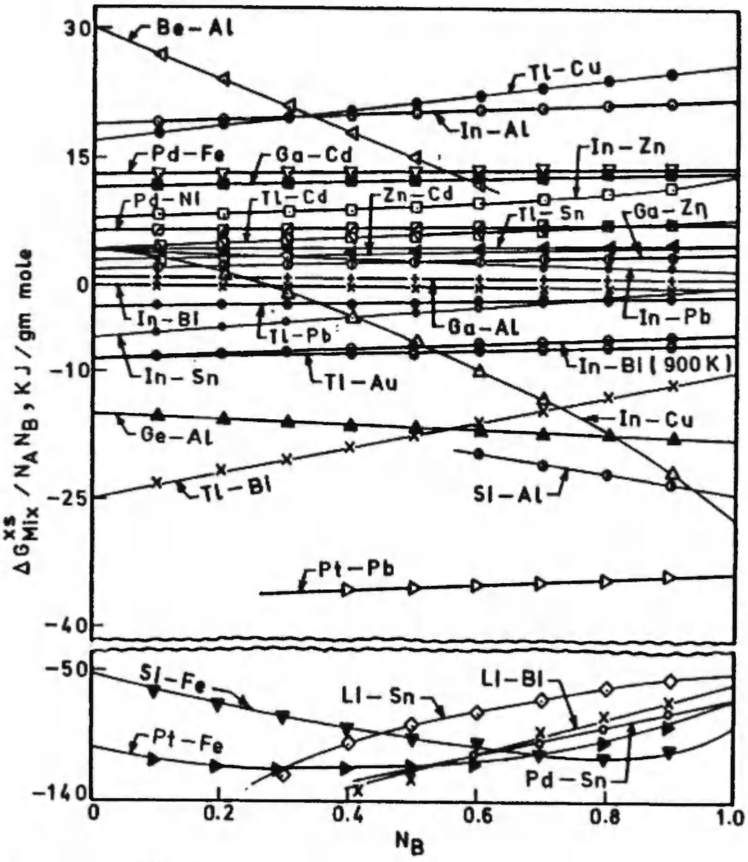

Fig. 1: $\Delta G^{xs}_{mix}/N_A N_B$ vs. N_B for liquid rare-metals-B alloy systems.

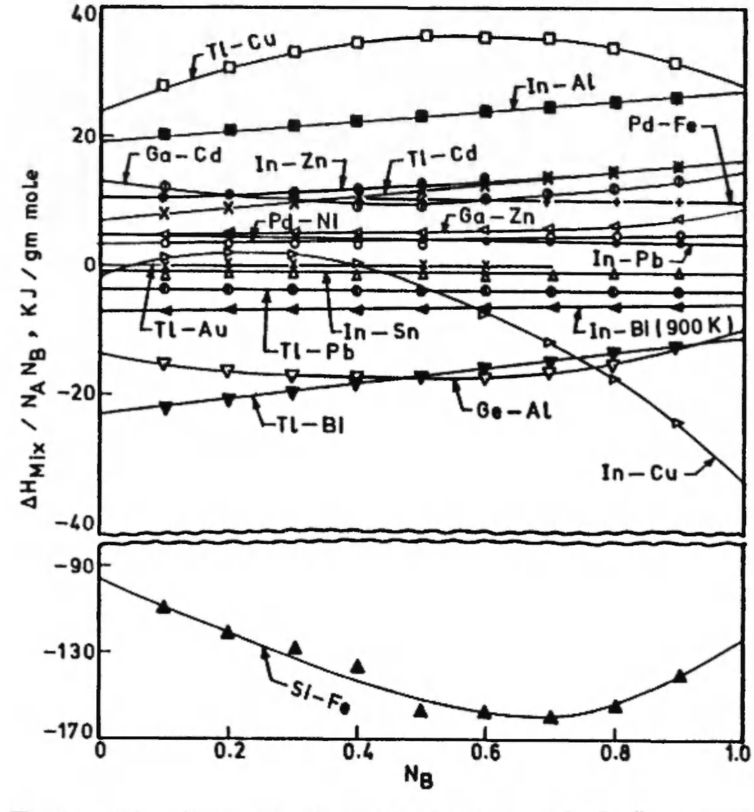

Fig. 2: $\Delta H_{mix}/N_A N_B$ vs. N_B for liquid rare-metals-B alloy systems.

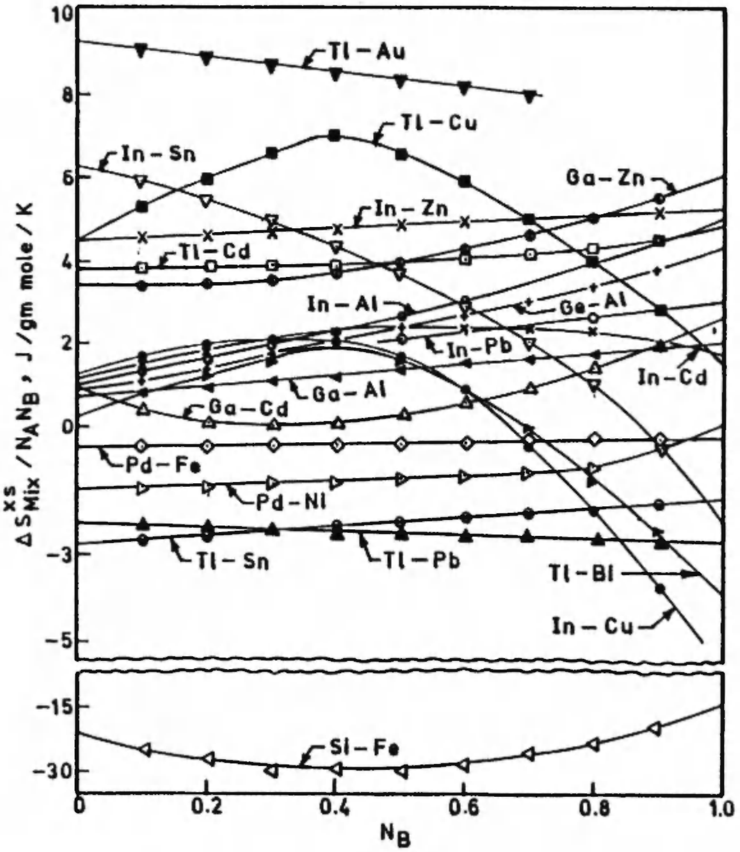

Fig. 3: $\Delta S^{xs}_{mix}/N_AN_B$ vs. N_B for liquid rare-metals-B alloy systems.

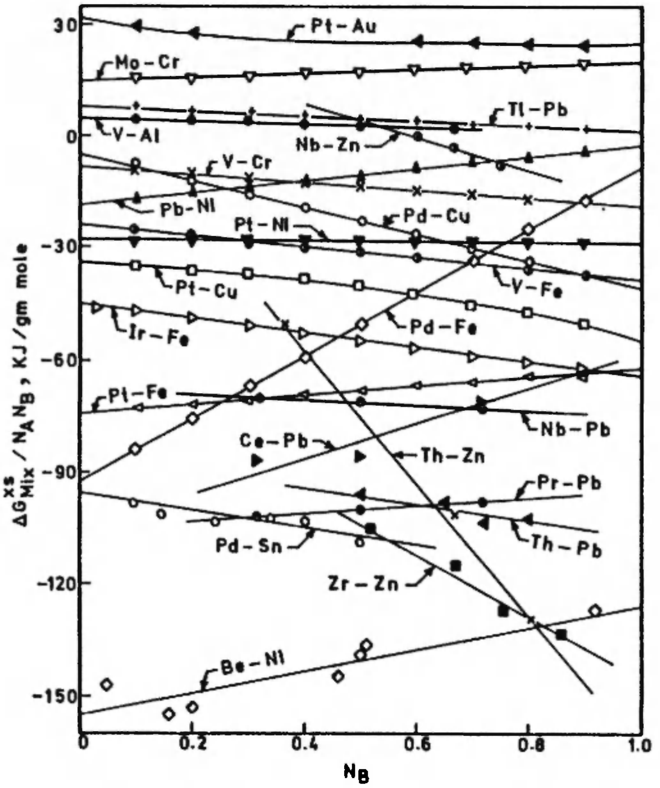

Fig. 4: $\Delta G^{xs}_{mix}/N_AN_B$ vs. N_B for solid rare-metals-B alloy systems.

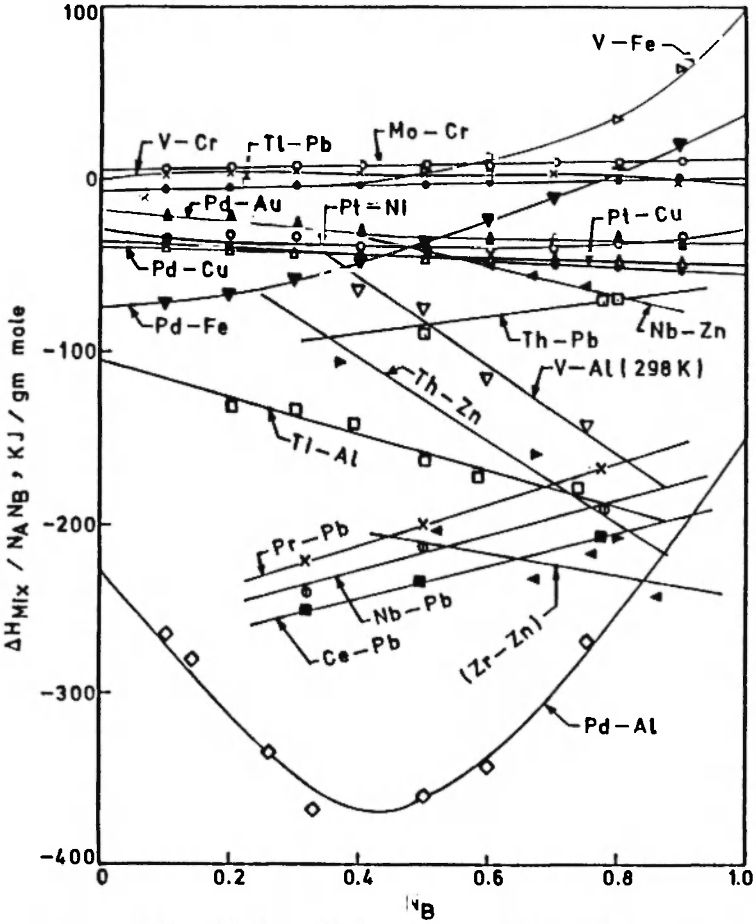

Fig. 5: $\Delta H_{mix}/N_A N_B$ vs. N_B for solid rare-metals-B alloy systems.

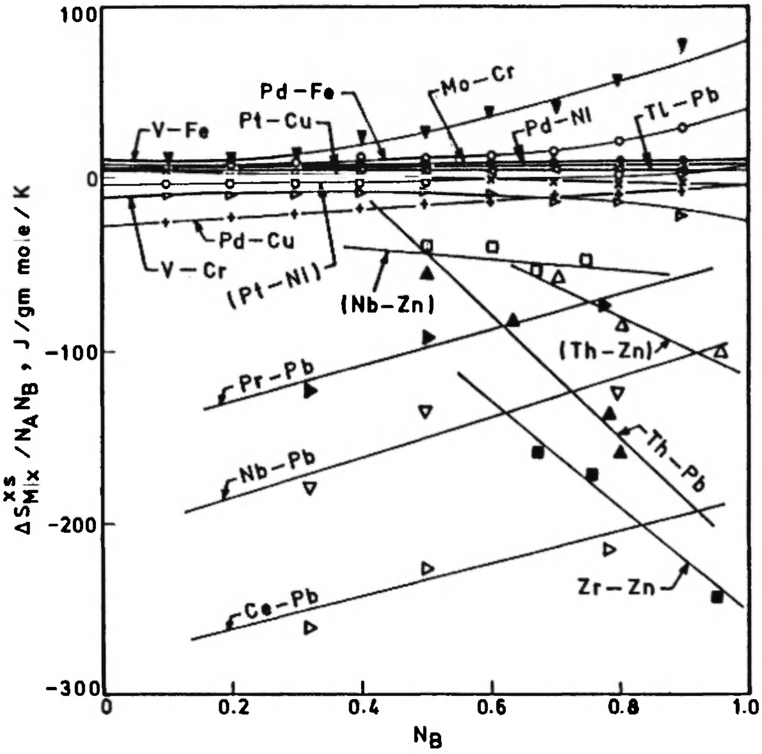

Fig. 6: $\Delta S^{xs}_{mix}/N_A N_B$ vs N_B for solid rare metals-N_B alloy systems.

TABLE 1
PARTIAL MOLAR PROPERTIES AT INFINITE DILUTION OF COMPONENTS OF RARE-METAL BEARING SUBSTITUTIONAL ALLOY SYSTEMS

S. No.	Binary Alloy System (A + B)	Tempera-ture (°K)	State	$\Delta\bar{G}^{ex,\infty}_{A(B)}$	$\Delta\bar{G}^{ex,\infty}_{B(A)}$	$\Delta\bar{H}^{\infty}_{A(B)}$	$\Delta\bar{H}^{\infty}_{B(A)}$	$\Delta\bar{S}^{ex,\infty}_{A(B)}$	$\Delta\bar{S}^{ex,\infty}_{B(A)}$
1	In-Pb	673	liquid	1.75	2.75	3.00	4.50	0.0030	0.0012
2	In-Cu	1073	-do-	-27.33	3.33	-32.50	-2.00	-0.0060	0.0018
3	In-Zn	700	-do-	13.00	7.66	16.20	10.50	0.0054	0.0044
4	In-Sn	700	-do-	0.00	-6.37	-0.75	-0.75	-0.0021	0.0062
5	In-Al	1173	-do-	22.00	19.00	27.00	19.00	0.0050	0.0010
6	In-Ag	1100	-do-	-14.70	-3.78	-35.70	-3.78	–	–
7	In-Bi	900	-do-	-5.50	-8.50	-6.00	-7.50	-0.0010	0.0016
8	In-Cd	800	-do-	5.33	3.00	7.12	4.50	0.0017	0.0012
9	In-Sb	900	-do-	-11.50	-16.50	-11.00	-12.50	0.0020	0.0045
10	In-Pb	315	solid	–	–	4.00	5.00	–	–
11	In-Sn	390	-do-	–	–	12.50	5.50	–	–
12	Tl-Cd	750	liquid	7.83	4.16	11.50	7.12	0.0480	0.0038
13	Tl-Cu	1573	-do-	26.00	17.33	28.50	24.50	0.0015	0.0045
14	Tl-Sn	723	-do-	5.00	3.87	3.75	1.75	-0.0018	-0.0028
15	Tl-Au	973	-do-	-6.50	-8.50	0.00	0.00	0.0075	0.0092
16	Tl-Bi	750	-do-	-10.00	-2.50	-11.00	-23.00	-0.0035	-0.0006
17	Tl-Pb	723	-do-	-1.50	-2.50	-4.00	-4.00	-0.0026	-0.0028
18	Tl-Pb	523	solid	1.25	8.00	-1.00	-7.50	-0.0057	-0.0057
19	Pd-Sn	1050	liquid	-68.25	-164.25	–	–	–	–
20	Pd-Fe	1873	-do-	14.00	12.50	10.00	10.50	-0.0015	-0.0020
21	Pd-Ni	1873	-do-	7.67	6.66	5.00	3.75	0.0000	-0.0014
22	Pd-Cu	1350	solid	-41.00	-5.00	-49.50	-39.50	-0.0036	-0.0270
23	Pd-Sn	1050	-do-	-119.25	-95.62	–	–	–	–
24	Pd-Fe	1273	-do-	-9.00	-92.50	-101.00	-9.50	0.0385	0.0075
25	Pd-Al	373	-do-	–	–	-150.00	-225.00	–	–
26	Pd-Au	298	-do-	–	–	-37.00	-20.00	–	–
27	Pd-Ni	1273	-do-	-2.50	-18.75	7.50	-11.25	0.0080	0.0056
28	Pt-Fe	1880	liquid	-69.00	-114.00	–	–	–	–
29	Pt-Pb	1273	-do-	-33.50	-37.00	–	–	–	–
30	Pt-Cu	1350	solid	-53.50	-33.50	-53.00	-39.50	-0.0048	0.0039

TABLE 1 (continued)

S. No.	Binary Alloy System (A+B)	Tempera-ture (°K)	State	$\Delta\bar{G}^{ex,\infty}_{A(B)}$	$\Delta\bar{G}^{ex,\infty}_{B(A)}$	$\Delta H^{\infty}_{A(B)}$	$\Delta H^{\infty}_{B(A)}$	$\Delta\bar{S}^{ex,\infty}_{A(B)}$	$\Delta\bar{S}^{ex,\infty}_{B(A)}$
31	Pt-Fe	1123	solid	-62.00	-74.50	–	–	–	–
32	Pt-Au	1423	-do-	25.00	31.66	–	–	–	–
33	Pt-Ni	625	-do-	-29.25	-28.12	-31.25	-32.50	0.0064	-0.0046
34	Ga-Zn	750	liquid	4.00	2.66	8.40	4.80	0.0060	0.0034
35	Ga-Sb	1000	-do-	–	–	-140.00	-14.00	–	–
36	Ga-Al	1023	-do-	1.00	1.00	3.00	2.00	0.0020	0.0008
37	Ga-Ag	1000	-do-	-26.88	-15.44	-20.58	58.88	–	–
38	Ga-Cd	700	-do-	-12.66	11.66	14.50	12.50	0.0026	0.0010
39	Pr-Pb	1000	solid	-94.50	-105.00	-140.00	-260.00	-0.0478	-0.1514
40	V-Fe	1600	-do-	-38.50	-24.00	-37.50	-73.00	0.0800	0.0100
41	V-Cr	1550	-do-	-19.00	-8.67	-22.00	-8.00	-0.0016	0.0016
42	V-Al	1273	-do-	1.00	5.00	–	–	–	–
43	V-Al	298	-so-	–	–	-200.00	45.00	–	–
44	Si-Ag	1700	liquid	6.51	19.11	–	–	–	–
45	Si-Al	1100	-do-	-24.50	-13.00	–	–	–	–
46	Si-Fe	1873	-do-	-100.00	-54.00	-123.00	-97.00	-0.0145	-0.0210
47	Ge-Al	1200	-do-	-18.000	-15.00	-10.00	-14.00	0.0042	0.0008
48	Ge-Ag	1250	-do-	-9.66	3.78	-13.02	15.96	–	–
49	Nb-Zn	1100	solid	-18.66	26.66	-86.00	0.00	-0.0600	-0.0280
50	Nb-Pb	1000	-do-	-74.50	-67.50	-165.00	-267.00	0.0928	-0.2085
51	Th-Zn	1000	-do-	-163.99	13.33	-246.00	-7.00	-0.1160	0.0600
52	Th-Pb	1000	-do-	-107.50	-85.50	-325.50	40.00	-0.2214	0.1328
53	Ti-Ag	975	liquid	6.51	11.34	-12.39	-9.03	–	–
54	Ti-Al	298	solid	–	–	-210.00	-103.75	–	–
55	Be-Al	1600	liquid	0.0	19.50	–	–	–	–
56	Be-Ni	1100	solid	-125.62	-155.00	–	–	–	–
57	Ir-Fe	1473	-do-	-64.00	-45.00	–	–	–	–
58	Mo-Cr	1471	-do-	20.00	15.34	39.67	22.67	0.0100	0.0048
59	Li-Sn	1000	liquid	-51.00	-165.00	–	–	–	–
60	Ce-Pb	1000	solid	-57.50	-105.50	-186.00	-282.00	-0.1185	-0.1857
61	Zr-Zn	800	solid	-146.66	-63.99	-242.00	-178.00	-0.2520	0.0540

All values are in kJ (gm atom)$^{-1}$ units.

TABLE 2
SELF-INTERACTION PARAMETERS OF COMPONENTS OF BINARY RARE-METAL BEARING SUBSTITUTIONAL ALLOY SYSTEMS

S. No.	Binary Alloy System (A+B)	Temperature (°K)	State	$\epsilon^{A}_{A(B)}$	$\epsilon^{B}_{B(A)}$	$\rho^{A}_{A(B)}$	$\rho^{B}_{B(A)}$	$\sigma^{A}_{A(B)}$	$\sigma^{B}_{B(A)}$
1	In-Pb	673	liquid	-1.50	-7.50	-3.00	-12.00	-0.0096	-0.0012
2	In-Cu	1073	-do-	141.32	-46.66	200.00	26.00	0.0468	0.0024
3	In-Zn	700	-do-	-38.66	-8.00	-44.40	12.00	-0.0126	-0.0069
4	In-Sn	700	-do-	-12.74	25.48	1.50	1.50	0.0370	-0.0220
5	In-Al	1173	-do-	-50.00	-32.00	-70.00	-22.00	-0.0220	0.0040
6	In-Ag	1100	-do-	6.79	-1.24	158.76	-17.22	--	--
7	In-Bi	900	-do-	5.00	23.00	9.00	18.00	0.0110	-0.0088
8	In-Ci	800	-do-	-15.32	-1.32	-19.56	-3.76	0.0004	-0.0016
9	In-Sb	900	-do-	5.40	26.40	13.00	34.00	-0.0012	-0.0220
10	In-Pb	315	solid	--	--	-6.00	-12.00	--	--
11	In-Sn	390	-do-	--	--	-39.00	3.00	--	--
12	Tl-Cd	750	liquid	-23.00	-0.98	-31.76	-5.56	-0.0116	-0.0056
13	Tl-Cu	1573	-do-	-69.34	-17.32	-24.00	5.00	0.0246	0.0120
14	Tl-Sn	723	-do-	-12.26	-5.48	-12.50	-1.50	0.0017	0.0077
15	Tl-Au	973	-do-	9.00	21.00	0.00	0.00	-0.0115	-0.0220
16	Tl-Bi	750	-do-	-10.00	80.00	-2.00	70.00	0.0470	0.0108
17	Tl-Pb	723	-do-	1.00	7.00	8.00	8.00	0.0060	0.0036
18	Tl-Pb	523	solid	11.00	-29.50	-11.00	-28.00	0.0114	0.0114
19	Pd-Sn	1050	liquid	-55.50	520.50	--	--	--	--
20	Pd-Fe	1873	-do-	-31.00	-22.00	-19.00	-22.00	0.0020	0.0050
21	Pd-Ni	1873	-do-	17.34	-11.31	-12.50	-5.00	-0.0068	0.0032
22	Pd-Cu	1350	solid	154.00	-62.00	119.00	59.00	-0.0396	0.1008
23	Pd-Sn	1050	-do-	285.76	143.98	--	--	--	--
24	Pd-Fe	1273	-do-	-149.00	352.00	-872.00	-2.00	-0.3020	-0.0105
25	Pd-Al	373	-do-	--	--	1200.00	-675.00	--	--
26	Pd-Au	298	-do-	--	--	68.00	-6.00	--	--
27	Pd-Ni	1273	-do-	-27.50	70.00	--	--	--	--
28	Pt-Fe	1880	liquid	-146.00	179.25	--	--	--	--
29	Pt-Pb	1273	-do-	60.00	81.00	--	--	--	--
30	Pt-Cu	1350	solid	164.00	49.00	162.00	52.00	0.0162	-0.0504

TABLE 2 (continued)

S. No.	Binary Alloy System (A + B)	Temperature (°K)	State	$\epsilon^{A}_{A(B)}$	$\epsilon^{B}_{B(A)}$	$\rho^{A}_{A(B)}$	$\rho^{B}_{B(A)}$	$\sigma^{A}_{A(B)}$	$\sigma^{B}_{B(A)}$
31	Pt-Fe	1123	solid	99.00	174.00	--	--	--	--
32	Pt-Au	1423	-do-	-59.33	-90.00	--	--	--	--
33	Pt-Ni	625	-do-	60.75	54.00	47.5	52.5	-0.0484	0.0212
34	Ga-Zn	750	liquid	-10.66	-2.66	-24.00	-2.40	-0.0186	-0.0040
35	Ga-Sh	1000	-do-	--	--	8.00	8.00	--	--
36	Ga-Al	1023	-do-	-2.00	-2.00	-8.00	-2.00	-0.0064	0.0008
37	Ga-Ag	1000	-do-	12.32	3.73	70.56	-41.16	--	--
38	Ga-Cd	700	liquid	-43.32	-28.00	-59.00	-35.00	-0.0196	-0.0112
39	Pr-Pb	1000	solid	168.00	231.00	40.00	760.00	-0.1116	-0.5100
40	V-Fe	1600	-do-	106.00	19.00	-427.56	259.00	-0.4074	-0.0200
41	V-Cr	1550	-do-	58.67	3.34	101.33	-29.33	0.0232	0.0160
42	V-Al	1273	-do-	6.00	-18.00	--	--	--	--
43	V-Al	298	-do-	--	--	890.00	-580.00	--	--
44	Si-Ag	1700	liquid	0.86	-4.48	--	--	--	--
45	Si-Al	1100	-do-	72.00	3.00	--	--	--	--
46	Si-Fe	1873	-do-	26.09	-64.00	-216.50	-46.00	-0.0640	-0.0060
47	Ge-Al	1200	-do-	42.00	24.00	-10.00	16.00	-0.0188	0.0020
48	Ge-Ag	1250	-do-	6.10	-1.53	126.00	-46.20	--	--
49	Nb-Zn	1100	solid	125.99	-141.99	344.00	-172.00	0.1840	-0.0080
50	Nb-Pb	1000	-do-	163.00	121.00	126.00	738.00	-0.0458	0.6484
51	Tb-Zn	1000	-do-	682.64	-381.31	978.00	-464.00	0.5840	-0.4720
52	Tb-Pb	1000	-do-	259.00	127.00	1380.00	-810.00	1.1512	-0.9740
53	Ti-Ag	975	liquid	-0.41	-3.99	31.50	11.34	--	--
54	Ti-Al	298	solid	--	--	632.50	-5.00	--	--
55	Be-Al	1600	liquid	39.00	-78.00	--	--	--	--
56	Be-Ni	1100	solid	192.50	368.75	--	--	--	--
57	Ir-Fe	1473	-do-	166.00	52.00	--	--	--	--
58	Mo-Cr	1471	-do-	-49.33	-21.33	-113.33	-11.33	-0.0288	0.0024
59	Li-Sn	1000	liquid	42.00	652.00	--	--	--	--
60	Ce-Pb	1000	solid	19.00	307.00	180.00	756.00	0.1026	0.5058
61	Zr-An	800	solid	458.67	-37.33	612.00	-228.00	1.1180	-0.7200

All values are in kJ (gm atom)$^{-1}$ units.

TABLE 3
CHARACTERISTICS OF COMPONENTS OF BINARY RARE-METAL BEARING SUBSTITUTIONAL ALLOY SYSTEMS

		Position in Periodic Table						
S. No.	Element	Group	Period	Atomic Number	Atomic Radius	Atomic Volume	Crystal Structure	Electro-negativity
1	Al	III-A	III	13	1.43	10.0	F.C.C.	1.5
2	Sb	V-A	V	51	1.59	18.4	Rhombohedral	1.9
3	Be	II-A	II	4	1.12	5.0	H.C.P.	1.5
4	Bi	V-A	VI	83	1.70	21.3	Rhombohedral	1.9
5	Cd	II-B	V	48	1.54	13.1	H.C.P.	1.7
6	Ce	III-B	VI	58	1.81	--	F.C.C.	1.1
7	Cr	VI-B	IV	24	1.27	7.23	B.C.C.	1.6
8	Cu	I-B	IV	29	1.28	7.1	F.C.C.	1.9
9	Ga	III-A	IV	31	1.41	11.8	Cubic	1.6
10	Ge	IV-A	IV	32	1.37	13.6	Diamond	1.8
11	Au	I-B	VI	79	1.44	10.2	F.C.C.	2.4
12	In	III-A	V	49	1.66	15.7	Tetragonal	1.7
13	Ir	VIII	VI	77	1.36	–	F.C.C.	2.2
14	Fe	VIII	IV	26	1.26	7.1	B.C.C.	1.8
15	Pb	IV-A	VI	82	1.75	18.3	F.C.C.	1.8
16	Li	I-A	II	3	1.55	13.1	B.C.C.	1.0
17	Mo	VI-B	V	42	1.39	9.40	B.C.C.	1.8
18	Ni	VIII	IV	29	1.24	6.6	F.C.C.	1.8
19	Nb	V-B	V	41	1.46	10.8	B.C.C.	1.6
20	Pd	VIII	V	46	1.37	8.9	F.C.C.	2.2
21	Pt	VIII	VI	78	1.38	9.10	B.C.C.	2.2
22	Pr	III-B	VI	59	1.81	–	H.C.P.	1.1
23	Si	IV-A	III	14	1.32	12.1	Diamond	1.8
24	Ag	I-B	V	47	1.44	10.3	F.C.C.	1.9
25	Tl	III-A	VI	81	1.71	17.2	H.C.P.	1.8
26	Th	III-A	VII	90	--	19.9	F.C.C.	1.3
27	Sn	IV-A	V	50	1.62	16.3	Tetragonal	1.8
28	Ti	IV-B	IV	22	1.47	10.6	H.C.P.	1.5
29	V	V-B	IV	23	1.34	8.35	B.C.C.	1.6
30	Zn	II-B	IV	30	1.38	9.2	H.C.P.	1.6

TABLE 3 (continued)

S. No.	Element	Position in Periodic Table Group	Period	Atomic Number	Atomic Radius	Atomic Volume	Crystal Structure	Electro-negativity
28	Ti	IV-B	IV	22	1.47	10.6	H.C.P.	1.5
29	V	V-B	IV	23	1.34	8.35	B.C.C.	1.6
30	Zn	II-B	IV	30	1.38	9.2	H.C.P.	1.6
31	Zr	IV-B	V	40	1.60	14.1	H.C.P.	1.4

silver (both of the I-B group), $\Delta\bar{H}_{i(j)}^{\infty}$ and $\rho_{i(j)}^{i}$ decrease for both components. However, for a similar variation from zinc to cadmium solutes (of group II-B), $\Delta\bar{G}_{i(j)}^{xs,\infty}$ and $\Delta\bar{H}_{i(j)}^{\infty}$ decrease; whereas $\Delta\bar{S}_{i(j)}^{xs,\infty}$, $\epsilon_{i(j)}^{i}$ and $\sigma_{i(j)}^{i}$ increase for both components of the solution and from tin to lead solutes (both of group IV-A), values of $\Delta\bar{G}_{i(j)}^{xs,\infty}$ and $\Delta\bar{H}_{i(j)}^{\infty}$ increase and $\rho_{i(j)}^{i}$ decreases for liquid alloys.

2. In relation to the effect of distance of solute from the solvent, in the periodic table, values of $\Delta\bar{G}_{i(j)}^{xs,\infty}$, $\Delta\bar{H}_{i(j)}^{\infty}$ and $\epsilon_{i(j)}^{i}$ decrease for both components from cadmium to silver (both of 5th period); but values of $\Delta\bar{G}_{i(j)}^{xs,\infty}$, $\Delta\bar{H}_{i(j)}^{\infty}$ and $\Delta\bar{S}_{i(j)}^{xs,\infty}$ decrease and $\epsilon_{i(j)}^{i}$ and $\rho_{i(j)}^{i}$ increase from zinc to copper (both of 6th period). Similarly, $\Delta\bar{G}_{i(j)}^{xs,\infty}$, $\Delta\bar{H}_{i(j)}^{\infty}$ and $\rho_{i(j)}^{i}$ decrease, but $\epsilon_{i(j)}^{i}$ increases from tin to antimony (both of 5th period); whereas $\Delta\bar{G}_{i(j)}^{xs,\infty}$ and decrease and $\epsilon_{i(j)}^{i}$ and $\rho_{i(j)}^{i}$ increase from lead to bismuth (both of 6th period).

Incidentally, electronegativity increases from zinc to cadmium (both of Group II-B), but it has the same value for copper and silver (both of Group I-B) and tin and lead (both of Group IV-A). Therefore, its effect is not clear in these binary alloy systems.

3. In liquid binary alloys of indium, amongst F.C.C. solutes, $\Delta\bar{G}_{i(j)}{}^{xs,\infty}$ increases from silver to lead to aluminium but $\Delta\bar{H}_{i(j)}^{\infty}$ increases in the order silver to copper to lead to aluminium. However, among the H.C.P. solutes, $\Delta\bar{G}_{i(j)}^{xs,\infty}$, $\Delta\bar{H}_{i(j)}^{\infty}$ and $\Delta\bar{S}_{i(j)}^{xs,\infty}$ decrease but $\epsilon_{i(j)}^{i}$ and $\sigma_{i(j)}^{i}$ increase from zinc to cadmium; and with rhombohedral solutes, $\Delta\bar{G}_{i(j)}^{xs,\infty}$ and $\Delta\bar{H}_{i(j)}^{\infty}$ decrease, but $\Delta\bar{S}_{i(j)}^{xs,\infty}$, $\epsilon_{i(j)}^{i}$ and $\rho_{i(j)}^{i}$ increase from bismuth to antimony.

3.3. Binary Alloys of Thallium

1. With increase in both atomic number and atomic radius of the solutes of the same group, values of $\Delta\bar{G}_{i(j)}^{xs,\infty}$, $\Delta\bar{H}_{i(j)}^{\infty}$, $\Delta\bar{S}_{i(j)}^{xs,\infty}$ and $\sigma_{i(j)}^{i}$ decrease, but $\rho_{i(j)}^{i}$ and $\rho_{i(j)}^{i}$ increase from copper to gold; whereas $\bar{G}_{i(j)}^{xs,\infty}$, $\Delta\bar{H}_{i(j)}^{\infty}$ and $\sigma_{i(j)}^{i}$ decrease and $\epsilon_{i(j)}^{i}$ and $\rho_{i(j)}^{i}$ increase from tin to lead.

Electronegativity increases from copper to gold but has the same value for tin and lead, so that its effect is also not clearly established in these thallium-base alloys.

2. In relation to the effect of distance of solute from solvent in the periodic table, $\rho_{i(j)}^{i}$, $\sigma_{i(j)}^{i}$, $\Delta\bar{G}_{i(j)}^{xs,\infty}$ and $\Delta\bar{H}_{i(j)}^{\infty}$ increase, but $\epsilon_{i(j)}^{i}$ decreases from cadmium to copper; whereas $\Delta\bar{S}_{i(j)}^{xs,\infty}$, $\epsilon_{i(j)}^{i}$, $\rho_{i(j)}^{i}$ and $\sigma_{i(j)}^{i}$ increase, but $\Delta\bar{G}_{i(j)}^{xs,\infty}$ and $\Delta\bar{H}_{i(j)}^{\infty}$ decrease from cadmium to gold. Similarly, values of $\Delta\bar{G}_{i(j)}^{xs,\infty}$ and $\Delta\bar{H}_{i(j)}^{\infty}$ decrease, but $\epsilon_{i(j)}^{i}$, $\rho_{i(j)}^{i}$ and $\sigma_{i(j)}^{i}$ increase from tin to bismuth; whereas values of $\Delta\bar{H}_{i(j)}^{\infty}$ and decrease, but $\sigma_{i(j)}^{i}$ increases from lead to bismuth.

3. For binary alloys of thallium, among F.C.C. solutes, $\sigma_{i(j)}^{i}$ and $\Delta\bar{G}_{i(j)}^{xs,\infty}$ increase from Au to Pb to Cu; only $\Delta\bar{H}_{i(j)}^{\infty}$ increases from Pb to Au to Cu; only $\Delta\bar{S}_{i(j)}^{xs,\infty}$ increases from Pb to Cu to Au; only $\epsilon_{i(j)}^{i}$ increases from Cu to Pb to Au; only $\rho_{i(j)}^{i}$ increases from Cu to Au to Pb.

3.4. Binary Alloys of Palladium

1. With increase in atomic number of the solute, values of $\Delta\bar{G}_{i(j)}^{xs,\infty}$ and $\Delta\bar{H}_{i(j)}^{\infty}$ decrease, but $\Delta\bar{S}_{i(j)}^{xs,\infty}$, $\epsilon_{i(j)}^{i}$ and $\rho_{i(j)}^{i}$ increase for liquid alloys from iron to nickel; but only $\Delta\bar{G}_{i(j)}^{xs,\infty}$ and $\rho_{i(j)}^{i}$ increase and $\Delta\bar{S}_{i(j)}^{xs,\infty}$ decreases for their solid alloys; also, only $\Delta\bar{H}_{i(j)}^{\infty}$ increases $\rho_{i(j)}^{i}$ and decreases for solid alloys from copper to gold.

Incidently, the atomic radius increases for these solutes in the order Ni to Fe and from Cu to Au, and the electronegativity is the same for Fe and Ni and increases from Cu to Au.

2. With reference to effect of distance of solute from solvent in the periodic table, the value of $\Delta\bar{G}^{xs,\infty}_{i(j)}$ increases and $\epsilon^{i}_{i(j)}$ decreases from solute to Sn to Cu, but only $\Delta\bar{H}^{\infty}_{i(j)}$ increases from Al to Cu and from Al to Au.

3. Among F.C.C. solutes in solid alloys, values of $\Delta\bar{S}^{xs,\infty}_{i(j)}$ and $\rho^{i}_{i(j)}$ increase from Cu to Ni, but $\Delta\bar{H}^{\infty}_{i(j)}$ increases from Al to Cu to Au to Ni for both components.

3.5. Binary Solid State Alloys of Platinum

1. With an increase in atomic number of the solute, values of $\Delta\bar{G}^{xs,\infty}_{i(j)}$ increase and of $\epsilon^{i}_{i(j)}$ decrease from Cu to Au and from Fe to Ni.

The atomic radius for these solutes increases from Cu to Au and from Ni to Fe. The electronegativity increases from Cu to Au and has the same value for Fe and Ni.

2. Among F.C.C. solutes, $\Delta\bar{G}^{xs,\infty}_{i(j)}$ increases from Cu to Ni to Au, but $\Delta\bar{H}^{\infty}_{i(j)}$ increases only from Cu to Ni.

3. No defined regular effect of the distance of solute from solvent in the periodic table is observed in alloys of this group.

3.6. Liquid Alloys of Gallium

1. With increase in atomic number, atomic radius and electronegativity, values of $\Delta\bar{G}^{xs,\infty}_{i(j)}$ and $\Delta\bar{H}^{\infty}_{i(j)}$ increase, but those of $\Delta\bar{S}^{xs,\infty}_{i(j)}$, $\epsilon^{i}_{i(j)}$, $\rho^{i}_{i(j)}$ and $\sigma^{i}_{i(j)}$ decrease from Zn to Cd. However, no regularity is observed for alloys with Al, Si or Sb as solutes.

2. Among F.C.C. solutes, values of $\Delta\bar{G}^{xs,\infty}_{i(j)}$ decrease and $\epsilon^{i}_{i(j)}$ increase from Al to Si. However, among H.C.P. solutes, values of both $\Delta\bar{G}^{xs,\infty}_{i(j)}$ and $\Delta\bar{H}^{\infty}_{i(j)}$ increase; but of $\Delta\bar{S}^{xs,\infty}_{i(j)}$, $\epsilon^{i}_{i(j)}$ and $\rho^{i}_{i(j)}$ decrease from Zn to Cd.

3. With reference to the effect of distance of solute from solvent in the periodic table, values of $\Delta\bar{G}^{xs,\infty}_{i(j)}$ and $\Delta\bar{H}^{\infty}_{i(j)}$ increase and $\epsilon^{i}_{i(j)}$ and $\rho^{i}_{i(j)}$ decrease from Al to Zn to Cd, but $\Delta\bar{S}^{xs,\infty}_{i(j)}$ increases from Al to Zn and then decreases to Cd. Further, $\Delta\bar{H}^{\infty}_{i(j)}$ decreases but $\rho^{i}_{i(j)}$ increases from Al to Sb.

3.7. Binary Solid Alloys of Vanadium and Liquid Alloys of Germanium

It is also important to note that in the binary solid alloys of vanadium among B.C.C. solutes, values of $\Delta\bar{G}^{xs,\infty}_{i(j)}$ and $\sigma^{i}_{i(j)}$ increase, but $\Delta\bar{S}^{xs,\infty}_{i(j)}$ and $\epsilon^{i}_{i(j)}$ decrease from Fe to Cr; whereas for liquid alloys of germanium among F.C.C. solutes, $\Delta\bar{G}^{xs,\infty}_{i(j)}$ increases and $\epsilon^{i}_{i(j)}$ decreases from Al to Mg.

4. CONCLUSIONS

With the present status of knowledge, it is clearly not possible to quantitatively predict and theoretically calculate the effect of characteristics of solutes on infinite dilution thermodynamic properties of the components of a binary solution using generalized expressions. Nevertheless, the excellent agreement between these theoretically calculated parameters and empirical data shows that the new approach can be very successfully applied to rare-metal bearing binary substitutional solutions, so that future advances are hopeful.

REFERENCES

1. I.Z. Ising, *Physik*, **31**, 253 (1925).
2. J.H. Hildebrandt, *J. Am. Chem. Soc.*, **6**, 221 (1929).
3. J.G. Kirkwood, *J. Chem. Phys.*, **6**, 70 (1938).
4. E.A. Guggenheim, *Mixtures*, Oxford University Press (1952).
5. H.K. Hardy, *Acta Met.*, **1**, 202 (1953).
6. J.C. Mathieu, F. Durand and E. Bonnier, *J. Chim. Phys.*, **11-12**, 1289 (1965).
7. C.H.P. Lupis and J.F. Elliot, *Acta Met.*, **15**, 265 (1967).
8. C. Wagner, *Acta Met.*, **21**, 1297 (1973).
9. M.L. Kapoor, *Int. Met. Reviews*, **20**, 150 (1975).
10. M.L. Kapoor, *Trans. Japan Inst. Metals*, **19**, 109 (1978).
11. R.D. Agrawal, V.N.S. Mathur and M.L. Kapoor, *Z. Metallkunde*, **70**, 536 (1979).
12. R.D. Agrawal, V.N.S. Mathur and N.L. Kapoor, *Metallkunde*, **70**, 722 (1979).
13. R.D. Agrawal, V.N.S. Mathur and M.L. Kapoor, *Trans. Japan Inst. Metals*, **20**, 329 (1979).
14. R.D. Agrawal, V.N.S. Mathur and M.L. Kapoor, *Proc. National Conf. Aluminium Metallurgy*, pp. 67-73, Ind. Inst. Science, Bangalore (1979).

15. R.D. Agrawal, V.N.S. Mathur and M.L. Kapoor, *Z. Metallkunde*, **71**, 76 (1980).
16. R.D. Agrawal, V.N.S. Mathur and M.L. Kapoor, *Trans. Ind. Inst. Metals*, **33**, 237 (1980).
17. R.D. Agrawal, V.N.S. Mathur and M.L. Kapoor, *Trans. Ind. Inst. Metals*, **33**, 501 (1980).
18. R.D. Agrawal, V.N.S. Mathur and M.L. Kapoor, *Ind. J. Pure & Appl. Phys.*, **18**, 494 (1980).
19. R.D. Agrawal, V.N.S. Mathur and M.L. Kapoor, *Ind. J. Tech.*, **18**, 70 (1980).
20. R.D. Agrawal, V.N.S. Mathur and M.L. Kapoor, *Trans. Japan Inst. Metals*, **21**, 1 (1980).
21. R.D. Agrawal, V.N.S. Mathur and M.L. Kapoor, *J. Phy. F: Metal Physics*, **10**, 2395 (1980).
22. R.D. AGrawal, V.N.S. Mathur and M.L. Kapoor, *Metals Forum, Aust. Inst. Metals*, **3**, 121 (1980).
23. R.D. Agrawal, V.N.S. Mathur and M.L. Kapoor, *Metals Forum, Aust. Inst. Metals*, **3**, 129 (1980).
24. R. Hultgren, P.D. Desai, D.T. Hawkins, M. Gleiser and K.K. Kelly, *Selected values of the thermodynamic properties of binary alloys*, ASM (1973).
25. A.R. Miedema, *J. Less Common Metals*, **46**, 67 (1976).