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Sustainable Process For The Estimation Of Germanium-Carbon Alloy System Structural Parameters

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Abstract
Development of Materials system from experimental approach consumes huge manpower and time. In case of materials system constitute more number of elements increase these efforts further. There are various analytical techniques developed for generating materials system data and evaluating thermodynamic properties such as CALPHAD and MC simulations etc. These approaches in general not consider multi atom interactional parameters beyond pair interactions. An appropriate method which considers multi atom interactions and vibration effects is Cluster Expansion Cluster Variation Method (CE-CVM). Hence this approach is adopted in this work to predict more accurate and reliable materials parameters/data for developing materials system. Successful optimization of various data of materials elements to generate complete materials system requires initial guess values of bonding energies and other structural parameters. Optimization process can be carried smoothly only if these predicted guess values are close to true values. Also for estimating errors in each iteration in the process of optimization requires suitable guess values of these parameters as input. In the present work Germanium Carbon alloy system is selected to apply these procedures to estimate structural parameters using CE-CVM approach. Validation of these parameters have been carried by comparative analysis made between CE-CVM and CALPHAD based ThermoCalc software through estimation of enthalpy, entropy and Gibbs free energy for Germanium-Carbon binary alloy system.

Keywords: *Thermodynamic Activity, Cluster Expansion Cluster Variation Method, Alloy System, structural parameters, optimization.*

1. INTRODUCTION

Sound thermodynamic formulation is essential for optimizing the material system and generates the data for computation of material system. Inorder to optimize various types of data such as pure elemental, stuructural, and available experimental data at different thermodynamic conditions need initial estatimation of material parameters. These guessing or initial estimated parameters required for carrying uninterrupted optimization process. Hence the data base for the material system can be generated. This work is an effort to compute various structural parameters for computing and validating Germanium-Carbon materials system using thermodynamic formulation as well as a commercial software named Thermo-Calc and a comparative study has been made between free energy estimated using both approaches. From the literature survey it has been observed that the CE-CVM method was found to be more reliable as it considers the structural, vibrational and energy parameters. Energy parameters for a tetrahedron element were developed using CE-CVM method and the phase equilibria optimization process carried out successfully. CE-CVM was found to be quiet successful. Many numerical methods were inherited for the optimization process such as Numerical Iteration method, Secant method, Newton's method etc., amongst which Newton Raphson's Method has been found to be easier and suitable procedure.

G. Srinivasa Gupta et al.[1] made an attempt to estimate CE-CVM energy parameters for body centred cubic crystal structure by considering tetrahedron as the basic cluster. These parameters estimated through interpolation of data of miscibility gap as feature selected from phase diagram. Author elaborated how these energy parameters are useful as an initial values for optimizing the various data of relevant materials system. B. Nageswara Sarma et al. [2] developed a consistent procedure which is estimating model parameters (Cluster expansion coefficients) for multi component systems in terms of simple binary systems. These procedures also included for representation of interactions as independent parameters of multi component systems and transformations of Cluster expansion coefficients from one basis to other in a chosen system.Naoya Kiyokane et al. [3] studied and developed zero potential free energy formulation through minimization of free energy. Constant zero pressure and chemical potentials temperature dependency graph of this analysis reveals that the long range order parameter is so sensitive to variation of temperature near the transition zone.

M. Anoune et al. [4] have developed a CVM method as the Natural Iteration Method through compatibility of cluster probabilities from input and output maxima in this procedure. Equilibrium of phases is set up by giving proper value of chemical potential as guess. This guess value is keep on modifying till reach the value equal to ground potential value. F. Lanzini et al. [5] have studied cluster variation method by considering irregular tetrahedron as basic cluster for equilibrium of short range as well as long range order structures in Cu-Al-Zn. In this study Author applied energy parameters of transition temperature order-disorder state. Mere pair interchange energies itself reflects precise values of transition temperatures of Copper-Aluminium and Copper-Zinc systems. Ney Sodre et al. [6] explains the development of meta stable body centered ordered equilibrium phase diagram of Fe-Al-Mo material system evaluated through truncated cluster expansion and full-potential linear augmented plane wave (FP-LAPW), electronic structure calculations and of cluster variation method combination, thermodynamic calculations in the irregular tetrahedron approximation. The electronic structure calculations were valid for the ground state of the given compounds (T-0K). The effect of temperature upon the electronic structure was neglected.

Shrikant Lele et al. [7] have presented CE-CVM procedures that have been adopted to carryout optimization process which involves simultaneous optimization of available experimental, structural and thermodynamic data. An independent set of functions have been defined corresponding to basic and sub clusters in the structure. Individual phase, two and three phase coexistence equilibrium was discussed through Newton-Raphson's iteration technique. Marjon I. Pekelharing et al. [8] explained process of predicting equilibrium transformation under cubic cluster using cluster variation approach. The structural aspects while addition of various elements as alloying and its influence on vacancies of face centred cubic structure transitions. Authors adopted zero value as effective chemical potential and varied the interstitial sub lattice chemical potential for finding stable state at specified temperature. Analysis of cubic arrangement variables reveals transitions of lattice and sub lattices have been coupled. F. Lanzini et al. [9] analyzed body centered cubic Copper-Aluminum material system for order-disorder transformations and equilibrium of phases using theoretical method. Authors estimated total energy of body centered cubic lattice shared ordered compound using density functional theory, also under irregular tetrahedron as basic cluster in Cluster variation method approach. Ground state energies wise equilibrium diagram exhibits symmetric in nature, a good transition is revealed at 800K for compositions near to Cu_3Al. Tetsuo Mohri [10] has given a presentation on first-principles by formulating L10 equilibrium diagram, ordering temperature for spinodal boundary as well as intensity spectrum for ordered Fe-Pt alloy. Gibbs energy derived for the phase as the totality of heat of formation, lattice vibration energy and vibration entropy. P. E. A. Turchi [11] has presented quantum mechanical-based methods for estimating equilibrium nature of materials. Basic clusters and ordered arrangement of

structure is adopted. Linear equations are solved for determining interaction parameters. Each structural configuration is estimated in an electronic structure code only through formation of energies for the materials system.Michael K. Gilson et al. [12] made a special effort to define units and standard states clearly. In order to provide a basis for the discussion of specific computational methods, a fairly detailed derivation of the free energy of binding is provided. Present derivation of binding energy is utilized to deduce various important free energy components, including the commonly used translational and rotational entropy, configurational entropy and solvent entropy.

The best procedure suitable for the optimization is analyzed through the literature as Newtons Raphson's method and is used in the present work. In this project, Gibbs free energy formulations are made for orthogonal basis systems using CE-CVM method. Energy parameter was also taken from the literature and the structural parameters were deduced using Cluster expansion - Cluster variation method which is the most important parameter of present work as a novelty. Validation of the present work is done for Germanium-Carbon binary alloy system. Gibbs free energy and Enthalpy values are calculated at selected composition and temperature conditions using CVM method as well as through Thermo-calc software.

2. CLUSTER VARIATION METHOD - FREE ENERGY FORMULATION

Cluster variation method considers the basic and derived cluster involved in basic cluster probability and its appropriateness. The accuracy of prediction entirely depends on number and size of cluster and sub clusters. The basic and sub clusters can be triangular, tetrahedron or octahedral as shown in the Fig. 2.1. This work is an essence of cluster variation energy formulation on triangle as the basic lattice consideration. This main lattice involves three sub lattices such as triangle, pair and point and their probability functions. Accordingly there are following probabilities for pair and triangular clusters, i.e., <pAA>, <pAB>, <pBB>, <pAAA>, <pBBB>,<pAAB>, <pBBA> as shown in the below figure 2.1. These probabilities are linear combinations of variables which are called correlation functions, of these, the point correlation functions are denoted with σi, σj and σk. Which are related to composition and is fixed for an alloy or a composition. If x_1 and x_2 are the compositions of a binary alloy of A and B elements respectively, then $x_1+x_2=1$. The total probability of occupation being 1, i.e., pAi + pBi = 1, and correlation function relation with probabilities is given by, σi or σj or σk = tA.pAi+tB.pBi. There are three sites for a triangular cluster, namely i, j and k; the point probabilities at these sites in a matrix form are given by ;

$$\begin{bmatrix} 1 & 1 \\ tA & tB \end{bmatrix} . \begin{bmatrix} pAi \\ pBi \end{bmatrix} = \begin{bmatrix} 1 \\ \sigma i \end{bmatrix}$$

Solving the above matrix, to find the column matrix $\begin{bmatrix} pAi \\ pBi \end{bmatrix}$. Hence pAi and pBi are written as

$$pAi = 1\text{-}pBi \quad (1)$$

$$pBi = (-tA + \sigma i)/(tB - tA) \quad (2)$$

$$pAj = 1\text{-}pBj \quad (3)$$

$$pBj = (-tA+\sigma j)/(tB\text{-}tA) \quad (4)$$

$$pAk = 1\text{-}pBk \quad (5)$$

$$pBk = (-tA+\sigma k)/(tB\text{-}tA) \quad (6)$$

Where, pAi is the A atom occupancy in site "i" and pBi is the B atom occupancy in site "i". so that
pAi is the point probability of the ith site by A
pBi is the point probability of the ith site by B
pAj is the point probability of the jth site by A

pBj is the point probability of the jth site by B
pAk is the point probability of the kth site by A
pBk is the point probability of the kth site by B
σi, σj, σk are site operators and tA and tB are the labels.

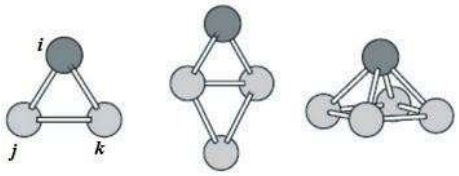

Fig: 2.1 Types of clusters

2.1 Pair probabilities:
As calculated the point probabilities of the point clusters of the considered triangular basic cluster, pair probabilities are also calculated. Pair probabilities of i, j sites in a binary alloy system are achieved by multiplying the point probability functions such as

<pAA>=pAi*pAj (7)
<pAB>=pAi*pAj (8)
<pBA>=pBi*pAj (9)
<pBB>=pBi*pBj (10)

<pAA>, <pAB>, <pBA>, <pBB> are the pair probability functions.

pAA suggests the probability of occupation of the two sites with A.

pAB suggests the probability of occupation of the one site with A and the other with B. pBA suggests the probability of occupation of the one site with B and the other with A.

Substituting the point probabilities in the equations (7), (8), (9) and (10), pair correlation functions are achieved. pBB suggests the probability of occupation of the two sites with B. From the above correlation functions, it is observed that pAB=pBA.

2.2 Triangular probabilities of a triangular cluster:
Triangular probabilities are achieved by multiplying single point probabilities, as in pair probabilities. So, all possible triangular probabilities are denoted as pAAA, pABB, pBAB, pBBA, pAAB, pABA, pBBA and pBBB. The calculated triangular probabilities are,

<pAAA>=pAi*pAj*pAk (11)
<pABB>=pAi*pBj*pBk (12)
<pBAB>=pBi*pAj*pBk (13)
<pBBA>=pBi*pBj*pAk (14)
<pAAB>=pAi*pAj*pBk (15)
<pABA>=pAi*pBj*pAk (16)
<pBAA>=pBi*pAj*pAk (17)
<pBBB>=pBi*pBj*pBk (18)

pAAA suggests the probability of occupation of the three sites with A.
pAAB is the probability of occupation of the first two sites with A and the other with B.
pABA is the probability of occupation of the first and last sites with A and the other with B.
pBAA is the probability of occupation of the first site with B and the other two sites with A.
pBBA is the probability of occupation of the two sites with B and the other with A.
pBAB is the probability of occupation of the first and last sites with B and the other with A.
pABB is the probability of occupation of the first site with A and the other two sites with B.
pBBB suggests the probability of occupation of the three sites with A.

From the above 6 probabilities, it is observed that pAAB, pABA, pBAA are equal and pBBA, pBAB, pABB are also equal. Hence the total number of probabilities including point, pair and triangle are 9. Point probabilities= 2, Pair probabilities= 3, Triangular probabilities= 4.

2.3 Configurational entropy formulations:

Boltzmann's Entropy concept is applied for finding structural entropy which can be given as $S_e = k \ln w$. In this k is Boltzmann's constant and w is the number of possible arrangements of atoms in a chosen lattice. Here the assumption made is binary system that is A and B atoms and their distribution is random in the chosen cluster. The bonding between the atoms and their number depends on the composition of the solid solution.

A single solution is a solution being defined as a mixture of the components on the atomic scale. Solid solutions may be substitutional or interstitial. In the substitutional the atomic species substitute for each other on the various lattice sites and in the latter the solute atoms reside in the interstices between the solvent atoms. The positional randomness of 'A' atoms in pure A are not the same as those of A atoms in the solution. Let 'n' be the closest atoms in the structure, n/2 bonds in each atom exist. So there are A type atoms of N_A and B type atoms of N_B exist in the lattice. So A atom occupancy probability is given by $N_A/(N_A+N_B)=x_A$ and the B atom occupancy probability is given by,

$N_B/(N_A+N_B)=x_B$ Since, $x_A+x_B=1$. Also the total number of A atoms and B atoms are equal to the Avogadro's number (N).i.e., $N_A+N_B =N$. Number of different ways in which the A and B atoms can be arranged in a given lattice is $\omega= N!/(N_A!.N_B!)$. Applying Stirling's approximation to above equation for $\ln \omega =$

$[N \ln N-N]-[N_A \ln N_A-N_A+ N_B \ln N_B-N_B] = N\{[\ln N-1]-[X_A \ln N_A-X_A+X_B \ln N_B-X_B]\} =N[(X_A+X_B] \ln N-[X_A \ln N_A+X_B \ln N_B]$

Therefore, $\ln \omega =-N[X_A \ln X_A+X_B \ln X_B]$ as the Entropy $(S)=k \ln \omega$

$S= -kN[x_A \ln x_A+x_B \ln x_B]$

Here values of N and k are, N=6.022*10^-23 particles/mole and k=1.3807*10^23 J/K.

N*k= 6.022*10^-23*1.3807*10^23 J/mol-K =8.3145 J/mol-K

This value is equal to Universal Gas constant (R). Hence N*k is replaced by R, therefore, Entropy (S)= -R $[x_A \ln x_A+x_B \ln x_B]$

Point entropy (Sp):

$s_p = x_1 \text{ Log } x_1 + x_2 \text{ Log } x_2$

Since, $x_1+x_2 = 1$ which implies, $x_2 = 1- x_2$. Substituting x_1 in the above equation,

$$Sp = -R[(1 - x_2)\text{Log}[1 - x_2] + x_2\text{Log}[x_2]] \quad (19)$$

where, x_1 and x_2 are the compositions of element A and element B respectively.

Pair entropy (s_{pr}):

$$s_{pr} = -R*(2*pAB \text{ Log}[pAB]+ pAA \text{ Log}[pAA] + pBB \text{ Log}[pBB]) \quad (20)$$

From pair correlation functions, as seen pAB=pBA, which implies pAB and pBA can be summed up making 2pAB. Hence three types of cluster probabilities namely pAB, pAA and pBB are achieved. On substituting them in the equation (20) and calculated total pair entropy is s_{pr}

Triangular entropy (s_t):

$$s_{tr} = -R(pAAA \text{ Log}[pAAA] + pBBB \text{ Log}[pBBB] + 3 * pABB \text{ Log}[pABB] + 3 *pAAB \text{ Log}[pAAB]) \quad (21)$$

As in the case of pair entropy, from triangular correlation functions, pABB = pABA = pBBA and also pAAB = pABA = pBAA. Hence it can be written as 3* pAAB and 3* pABB. Substituting the cluster probabilities in the above equation (21), resulting the triangular entropy (str)

2.4 Total configurational entropy (S):

$$s = s_{tr} - s_{pr} + s_p \qquad (22)$$

Substituting the terms from equations (19), (20) and (21) in the equation (22), and to reduce the ambiguity of equation, as $\sigma i = \sigma j = \sigma k = \sigma i$. As, $\sigma i\sigma j = \sigma j\sigma k = \sigma k\sigma i$, substituting it by k1 and $\sigma i\sigma j\sigma k$ is substituting it by k2. Hence the total configurational entropy (S) is:

$$\begin{aligned}
s = {} & \boldsymbol{R}\left(\left(\frac{k1}{(-tA+tB)^2}+\frac{tA^2}{(-tA+tB)^2}-\frac{2tA\sigma i}{(-tA+tB)^2}\right)\boldsymbol{Log}\left[\frac{k1}{(-tA+tB)^2}+\frac{tA^2}{(-tA+tB)^2}-\frac{2tA\sigma i}{(-tA+tB)^2}\right]+\left(\mathbf{1}+\right.\right. \\
& \left.\left.\frac{k1}{(-tA+tB)^2}+\frac{tA^2}{(-tA+tB)^2}+\frac{2tA}{-tA+tB}-\frac{2tA\sigma i}{(-tA+tB)^2}-\frac{2\sigma i}{-tA+tB}\right)\boldsymbol{Log}\left[\mathbf{1}+\frac{k1}{(-tA+tB)^2}+\frac{tA^2}{(-tA+tB)^2}+\frac{2tA}{-tA+tB}-\right. \\
& \left.\frac{2tA\sigma i}{(-tA+tB)^2}-\frac{2\sigma i}{-tA+tB}\right]+\mathbf{2}\left(-\frac{k1}{(-tA+tB)^2}-\frac{tA^2}{(-tA+tB)^2}-\frac{tA}{-tA+tB}+\frac{2tA\sigma i}{(-tA+tB)^2}+\frac{\sigma i}{-tA+tB}\right)\boldsymbol{Log}\left[-\frac{k1}{(-tA+tB)^2}-\right. \\
& \left.\frac{tA^2}{(-tA+tB)^2}-\frac{tA}{-tA+tB}+\frac{2tA\sigma i}{(-tA+tB)^2}+\frac{\sigma i}{-tA+tB}\right])-\boldsymbol{R}\left(\left(\frac{k2}{(-tA+tB)^3}-\frac{3k1tA}{(-tA+tB)^3}-\frac{tA^3}{(-tA+tB)^3}+\right.\right. \\
& \left.\left.\frac{3tA^2\sigma i}{(-tA+tB)^3}\right)\boldsymbol{Log}\left[\frac{k2}{(-tA+tB)^3}-\frac{3k1tA}{(-tA+tB)^3}-\frac{tA^3}{(-tA+tB)^3}+\frac{3tA^2\sigma i}{(-tA+tB)^3}\right]+\mathbf{3}\left(-\frac{k2}{(-tA+tB)^3}+\frac{3k1tA}{(-tA+tB)^3}+\right. \\
& \left.\frac{tA^3}{(-tA+tB)^3}+\frac{k1}{(-tA+tB)^2}+\frac{tA^2}{(-tA+tB)^2}-\frac{3tA^2\sigma i}{(-tA+tB)^3}-\frac{2tA\sigma i}{(-tA+tB)^2}\right)\boldsymbol{Log}\left[-\frac{k2}{(-tA+tB)^3}+\frac{3k1tA}{(-tA+tB)^3}+\frac{tA^3}{(-tA+tB)^3}+\right. \\
& \left.\frac{k1}{(-tA+tB)^2}+\frac{tA^2}{(-tA+tB)^2}-\frac{3tA^2\sigma i}{(-tA+tB)^3}-\frac{2tA\sigma i}{(-tA+tB)^2}\right]+\left(\mathbf{1}-\frac{k2}{(-tA+tB)^3}+\frac{3k1tA}{(-tA+tB)^3}+\frac{tA^3}{(-tA+tB)^3}+\right. \\
& \left.\frac{3k1}{(-tA+tB)^2}+\frac{3tA^2}{(-tA+tB)^2}+\frac{3tA}{-tA+tB}-\frac{3tA^2\sigma i}{(-tA+tB)^3}-\frac{6tA\sigma i}{(-tA+tB)^2}-\frac{3\sigma i}{-tA+tB}\right)\boldsymbol{Log}\left[\mathbf{1}-\frac{k2}{(-tA+tB)^3}+\frac{3k1tA}{(-tA+tB)^3}+\right. \\
& \left.\frac{tA^3}{(-tA+tB)^3}+\frac{3k1}{(-tA+tB)^2}+\frac{3tA^2}{(-tA+tB)^2}+\frac{3tA}{-tA+tB}-\frac{3tA^2\sigma i}{(-tA+tB)^3}-\frac{6tA\sigma i}{(-tA+tB)^2}-\frac{3\sigma i}{-tA+tB}\right]+\mathbf{3}\left(\frac{k2}{(-tA+tB)^3}-\right. \\
& \left.\frac{3k1tA}{(-tA+tB)^3}-\frac{tA^3}{(-tA+tB)^3}-\frac{2k1}{(-tA+tB)^2}-\frac{2tA^2}{(-tA+tB)^2}-\frac{tA}{-tA+tB}+\frac{3tA^2\sigma i}{(-tA+tB)^3}+\frac{4tA\sigma i}{(-tA+tB)^2}+\right. \\
& \left.\frac{\sigma i}{-tA+tB}\right)\boldsymbol{Log}\left[\frac{k2}{(-tA+tB)^3}-\frac{3k1tA}{(-tA+tB)^3}-\frac{tA^3}{(-tA+tB)^3}-\frac{2k1}{(-tA+tB)^2}-\frac{2tA^2}{(-tA+tB)^2}-\frac{tA}{-tA+tB}+\frac{3tA^2\sigma i}{(-tA+tB)^3}+\right. \\
& \left.\frac{4tA\sigma i}{(-tA+tB)^2}+\frac{\sigma i}{-tA+tB}\right])-\boldsymbol{R}[(\mathbf{1}-\boldsymbol{x2})\boldsymbol{Log}[\mathbf{1}-\boldsymbol{x2}]+\boldsymbol{x2}\boldsymbol{Log}[\boldsymbol{x2}]]
\end{aligned}$$

2.5 Entropy of orthogonal system (s_o):

Entropy of an orthogonal basis system is achieved by substituting $tA = -1$ and $tB = 1$ in achieved equation (22) of s gives entropy of orthogonal basis (so).

2.6 Formulations of Gibbs free energy:

As the Gibbs free energy is the hierarchical function of effective cluster interactions/cluster expansion coefficients(ECI/CEC), temperature, composition and microscopic/internal variables so it is supposed to calculate the internal energy (U) of A basis system, B basis system, as well as orthogonal system. The total free energy can be written as

$G_{total} = G_{mixture} + G_{xs} + G_{ideal}$ where $G_{xs}+G_{ideal}$ is called the G_{mixing}.

In CVM Internal Energy (U) of an alloy is expressed as a bilinear sum of the products of the CEC's and the corresponding internal variables.

Internal energy of a system is given by:

$$U = e_1 * m_1 * \xi_1 + e_2 * m_2 * \xi_2 + e_3 * m_3 * \xi_3 \qquad (23)$$

where,

e_1=energy parameters of the point.

e_2=energy parameters of pair.

e_3=energy parameters of triangle.

m_1, m_2 and m_3 are the multiplicities of a motif/sub motif corresponding to the respective correlation function. The multiplicities are defined as the number of symmetry-equivalent motifs/sub-motifs per site present in the structure. In a lattice structure, it is composed of many clusters. Considering a triangular cluster, every atom is surrounded or shared by 6 atoms, and a triangular cluster is formed by 3 atoms itself, The multiplicity of a Triangular (m3) cluster is given by 6/3 = 2.
Similarly, every pair, is shared by two adjacent pairs, which gives 6/2 = 3, hence the multiplicity of a pair cluster (m2) is 2 and for the point, every point has 6 neighbour points, i.e., 6/6 = 1. Point multiplicity (m1) being 1.
$m_1 = 1$, $m_2 = 3$, $m_3 = 2$, which are the multiplicities of the point, pair and triangular clusters respectively.
$\xi_1 = si$, $\xi_2 = k1$, $\xi_3 = k2$, are the structural parameters of the point,pair and triangle respectively. So, the total internal energy of the system is given by substituting the multiplicities in equation (23),

$$U_t = 3e_2k1 + 2e_3k2 + e_1(-1 + 2x_2) \quad (24)$$

2.7 Gibbs free energy of Orthogonal basis system (Gb):
Internal energy of pure A: (tA = - 1,tB = +1)
The correlation function pAA = 1, gives $\sigma i = -1$, k1 = 1 and k2 = −1. Substituting in equation (24), the internal energy of pure A is,

$$U_{oa} = -e_1 + 3e_2 - 2e_3$$

Internal energy of pure B:
The correlation function pBB=1, gives gives $\sigma i=1$, k1=1 and k2=1.
Substituting the values in equation (24), the internal energy of pure B in orthogonal basis system (Uob) is,

$$Uob = e_1 + 3e_2 + 2e_3$$

Now to calculate the Internal energy of mixing in Orthogonal-Basis system (Umo), Which can be given as

$$Umo = Ut\text{-}Uoa\text{-}Uob \quad (25)$$

substituting equations (24), (Uoa), (Uob) in equation of (25),

$$Umo = 3e_2(-1 + k1) + 2e_3(1 + k2 - 2x_2) \quad (26)$$

Gibbs free energy for the Orthogonal-basis (G_o) system is given by

$$Go=Umo-T*So \quad (27)$$

Substituting equation of (Umo) and (So) in the equation(27) gives G_0.
Summary:
In this chapter, considering the triangle as a basic cluster, CE method is used for formulation of Configurational enthalpy and CVM for Configurational Entropy of mixing which together offer Gibbs free energy formulations.

3. ESTIMATION OF STRUCTURAL PARAMETERS:
Structural parameters play the most vital role in the behaviour of an alloy system. It has a critical influence on the construction of a phase diagram. Every element has a different structure, and every element reacts with the other to form an unique compound, thereby changing its physical structure and properties. As the structure changes, the distances between the adjacent atoms change, and also the number of combinations and clusters change. As it is already seen that the CVM depends upon the mathematical combinatorics; entropy, internal energy as well as Gibbs free energy result in a different and unique way. As the reaction in an alloy proceeds, at every point crystal or alloy structure keeps on changing, which results in different values. Structural parameters and energy parameters go hand in hand. This is observed in the Gibbs free energy formulations as the initial cluster probabilities itself are taken considering the alloy structure.
In order to find the stability of a phase the free energy need to be minimized with respect to internal variables. A versatile method called Newton Raphson's method is applicable well for evaluating internal

variables through minimization of CVM free energy. while deriving Cluster probabilities, it is observed that the probability of any cluster or sub cluster is the linear combination of set of independent variables, these are called internal or microscopic variables or correlation functions, the higher order derivatives are represented by a matrix, and matrix inversion also can be in the Newton Raphson's method.

The constraints between which the independent variables i.e., σi*σj which is assumed as k1 and σi*σj*σk which is assumed as k2 lies between are 0 and 1. It is also required to know the initial guesses of these parameters which need to be close enough to the true value. These internal variables are successfully applied as initial values in the optimization process in CVM.

The conditions for the system to be in equilibrium are:

$$\frac{\partial G}{\partial Ki} = 0$$

where, in the above equation , i = 1, 2

For the chosen initial values of k1 and k2, the above non linear equations will not be satisfied, therefore the corrections on k1 and k2 are to be found. Hence Taylors series expansion is applied to the above equation so as to find the corrections involved in the ki terms. At every iteration the change or deviation (di, where i=1, 2) from the initial guess value is calculated and is added to the ki values. The iterations are proceeded till the difference between the Gnew and G is checked such that the difference is as small as 10^{-7}.

$$\frac{\partial G}{\partial Ki} = 0$$

Hence forth,

$$M1 = \begin{bmatrix} \frac{\partial^2 G}{\partial k1^2} & \frac{\partial^2 G}{\partial k1 \partial k2} \\ \frac{\partial^2 G}{\partial k1 \partial k2} & \frac{\partial^2 G}{\partial k2^2} \end{bmatrix}$$

$$M2 = \begin{bmatrix} \frac{\partial G}{\partial k1} \\ \frac{\partial G}{\partial k2} \end{bmatrix}$$

$$M3 = \begin{bmatrix} d1 \\ d2 \end{bmatrix}$$

where,

d1= Change of value of k1 from initial guess value.

d2= Change of value of k2 from initial guess value. Framing the matrices in the equation format, so as to find the deviation from the initial guesses., M1 * M3 = M2, Solving for matrix M3, M3 = Inverse[M1] * M2

Henceforth, for orthogonal basis system, the free energy expression "Go" is considered in place of "G" in the shown procedure. Since k1 and k2 lies between 0 and 1, a guess value is chosen for k1 and k2 at temperature T, R being 8.3145, at x_2 composition. e_2 and e_3 are the energy parameters taken from literature [1].

3.1 Estimation of structural parameters of Orthogonal system:

Orthogonal basis system was observed to be computable and could be arrived at the desired values.

In calculation of k1 and k2 values, the value of k2 was running to negative value. The values of k1 and k2 are subjected to lie between limits 0 and 1. In the Newton Rapson's i th iteration the following condition is implemented to readjust these k values accordingly

$If[knew[[i]] < 0, duf1[[i]] = -kold[[i]]/du[[i]]]; If[knew[[i]] > 1, duf2[[i]] = 1 - kold[[i]]/du[[i]]]$, Where,

knew=value of the iteration,where k1or k2 is either greater than 1 or less than 0 , kold=value of the previous iteration, du=knew-kold

Summary:
In this chapter, structural parameters are estimated by using a mathematical technique called Newton Raphson's method which is used to minimize the free energy. Feasibility of estimation of structural parameters is checked for the three transformation bases systems, and is observed that the structural parameters could be deduced only for orthogonal basis system. Number of iterations are made to optimize the Gibbs free energy. At the minimum value of free energy, structural parameters are found.

4. CALPHAD APPROACH : THERMOCALC SOFTWARE:

Thermo Calc software is based on the CALPHAD approach tool developed for computing material systems. This is a tool used for prediction stable materials phases and generate data base for materials systems of chosen elements combinations with proper understanding and knowledge of ability to forming various phases in the given conditions of composition and temperature ranges.
One of the tools regularly used by materials scientists and engineers for various materials system development and its applicability in industries. SGTE elemental data, structural data and any available limited experimental data is taken as interfacing to the tool to carry out optimization process. So that using this tool one can compute stability conditions and properties of various phases and also materials systems.
The basic difference between thermo Calc and Cluster variation method is the adopted thermodynamic model. In Thermo-Calc Redlich-Kister emphirical model is used for process of optimization which doesn't taken care multi atom interactions. Hence CVM is more appropriate than CALPHAD to develop materials system. The draw back with CVM model is that it is algebraically complex and more complex in case of multi component system development.
Present work Germanium and Carbon binary system is adopted to estimate enthalpy, entropy and free energy quantities at relevant temperature and composition conditions. These estimated quantities have been compared with the quantities generated from cluster variation method formulations.

5. RESULTS AND DISCUSSION:

For different compositions, at constant temperature of 312.747 K and energy parameters e2 = 250 J , e3 = 83.33 J for a Ge-C alloy Enthalpy and Gibbs Free energy values were computed using CVM method and the results were compared with that of Thermocalc values. These results are tabulated in the tables 5.1, 5.2 and 5.3 respectively. The graph X (composition) vs U (Enthalpy) is plotted as shown in the Fig. 5.1 in which CVM results are taken as U1 and Thermo-Calc as U2. Likewise, as per table 5.2, a graph X (Composition) vs G (Gibbs Free Energy) is plotted as shown in the Fig. 5.2 for the same energy parameters and at same constant temperature. Mathematically formulated free energy values are taken as G1 and Thermo-Calc as G2. Also Table 5.3 represents free energy comparison between CVM and Thermo-Calc at fixed composition while temperature is the variable.
From the table 5.1 and figure 5.1, initially at X2 = 0.45 the enthaply variation between thermo calc and mathematica is less than 5%. As the composition of X2 increases the deviation of enthalpy increases since it approaches B rich end. In case of free energy as shown in the table 5.2 the deviation between Mathematic and thermocalc decreases initially as the X2 composition increases. Then the deviation increases when X2 approaches more and more.
But at constant X2 = 0.4 from Table 5.3 and Figure 5.3 when the temperature increases the Free energy deviation from Mathermatical model and ThermoCalc is keep on increasing with higher temperatures. The increment or decrement based on the appropriate case the variation of enthalpy and free energy are exhibiting as per thermodynamic equilibrium. Also both Mathematical CVM model and thermo Calc show similar variation as well. Hence the results are proven appropriate.

From figures 5.1 and 5.2 it has been observed that the enthalpy and free energy values are same for both analytical and Thermo Calc models at the Ge composition of 0.55. Hence the deviations in other

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compositions might be consideration of variations in cluster configurations in thermoCalc and analytical models.

Table 5.1 Comparison of enthalpy values for a Ge-C alloy system

X Composition (Mole Fraction)		Enthalpy (J)	
Ge (X1)	C (X2)	Mathematica (U1)	Thermo-calc (U2)
0.55	0.45	697.593	730.003
0.50	0.50	607.015	675.5107
0.45	0.55	606.274	620.5107
0.40	0.60	595.339	565.7646
0.35	0.65	573.953	511.0184
0.30	0.70	541.585	456.2723
0.25	0.75	497.338	401.5261
0.20	0.80	439.791	346.78

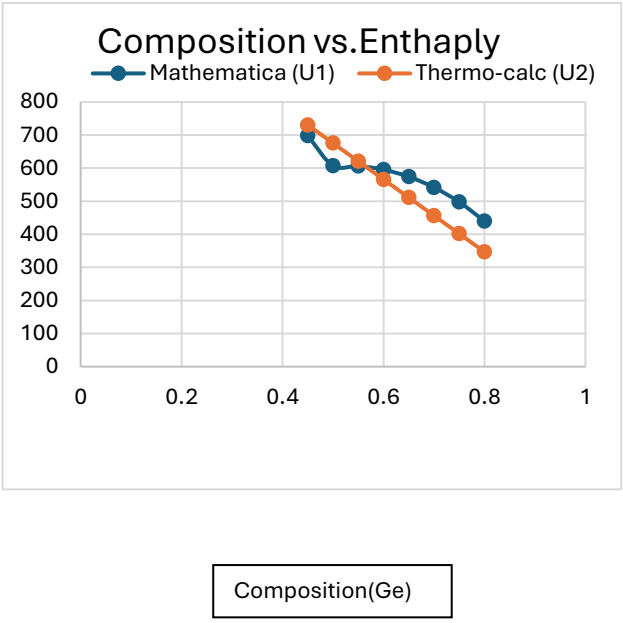

Figure 5.1 Composition vs. Enthalpy

Table 5.2 Comparison of Gibbs free energy values for a Ge-C alloy system

X Composition (Mole Fraction)		Gibbs free energy (G) (J)	
Ge (X1)	C (X2)	Mathematica (G1)	Thermo-calc (G2)
0.55	0.45	-5825.0	-6715.46
0.50	0.50	-5844.34	-6268.5
0.45	0.55	-5784.82	-5821.54
0.40	0.60	-5646.26	-5374.58
0.35	0.65	-5426.44	-4927.62
0.30	0.70	-5120.74	-4480.66
0.25	0.75	-4721.42	-4033.7
0.20	0.80	-4215.94	-3586.74

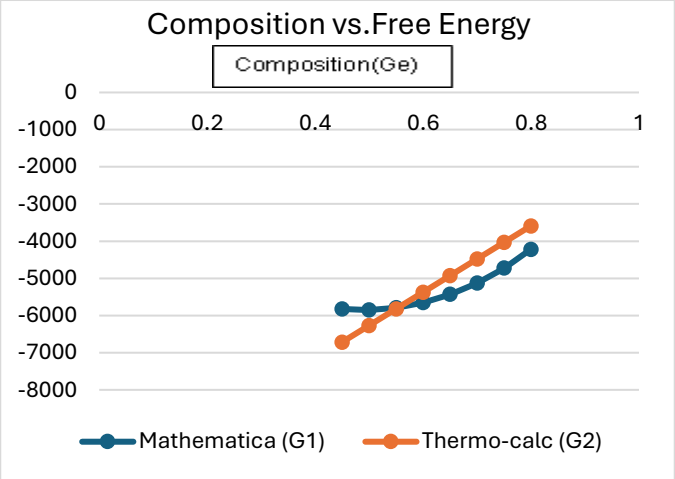

Figure 5.2 Composition vs. Free Energy

Table 5.3 Comparison of Gibbs free energy values for a Ge-C alloy system at constant X2 = 0.4

Temperature(K)	Gibbs free energy (J)	
	Mathematica	Thermo-calc
400	-7747.68	-7876.46
410	-7973.62	-8128.21
420	-8199.7	-8384.38
430	-8425.92	-8644.91
440	-8652.28	-8909.72
450	-8878.76	-9178.76
460	-9105.34	-9451.97

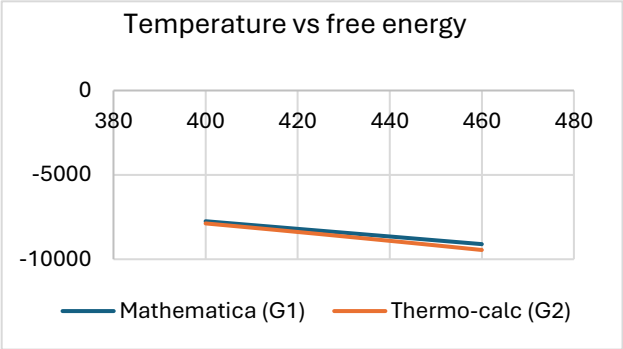

Figure 5.3 Temperature vs. Free Energy

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