THERMODYNAMIC DATA FROM DIFFUSION COUPLES—II

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Abstract—A non-linear least squares based algorithm which permits one to estimate the activity composition relationship from the interdiffusivity data was applied to nine isomorphous binary alloy systems: CuAu, PdCu, CuNi, PdNi, AgAu, PdFe, AuNi, PtNi and NbTi. The algorithm factors the interdiffusion coefficient into two terms: a thermodynamic term and another term representing the phenomenological coefficients. The problem is non unique hence; the algorithm leads to multiple solutions, one of which represents the thermodynamics of the systems whereas the others are spurious solutions. One additional piece of information such as the activity at one particular composition or the Henry's law constant at infinite dilution is needed to select the correct solution from the set of solutions. For eight of the ten binary systems the algorithm computed a possible solution that was close to the experimentally measured activity-composition curves confirming that it is possible to estimate activities from diffusion data. For the NbTi system the model provided fresh insight into its thermodynamics by suggesting the presence of a low temperature miscibility gap. The model may also be applied to systems exhibiting a miscibility gap.

Résumé—On applique un algorithme non linéaire basé sur les moindres carrés, qui permet d'estimer la relation entre composition et activité à partir des données d'interdiffusivité, à neuf systèmes d'alliages binaires isomorphes: CuAu, PdCu, CuNi, PdNi, AgAu, PdFe, AuNi, PtNi et NbTi. L'algorithme factorise le coefficient d'interdiffusion en deux termes: un terme thermodynamique et une autre représentant les coefficients phénoménologiques. Le problème n'est donc pas unique; l'algorithme conduit à des solutions multiples, l'une d'elles représente la thermodynamique des systèmes tandis que les autres sont des solutions fausses. Une information additionnelle telle que l'activité pour une composition particulière ou la constante de la loi d'Henry à dilution infinie, est nécessaire pour choisir la solution correcte parmi la série de solutions. Pour huit sur dix des systèmes binaires, l'algorithme calcule une solution possible qui est voisine des courbes composition-activité mesurées expérimentalement, confirmant qu'il est possible d'estimer les activités à partir de données de diffusion. Pour le système Nb-Ti, le modèle conduit à une vue nouvelle sur sa thermodynamique en suggérant la présence d'une lacune de miscibilité à basse température. Le modèle peut aussi être appliqué à des systèmes présentant des lacunes de miscibilité.

Zusammenfassung—Eine nichtlineare, auf dem kleinsten Fehlerquadrat aufbauende Methode ermöglicht es, den Zusammenhang zwischen Aktivität und Zusammensetzung aus Interdiffusionsdaten zu bestimmen. Die Methode wird auf neun isomorphe binäre Legierungssysteme angewandt: CuAu, PdCu, CuNi, PdNi, AgAu, PdFe, AuNi, PtNi und NbTi. Der Algorithmus teilt den Interdiffusionskoeffizienten in zwei Beiträge, einen thermodynamischen Term und einen Term, der die phänomenologischen Koeffizienten darstellt. Das Problem ist aber nicht eindeutig; der Algorithmus führt zu mehrfachen Lösungen, von denen eine die Thermodynamik des Systems darstellt, die anderen sind unecht. Eine zusätzliche Information, wie etwa die Aktivität bei einer bestimmten Zusammensetzung oder die Konstante aus dem Gesetz von Henry bei unendlicher Verdünnung, wird benötigt, um die richtige Lösung auszuwählen. Für acht der neun binären Legierungen ergab der Algorithmus eine mögliche Lösung, die nahe bei den gemessenen Aktivitäts-Zusammensetzungs-Kurven lag; hiermit wird die Möglichkeit bestätigt, Aktivitäten aus Diffusionsmessungen zu ermitteln. Bei dem System NbTi vermittelte das Modell neue Einsichten in seine Thermodynamik, indem es auf die Möglichkeit einer Mischungslücke bei tiefer Temperatur hinweist. Das Modell kann auch auf Systeme mit einer Mischungslücke angewendet werden.

INTRODUCTION

This is the second paper in a series covering an investigation aimed at obtaining chemical potential information from diffusion couples. In the previous paper [1] a non-linear least squares approach was proposed which models the interdiffusion coefficient as a product of two functions, one arising from the thermodynamic contribution and the other representing the contributions of the phenomono-

logical coefficients. In this paper the proposed computation scheme will be applied to 10 isomorphous binary alloy systems. For each system, diffusivity data describing the variation of the interdiffusion coefficient as a function of composition were obtained from the text by Borovskii *et al.* [2]. The results of the calculations were compared with the experimentally reported activity-composition data summarized in the handbook by Hultgren *et al.* [3].

MODEL SUMMARY

The proposed scheme models the interdiffusion coefficient as a product of two functions

$$\tilde{D} = f(c) \cdot \phi(c) \quad (1)$$

$$\tilde{D}_i \approx \left(\sum_{j=1}^4 (\tau_j c_i^{4-j}) \right) \left(\exp \left(\sum_{k=5}^9 (\tau_k c_i^{10-k}) \right) \right). \quad (2)$$

In addition the following constraints were imposed on the variables [1]

$$\phi(c=0) = 1.0 \quad \text{and} \quad \phi(c=1) = 1.0 \quad (3)$$

$$l_i \leq \phi(c_i) \leq u_i \quad \text{at} \quad c_i = [0.1, 0.2, \dots, 0.9] \quad (4)$$

Thus the diffusivity was modelled as a product of two functions: $P_3[\exp(P_5)]$. It should be noted that these functions were chosen based on preliminary analyses and that these functions may be modified as needed. During this investigation it became necessary to alter the modelling function to $P_4[\exp(P_6)]$. For this modelling function the diffusivity may be expressed as follows

$$\tilde{D}_i \approx \left(\sum_{j=1}^5 (\tau_j c_i^{5-j}) \right) \left(\exp \left(\sum_{k=6}^{11} (\tau_k c_i^{12-k}) \right) \right). \quad (5)$$

The least squares error function for these models may be expressed as follows

$$E^2 = \sum_{i=1}^{i=100} \{(\tilde{D}_i - h_i)w_i\}^2 \quad (6)$$

where, h_i is given by right hand side of equation (2) or equation (5) (depending on the model being used) and $w_i = 1.0/\tilde{D}_i$.

Using the Fortran routine E04VCF from the NAG library [4] the least squares problem of equation (6) was solved subject to the constraints embodied in equations (3) and (4). Solution of the least squares problem amounts to minimizing E^2 with respect to the variables τ_i and subject to the imposed constraints [equations (3) and (4)]. The constraints in equation (3) are based on thermodynamic knowledge and follow directly from an understanding of solution behavior. However, the constraints in equation (4) serve to restrict the least squares search to a subset of the $\phi(c)$ - c space and thereby aid in locating a possible minimum in the subset of the $\phi(c)$ - c space. Several runs were performed, each with a different set of upper and lower bounds $[l_i, u_i]$. A minimum in E^2 - c space was located for each set of bounds. For each such set, the fit to the interdiffusion coefficient was checked graphically and if found satisfactory, the particular minimum was accepted as a possible solution to the problem. In this manner a set of solutions was determined.

Thus in essence the present scheme attempts to de-convolute or factor the interdiffusion coefficient into the thermodynamic term and another term representing the phenomenological coefficients. Such a decomposition is not unique. Hence multiple sol-

utions are inherent to this computational scheme since one is attempting to compute two unknown functions $[f(c)$ and $\phi(c)]$ given only their product $[\tilde{D}(c)]$. One expects that there will be several sets of functions $[f_i(c), \phi_i(c)]$ such that the product of each set will provide an adequate fit to the original diffusivity data. The constraints of equation (4) restrict one of the two functions, $\phi(c)$, to a certain region of the $\phi(c)$ - c space. Thus, for each set of bounds one searches a section of the $\phi(c)$ - c space. By searching different sections of the space, a set of feasible solutions can be determined.

The $\phi(c)$ - c data for each solution were then integrated to obtain γ - c data from which a set of curves were generated on the activity-composition diagram. Integration of the $\phi(c)$ - c data was carried out using a Runge-Kutta-Nystrom technique with a step size of 0.0001. The data were plotted every 2%. Each curve corresponded to a particular solution of the problem. The next task was that of selecting the appropriate solution from the set of possible solutions (as an example see Fig. 3 which depicts a set of possible solutions to the problem for the CuNi system).

The task of selecting the appropriate solution from the set of possible solutions demands one additional piece of information. This could be in the form of experimentally measured activity data at a single composition. If an experiment were to be performed, then observation of the set of computed solutions would suggest an appropriate composition range within which an experiment ought to be performed. The composition range selected for the experiments should be one wherein the computed solutions exhibit the maximum separation.

Alternately, one may utilize the slope of the Henry's law line at infinite dilution to select the appropriate solution from the set of solutions. In this study, *theoretical model predictions* of the heats of mixing at infinite dilution (by Miedema *et al.* [5]) were used to compute the Henry's law line for each of the systems under consideration. The procedural details have been presented in the earlier paper [1]. The theoretically predicted Henry's law line was used to select a solution from the set of feasible solutions. The selected solution was compared with the experimentally available activity data reported by Hultgren *et al.* [3] to determine the reliability of the proposed computational model.

The proposed scheme may fail for any of the following reasons. Firstly, it is possible that an inappropriate functional form was chosen to model the thermodynamic term or the function $f(c)$. This should manifest itself as an inability to obtain a good fit to the diffusivity data. Secondly, from the proposed set of solutions one may pick the wrong solution due to inaccuracies in the estimated slope of the Henry's law line. The first problem may be overcome by modifying the functional form of $f(c)$ or $\phi(c)$ and recomputing a new set of solutions. The

second problem may lead to an inability to select the correct solution from the set of possible solutions (assuming that the set of possible solutions does contain a correct solution). In such a case the additional piece of information can be obtained experimentally. Thirdly, it is possible that either the $\tilde{D}$ - c data or the activity data to which a comparison is being made are in error. These limitations should be kept in mind when reviewing the results of the computations for each of the 10 systems.

TREATMENT OF DIFFUSION DATA

All of the diffusivity data for this investigation were obtained from the text by Borovskii [2] *et al.* which exhaustively reviews the current literature on diffusion in alloys. As part of the review, plots depicting interdiffusion data from several investigations in the literature are presented. Hence this book was used as a central source for all of the diffusion data. In certain cases the data is not available at the ends, that is, the data is reported only on the range $0.05 < c < 0.9$. For such systems the data were extrapolated to the end points.[†] Similarly, for some systems, diffusivity data as a function of composition are presented at several temperatures. In such cases the data for the highest temperature were chosen to avoid any errors arising from grain boundary diffusion which dominates at lower temperatures.

The figures in Borovskii's book were magnified and digitized at approximately 100 points. The digitizing process introduces high wave-number noise in the data. To smooth out this noise and to obtain a suitable interpolant to the data, the raw data were fitted with a fourth order linear least squares spline. Details on spline fitting have been presented elsewhere [6]. The spline fit to the diffusivity data was evaluated at 100 equally spaced points on the compositional interval [0, 1]. This data served as input to the model.

[†]Initially it was hoped that one would be able to use the tracer diffusivity of the solute in the solvent as an approximation to the interdiffusion coefficient at infinite dilution. This is approximately valid at infinite dilution, since according to Darken's relationship the following equation holds:

$$\tilde{D} = (D_1^* c_2 + D_2^* c_1) \left(1 + \frac{\partial \ln \gamma}{\partial \ln c} \right).$$

Although Kirkaldy, Manning, Howard and Lidiard have modified the above expression, the difference between the modified expression and Darken's expression is of the order of 5% and the difference is less significant for dilute alloys. Hence at infinite dilution ($c_i \rightarrow 0.0$) the interdiffusion coefficient may be approximated by the tracer diffusivity of the solute in the solvent. However when the data on tracer diffusivity was examined from the Handbook by Smithell's [7], it was found to have a fairly large scatter and hence could not be used. Thus in some cases one resorted to extrapolation to obtain the interdiffusion coefficient at either end.

The diffusivity data presented by Borovskii are depicted on a semi-log scale, that is the diffusivity is plotted on a log scale whereas the composition is on a linear scale. The data were digitized as $\log(\tilde{D})$ - c data and the spline was also fit to the $\log(\tilde{D})$ - c data. After spline fitting, the data were converted to $\tilde{D}$ - c data. This is important because diffusivity data often varies over several orders of magnitude and hence if the spline fitting routines were provided with $\tilde{D}$ - c data, rather than $\log(\tilde{D})$ - c data, a poor spline fit may result.

During the subsequent computations, aimed at obtaining the thermodynamics of the system, the diffusivity data were scaled such that the smallest diffusivity in the entire range was typically of the order of unity. Scaling of the data is important to avoid loss of accuracy when performing computations on a machine with a finite precision. For the systems investigated, the diffusivity was of the order of 10^{-11} cm²/s. In absolute terms this is a small number and is much closer to the finite precision available on a digital computer than a number such as unity. Hence, if calculations were performed on unscaled data one would run the risk of an appreciable loss of accuracy. To avoid this, the diffusivity data were scaled by a constant factor (usually 10^{+11} or 10^{+10}) and then input to the model [equation (6)]. After the main calculations, the data were rescaled back to the original dimensions. It is apparent from equations (1), (3) and (4), that scaling affects only the quantity " $f(c)$ " and does not affect the quantity " $\phi(c)$ ".

It has already been stressed that the proposed solution scheme leads to multiple minima on an activity-composition diagram. Some of these minima exist in the section of the $\phi(c)$ - c space that corresponds to positive deviations from ideality whereas others exist in the region of the $\phi(c)$ - c space corresponding to negative deviations from ideality. In practice one is not interested in mapping out the entire $\phi(c)$ - c space, rather one would prefer to explore the $\phi(c)$ - c space in a neighborhood of the correct solution. This can lead to significant savings in the time expended in solving a particular system. This for instance, if it were known that the solution exhibits a positive deviation from ideality there would be little point in searching the subset of the $\phi(c)$ - c space that corresponds to solutions depicting negative deviations from ideality even though there may exist several minima (spurious solutions) in that subset of $\phi(c)$ - c space. Miedema's predictions were very helpful in defining the region of $\phi(c)$ - c space within which to concentrate the search. Thus in practice Miedema's data were first examined to decide whether the solution exhibited positive or negative deviations. For positive deviations from ideality, only the region corresponding to $0.0 \leq \phi(c) \leq 1.0$ was examined whereas for negative deviations from ideality, the region corresponding to $1.0 \leq \phi(c)$ was searched. Although the region of the $\phi(c)$ - c space is

unbounded above for solutions exhibiting negative deviations from ideality, in a practical sense one may choose an upper bound[†] of $\phi(c) \leq 10.0$.

COMPUTATION RESULTS

For sake of brevity, only the computed activity-composition data for each binary system is presented. The corresponding $\phi(c)$ - c curves and the $\ln(\gamma)$ - c curve for the selected solution along with the table of residuals are available elsewhere [7]. The tables of residuals are useful in comparing the goodness of fit between two computations each performed using different bounds.

Several activity-composition curves are presented for each alloy system. Each activity-composition curve corresponds to a different set of bounds on the function $\phi(c)$. The legend for each figure lists the bounds used for computing that curve. For each system, the activity composition diagram also depicts the theoretically estimated Henry's law line which was used to pick the correct solution. In addition, the experimental data reported in Hultgren are also presented.

In comparing the computed activities to the data presented by Hultgren, it should be noted that Hultgren's data represents a best fit to the experimental data from several investigations and does not necessarily reflect the actual experimental points. Hence minor deviations from Hultgren's data do not necessarily imply that the proposed algorithm is incorrect since it is possible that Hultgren's data itself may contain errors.

CoNi system

Results for this system were presented in the earlier paper [1]. Theoretical estimates of the Henry's law line based on Miedema's prediction were in good agreement with the data in Hultgren's handbook. Both indicate that the system is ideal in its solution behavior. Several solutions were computed by applying the computational scheme outlined above to the diffusivity data from the book by Borovskii. The correct solution was picked using the theoretically estimated Henry's law line. Thus the proposed computational scheme is successful at estimating the activity composition relation for the CoNi system.

CuAu system

Diffusivity data for this system was reported at 857°C whereas the data in Hultgren represent measurements made at 527°C. An excellent fit was obtained to the diffusivity data for all solutions. The solutions are depicted in Fig. 1 along with the estimated Henry's law line and the experimental

data-points reported by Hultgren. The estimated Henry's law line appears to match Hultgren's data. Examination of the activity composition curves (Fig. 1) and the table of residuals [7] indicates that the solutions computed using the bounds [0, 6] and [1, 6] are coincident and agree well with the estimated Henry's law line. In addition the computed activity data closely follow the trend exhibited by the experimental data reviewed by Hultgren. The computed data also lie closer to the ideal law line than Hultgren's data. This is consistent with the idea that all solutions tend to ideality at higher temperatures. Since the diffusivity data were obtained at a higher temperature than Hultgren's data, it is natural that the predicted activities will be closer to the ideal solution line than the data reported by Hultgren. Hence the curves corresponding to the bounds [0, 6] and [1, 6] are taken to represent the thermodynamics of the CuAu system at 857°C. Thus it is believed that the proposed computation scheme leads to good results for the CuAu system.

PdCu system

Diffusivity data for this system was reported at 1019°C whereas Hultgren *et al.* report activity data at 1077°C. Computational results for this system are depicted in Fig. 2 which depicts several activity-composition diagrams along with the estimated Henry's law line based on Miedema's data [7]. The corresponding $\phi(c)$ - c curves have been reported elsewhere [7]. The predicted Henry's law line (from Miedema's data) was helpful in confining the search to a region of $\phi(c)$ - c space that corresponds to negative deviations from ideality. For each of the curves depicted in Fig. 2, an excellent fit to the original diffusivity data was obtained. It is clear from

Fig. 1. Computed activities for the CuAu system at 857°C using the model function $P_3[\exp(P_3)]$. The Henry's law line computed from Miedema's theoretical predictions is also depicted. The activities computed by imposing the constraints [0, 6] and [1, 6] are coincident and are taken to represent the thermodynamics of the CuAu system at 857°C. Experimentally determined activities from Hultgren are also presented for comparison.

[†]Very strong negative deviations from ideality will lead to compound formation. Hence when one is considering a solid solution it is reasonable to impose an upper bound on $\phi(c)$.

Fig. 2 that the estimated Henry's law line, although close to Hultgren's data, does not match it exactly. Computations based on the diffusivity data predict two possible solutions in the region of interest. These correspond to computations performed with the bounds [1, 6] and [1, 3]. Based on the estimated Henry's law line, one would pick the solution corresponding to the bounds [1, 3] since it is closest to Miedema's prediction at infinite dilution. From Fig. 2 it is also clear that this solution closely matches the experimental data reported by Hultgren although there is a slight discrepancy in the lower compositional range. The residual for the solution computed using the bounds [1, 3], is 0.0072 whereas the residual for the solution computed using the bounds [1, 6] is 0.041 [7] suggesting that the solution computed using the bound [1, 3] fits the diffusivity data better. Thus examination of the residual also indicates that the correct solution is the one corresponding to the bounds [1, 3]. Hence, *the solution computed using the bounds [1, 3] is taken to represent the thermodynamics of the PdCu system at 1019°C*. Since the temperatures of the interdiffusion data and Hultgren's data are close, the computed activities are expected to lie close to the experimentally obtained data. Thus the proposed computational scheme yields good results when applied to the PdCu system.

CuNi system

Diffusivity data for the CuNi system at 1000°C were used for the computations while Hultgren *et al.* report activity data at 700°C. Results for the computation (activity-composition data) are depicted in Fig. 3 along with the estimated Henry's law line based on Miedema's prediction [7]. Hultgren's experimental data is also presented in Fig. 3. The corresponding $\phi(c)$ - c curves for the CuNi system have been re-

ported elsewhere [7]. It is clear from Fig. 3 that the estimated Henry's law line does not match Hultgren's experimental data. Hence use of the estimated Henry's law line will lead to selection of a spurious solution from the set of possible solutions. Nonetheless it is of interest to ascertain whether the computational scheme leads to any solutions which may be plausible. Miedema's data does suggest that the search should be confined to the region of $\phi(c)$ - c space corresponding to systems exhibiting positive deviations from ideality.

For each of the curves depicted in Fig. 3 an excellent fit was obtained to the original diffusivity data. Since the diffusivity was reported at a higher temperature than the temperature corresponding to the experimentally reported data, it is expected that the activity curve at 1000°C will lie between the experimentally determined activity curves at 700°C and the ideal alloy line. Hence the solution corresponding to the bounds [0.05, 1], must be a spurious solution. However it should be noted that this is precisely the solution one would have picked based on the estimated Henry's law line. Thus this example highlights one of the potential sources of error when using this technique, namely selection of an incorrect solution from a set of solutions that may contain the correct solution.

Knowledge of solution thermo-chemistry suggests that the activity curve at 1000°C should lie between Hultgren's data at 700°C and the ideal alloy line since all solutions tend to ideality with an increase in temperature. Referring to Fig. 3, this implies that any one of the solutions that lie between the ideal alloy line and Hultgren's data may represent the thermodynamics of the system. Based on the residual error at the minima [7] one would pick the solution corresponding to the bounds [0.2, 1] since it exhibits the

Fig. 2. Computed activities for the PdCu system at 1019°C using the model function $P_3[\exp(P_3)]$. The Henry's law line computed from Miedema's theoretical predictions is also depicted. The activities computed on imposing the bounds [1, 3] on $\phi(c)$ are taken to represent the thermodynamics of the PdCu system. Experimental data reported by Hultgren at 1077°C is also presented.

Fig. 3. Computed activities for the CuNi system at 1000°C using the model function $P_3[\exp(P_3)]$. The Henry's law line computed from Miedema's theoretical predictions is also depicted. Based on the residual at minimum the activity curve computed on imposing the constraints [0.2, 1] on $\phi(c)$ is taken to represent the system thermodynamics. Hultgren's data at 700°C is also depicted.

smallest residual at the minimum among the set of feasible solutions. These observations strongly suggest that the solution corresponding to the bounds [0.2, 1] represents the thermodynamics of the CuNi system at 1000°C. Thus the proposed computational scheme does provide the correct solution but in this case one had to rely on Hultgren's data at 700°C to guide one in selecting a plausible solution since the estimated Henry's law line was inconsistent with the experimental data.

PdNi system

Diffusivity data for this system at 1045°C was used for the computations whereas Hultgren *et al.* report the experimental activity data at 1000°C. Miedema's theoretical prediction suggests that this system exhibits ideal solution behavior [5]. This suggests that one should focus on a region of the $\phi(c)$ - c space that is relatively close to unity such as $0.5 < \phi(c) < 2.5$ rather than examining the entire space, $0.0 < \phi(c) < 8.0$. A series of simulations were conducted using the modelling function $P_3[\exp(P_5)]$. However a good fit to the interdiffusion coefficient could not be obtained⁷ in the region of interest ($0.5 \leq \phi(c) \leq 2.5$). Hence results for these preliminary computations are not presented. To obtain a better fit, the modelling function was altered and one degree of freedom was added to both $f(c)$ and $\phi(c)$. Thus the modelling function chosen was $P_4[\exp(P_6)]$. When the computations were rerun, a good fit was obtained to the diffusivity data (table of residuals [7]). Results for these computations are depicted in Fig. 4 along with Hultgren's data at 1000°C and the estimated Henry's law line. The corresponding $\phi(c)$ - c curves have been reported elsewhere [7]. From Fig. 4 it is seen that the estimated Henry's law line differs slightly from the experimentally measured data reported by Hultgren.

Fig. 4. Computed activities for the PdNi system at 1045°C using the model function $P_4[\exp(P_6)]$. The Henry's law line computed from Miedema's theoretical prediction is also depicted. Based on the residual at minimum the activities computed on imposing the bounds [0.7, 1.75] are taken to represent the system thermodynamics at 1045°C. Experimental data by Hultgren at 1000°C is also depicted.

From Fig. 4 it is clear the solutions corresponding to the bounds [0.9, 1.5] and [0.7, 1.75] are both close to the estimated Henry's law line although neither solution matches it exactly at infinite dilution. The residual at the minima is 0.019 for the solution corresponding to the bounds [0.7, 1.75] whereas for the solution corresponding to [0.9, 1.5] the residual is 0.043. This suggests that the solution corresponding to the bounds [0.7, 1.75] represents the system thermodynamics as computed from diffusion data. Comparison between the computed solutions and Hultgren's data indicates a fairly good match over most of the composition range except the low concentration range ($c < 0.3$). Thus for this system there is a slight discrepancy at the low composition end but the overall match between the activity data computed from the interdiffusion coefficient and Hultgren's data is fairly good.

AgAu system

Diffusivity data from this system was obtained at 900°C whereas Hultgren *et al.* report the activity data at 527°C. The Henry's law line computed from Miedema's prediction matches Hultgren's data very well (Fig. 5). Miedema's data suggests that one should concentrate the search in the section of $\phi(c)$ - c space corresponding to negative deviations from ideality [$1 < \phi(c)$]. Initial computations on this system used the modelling function $P_3[\exp(P_5)]$. A good fit was obtained to the diffusivity data when using this modelling function but none of the computed solutions in the region of interest were close to Miedema's prediction. Hence it was decided to rerun the computations using the more complex modelling function, $P_4[\exp(P_6)]$. Results for these computations are presented in Fig. 5, which depicts the activity composition curves along with the estimated Henry's

Fig. 5. Computed activities for the AgAu system at 900°C using the model function $P_4[\exp(P_6)]$. The Henry's law line computed from Miedema's theoretical predictions is also depicted. The activities computed on imposing the bounds [1, 6] are taken to represent the thermodynamics of the system. Hultgren's experimental data at 527°C is also depicted.

law line and Hultgren's data. The $\phi(c)$ - c curves are reported elsewhere [7]. A good fit was obtained to the diffusivity data in this case (table of residuals [7]). From Fig. 5, it is clear that the solution corresponding to the bounds [1, 6] closely matches the estimated Henry's law line. Further it exhibits the same general trend as Hultgren's data and in fact is coincident with Hultgren's data at both the dilute end and the high concentration end. At intermediate compositions ($0.2 < c < 0.8$), the computed activities are closer to the ideal alloy line than Hultgren's data. This is precisely what one would expect, since the diffusivity data were measured at a much higher temperature (900°C) than Hultgren's data (527°C). On the basis of these results, it is believed that the solution corresponding to the bounds [1, 6] in Fig. 9 represents the activity-composition data for the Ag-Au binary. A plot of $\ln(\gamma)$ as a function of composition for this solution is available elsewhere.⁷ Thus the proposed algorithm leads to good results when applied to the AgAu system.

PdFe system

Diffusivity data for this system was obtained at 1050°C whereas Hultgren *et al.* report the activity at 1000°C . The $\tilde{D}$ - c data for this system had to be extrapolated at the ends since the data reported by Borovskii covered the composition range [0.05, 0.95]. The system is peculiar in that it exhibits positive deviation for compositions in excess of 0.55 whereas for compositions below 0.55 it exhibits negative deviations from ideality. Consequently, one expects that the $\phi(c)$ - c curves will cross the line $\phi(c) = 1$ over the compositional interval [0, 1]. Thus using unity as an upper or lower bound will be counter productive.

Due to the peculiar thermodynamic behavior of this system it was expected that this system would challenge the proposed computational scheme and test its robustness.

It should be noted that for this system the estimated Henry's law line does not match Hultgren's experimental data very well. Hence, one expects that the estimated Henry's law line would in this case mislead one into picking the wrong solution from the set of possible solutions.

Initial computations were performed using the function $P_3[\exp(P_5)]$ to model the inter-diffusion coefficient. However the fit to the diffusivity data were not satisfactory. With some bounds, a reasonable fit was obtained but with others a good fit could not be achieved. Hence it was decided to change the modelling function to $P_4[\exp(P_6)]$. With this function a good fit was achieved to the original interdiffusivity data. Results for these computations are depicted in Fig. 6 which also presents the experimental data reported by Hultgren as well as the estimated Henry's law line at infinite dilution. The corresponding $\phi(c)$ - c graphs have been presented elsewhere [7]. From Fig. 6, it is clear that the estimated Henry's law line

does not match Hultgren's data. It is also clear from Fig. 6 that the computational scheme does predict one solution which depicts a general trend similar to that exhibited by Hultgren's data although there is a some difference between the computed data and Hultgren's data over the intermediate range of compositions ($0.3 < c < 0.75$). Despite this difference, it is encouraging to note that the computed solution does in fact correctly predict that the system exhibits a positive deviation in the higher compositional range and a negative deviation in the lower compositional range. In fact there is excellent agreement between the experimental and computed data at the dilute end ($c < 0.3$) and at the concentrated end ($c > 0.8$). Data depicting $\ln(\gamma)$ as a function of composition for the selected solution have been reported elsewhere [7]. Thus, while the computational scheme yields activities that differ from the data by Hultgren over the intermediate range of compositions, the scheme does predict the general trend in the data.

AuNi system

Diffusivity data for this system were obtained at 900°C whereas Hultgren's data represents the system thermodynamics at 875°C . The estimated Henry's law line based on Miedema's theoretical prediction does not match Hultgren's data but is helpful in focussing the search to a region of $\phi(c)$ - c space corresponding to positive deviations from ideality. Preliminary attempts at fitting the diffusivity data with the model function $P_3[\exp(P_5)]$ did not lead to a satisfactory fit. Hence the model was changed to $P_4[\exp(P_6)]$. This resulted in an adequate fit to the data. Results of the computations are depicted in Fig. 7 which plots the computed activities as a function of composition. The corresponding $\phi(c)$ - c

Fig. 6. Computed activities for the PdFe system at 1050°C using the model function $P_4[\exp(P_6)]$. The Henry's law line computed from Miedema's theoretical predictions is also depicted. The activities computed on imposing the constraints [0.1, 6] are taken to represent the system thermodynamics. Experimental data by Hultgren at 1050°C is also depicted.

curves have been reported elsewhere [7]. The solutions computed on imposing the bounds [0.001, 1] and [0.01, 1] are coincident. From Fig. 7, it is clear that the solution close to Miedema's prediction (i.e. the solution corresponding to the bounds [0.02, 1]) does not compare well with Hultgren's experimental data. However, the solution corresponding to the bounds [0.01, 1] leads to a good match at low concentrations ($c < 0.15$). Thereafter it exhibits the same general behavior as Hultgren's data but differs from it. Hence, the solution computed on imposing the constraints [0.001, 1] represents the thermodynamics of the AuNi system as computed from the diffusivity data. Thus in this system, one also notes that Miedema's prediction may misguide one into picking the wrong solution. However, the fitting process is capable of locating a solution that is similar to the actual data.

NiPt system

Diffusivity data were obtained at 1296°C whereas Hultgren *et al.* report experimental data at 1352°C. The estimated Henry's law line based on Miedema's prediction provides a good match to Hultgren's data. Miedema's prediction also indicates that the search should be confined to the region of $\phi(c)$ - c space representing negative deviations from ideality. Preliminary computations were performed on this system using the model function $P_3[\exp(P_5)]$. Results for these are shown in Fig. 8 which depicts the activity-composition curves. The corresponding $\phi(c)$ - c curves have been reported elsewhere [7]. A large number of runs were conducted and in each case a good fit was achieved to the diffusivity data. However none of the computed solutions were close to the estimated Henry's law line or to Hultgren's data. From Fig. 8 one notes that the computed solutions can be classified into two distinct families. The family

corresponding to the bounds [1, 6], [1, 3], [1, 6.25] and [1, 6.32] is degenerate in that all the solutions are identical. These solutions are closer to the ideal alloy line than the estimated Henry's law line. The second family of solutions shows a far greater deviation from ideality than that predicted by Miedema. The computed solutions are also a strong function of the bounds chosen. This is best illustrated by comparing the solutions corresponding to the bounds [1, 6.32] and [1, 6.4].

It was decided to use the more complex modelling function, $P_4[\exp(P_6)]$, in the hope of locating solutions closer to Miedema's prediction and to Hultgren's data. Results for these computations are depicted in Fig. 9. The general trend is similar to the trend seen in Fig. 8. Once again two families of solutions emerge but none of the computed solutions are close to Miedema's prediction or to Hultgren's experimental data.

The lack of existence of any solutions close to Hultgren's data could be caused by any of the following reasons. Firstly, it is possible that the diffusion data itself contains systematic errors. It has been estimated that diffusion data may contain up to 25% error [7]. Secondly it is possible that the functional forms chosen for $\phi(c)$ and $f(c)$ [see equation (1)] are inappropriate for this particular system. This implies that one is unable to satisfactorily model the variation of the two functions although their product does model the diffusivity satisfactorily.

Finally, the inability to locate an appropriate minimum for the NiPt system may be a result of the curve fitting procedures. A full discussion on this is deferred to a latter section. Lacking any additional data one is unable to comment further on which one of these reasons leads to a failure in computing the activities for the Ni-Pt system.

Fig. 7. Computed activities for the AuNi system at 900°C using the model function $P_4[\exp(P_6)]$. The Henry's law line computed from Miedema's theoretical predictions is also depicted. The activities computed on imposing the bounds [0.01, 1] and [0.001, 1] are coincident and are taken to represent the system thermodynamics. Experimental data by Hultgren at 873°C is also depicted.

Fig. 8. Computed activities for the NiPt system at 1296°C using the model function $P_3[\exp(P_5)]$. The Henry's law line computed from Miedema's theoretical predictions is also depicted. None of the computed solutions match either the predicted Henry's law line or the experimental data by Hultgren at 1352°C.

NbTi system

Diffusivity data for this system was reported at 1000°C. Only one investigation, that by Kuz'min *et al.*, has experimentally examined the thermodynamics of the Nb–Ti system [9]. Their data suggests that the system possesses a strong negative deviation from ideality. Hultgren *et al.* do not tabulate activity data for this system since they consider Kuz'min's data to be unreliable. Thus for this system there is no reliable thermodynamic data available. In sharp contrast to Kuz'min's data, the theoretical predictions of Miedema *et al.* indicate that the system exhibits a positive deviation from ideality. A value of +9 kJ/mol is predicted for the enthalpy of formation at infinite dilution which corresponds to a Henry's constant of $\gamma = 2.5$.

Initial computations were performed using the model function $P_3[\exp(P_5)]$. Subsequently, the model function was altered to $P_4[\exp(P_6)]$. Since both model functions yielded similar results, only the results for the model $P_4[\exp(P_6)]$ are presented. These are depicted in Fig. 10 along with the estimated Henry's law line. For both modelling functions *considerable difficulty was encountered in obtaining a good fit to the diffusivity data*. For both modelling functions only one solution (the one corresponding to the bounds [0.05, 1] in Fig. 10) led to a good fit (Table 1) to the diffusivity data. The fit to the diffusivity data for this solution is depicted in Fig. 11 whereas Fig. 12 depicts the fit corresponding to the bounds [0.4, 1]. The latter figure is representative of the difficulty in obtaining a good fit to the diffusivity data. Table 1 summarizes the results of the computations for the NbTi system.

Examination of Table 1 and Figs 11 and 12 would strongly suggest that the solution corresponding to the bounds [0.05, 1] represents the thermodynamics

of the NbTi system at 1000°C. This is the only solution for which a good fit has been achieved and it possesses the smallest residual at the minimum.

Two arguments may be presented challenging the validity of this solution. Firstly the selected solution clearly contradicts Kuz'min's data. Secondly, the selected solution does not match the estimated Henry's law line based on Miedema's prediction. However, as mentioned earlier Kuz'min's data is not considered reliable by Hultgren *et al.* As far as Miedema's prediction is concerned, the solution does agree with Miedema's prediction that the system exhibits a positive deviation from ideality. It has already been observed that the estimated Henry's law line can also contain errors (examples include the AuNi and CuNi systems discussed earlier). It should be recalled that Miedema's predictions were made for liquid alloys. Although some compensation has been made for the latent heat of fusion in estimating the partial molar enthalpy in the solid state¹ one is still unable to account for the strain energy. Further the assumption of regular solution behavior which is implicit in the estimation of the Henry's law line (see earlier paper [1]) may not be correct. This and the fact that in the present case the homologous temperature of the diffusion experiment is approximately 0.5, together imply that it is quite possible that the estimated Henry's law line contains large errors. If the system does exhibit a positive deviation from ideality then one would expect this tendency to be more prominent at lower temperatures, which is consistent with the observed behavior.

The discrepancy between Miedema's prediction and the computed solution can be resolved if a single bold assumption is made. If one assumes that the system contains a miscibility gap at temperatures lower than 1000°C then one would expect the system

Fig. 9. Computed activities for the PtNi system at 1296°C using the model function $P_4[\exp(P_6)]$. The Henry's law line computed from Miedema's theoretical prediction is also depicted. None of the computed solutions match either the predicted Henry's law line or the experimental data by Hultgren at 1352°C.

Fig. 10. Computed activities for the NbTi system at 1000°C using the model function $P_4[\exp(P_6)]$. The Henry's law line computed from Miedema's theoretical prediction is also depicted. The solution computed in imposing the constraints [0.05, 1] on $\phi(c)$ was taken to represent the thermodynamics of the system at 1000°C.

Fig. 11. Illustration of a relatively good fit to the original diffusivity data for the NbTi system computed by imposing the constraints [0.05, 1] on $\phi(c)$. The residual at the minimum was 0.82.

to exhibit the strong positive deviations that the calculations reveal. However, the binary phase diagram [9] for the Nb–Ti system does not reveal a miscibility gap. That in itself does not rule out the possibility of a low temperature miscibility gap since it is quite possible that a miscibility gap does exist but has not been discovered. The situation would be similar to the Fe–Ni binary, wherein recent studies [10–12] have revealed a low temperature miscibility gap formerly unknown. At the temperature of interest the diffusion coefficient is fairly small (10^{-14} cm²/s for the NbTi system at the Nb rich end). Such small diffusion coefficients can serve as kinetic barriers hindering the transformation to the low temperature phases and thereby impeding the detection of low temperature miscibility gaps.

Finally, one must also consider the possibility that the diffusivity data for the NbTi system contains

Fig. 12. Illustration of a relatively poor fit to the original diffusivity data for the NbTi system computed by imposing the constraints [0.4, 2] on $\phi(c)$. The residual at the minimum was 12.8.

Table 1. Results of least squares fitting for the NbTi system using the modelling function $P_3 \exp(P_5)$

Bounds	Final activity curve	Residual at minima
[0.05, 1.]	Strong positive deviation	0.82
[0.2, 1.]	Positive deviation	4.269
[0.4, 1.]	Positive deviation	12.8
[0.7, 1.]	Positive deviation	21.0
[0.7, 6.]	Negative deviation	5.06
[1., 8.0]	Negative deviation	5.60
[1., 4.0]	Negative deviation	8.47
[1.0, 12]	Negative deviation	5.365

errors. Such errors may originate from two sources in the present case. Firstly, measurement of small diffusion coefficients is a process intrinsically susceptible to large errors. Secondly, the temperature of the diffusion experiment (1000°C) corresponds to a homologous temperature of 0.46 at the Nb rich end and 0.64 at the Ti rich end. It is well known that for homologous temperatures less than 0.5, grain boundary diffusion can contaminate the results of a bulk diffusion experiment. If such errors were present in the diffusivity data then they would lead to errors in the computed activities.

To summarize, the thermodynamics of the Nb–Ti system remain elusive. The computations suggest that the system exhibits a strong positive deviation from ideality and that the system possesses a miscibility gap below 1000°C. Additional experimentation is necessary to fully evaluate this system although the computations based on the interdiffusion coefficient provide new insight to the thermodynamics of this system.

DISCUSSION

Summary of computational results

The computations on the ten isomorphous binaries may be summarized as follows. For eight systems, the computational scheme resulted in solutions that either matched very well with the experimental data, were close to the experimental data or exhibited a trend similar to the experimental data. Among these, in four systems the estimated Henry's law line was helpful in selecting the correct solution, for the other four a plausible solution was computed but if the estimated Henry's law line were used, an incorrect solution would have been picked. For these four systems the experimental data of Hultgren was relied on to help select the correct solution. For one system (PtNi) the solution scheme did not compute any solution close to the experimental data. Finally in the case of the NbTi system, since no reliable experimental data exists, a comparison is not possible. For this system, the computed solution does agree with Miedema's prediction in that the system should exhibit positive deviation from ideality. The computations also provide fresh insight into the system thermodynamics by suggesting the possibility of a low temperature miscibility gap.

A clear demonstration of the proposed scheme was its successful application to the Pd-Fe system for which the activity curves cross over from negative deviations to positive deviations. *The demonstration that the proposed scheme works for complex systems such as Pd-Fe is a clear indication of the robustness of the method.*

These results suggest that the proposed algorithm is generally capable of computing a set of solutions of which one is close to the correct activity composition curve.

Nonuniqueness problem

The computations have successfully demonstrated that in principle, activity data can be estimated from diffusivity data and that measurements of the interdiffusion coefficient can serve as a source of activity-composition data for isomorphous binaries. The main drawback to this computational scheme is the multiplicity of solutions. As mentioned earlier, this necessitates that some additional information be made available that would help in selecting the correct solution.

It was hoped that the estimated Henry's law line would provide that additional piece of information. However, *it is clear that the estimated Henry's law line cannot be relied on to pick the correct solution from the set of possible solutions.* Instead it is advisable to conduct a single experiment which will yield the activity at a particular composition and use the experimental data point to pick the correct solution. Thus one needs to input not only the diffusivity as a function of composition but also a single measured data-point.

One would prefer to have an algorithm that yields a unique solution but as has been shown, the problem itself is non unique and hence multiple solutions are unavoidable.

Role of the constraints

The present constraints embodied in equation (3) ensure that $\phi(c)$ is unity at either end of the composition range. These are based upon firm thermodynamic knowledge. It can be shown [7] (by considering the activity composition relationship corresponding to the regular solution model) that in the general case there are no intrinsic thermodynamic constraints on $\partial\phi/\partial c$. It is unclear at the present time whether additional higher order constraints need to be imposed on $\phi(c)$. Such constraints should be included only if they are known to hold true for *all* solutions.

It is important to note the critical role of the constraints embodied in equations (3) and (4). It is these constraints that allow one to *simultaneously* evaluate both the thermodynamics of the system and the function $f(c)$. Without the constraints one would possess a single quantity (Diffusivity as a function of composition) and attempt to compute two quantities [$f(c)$ and $\phi(c)$]. It is the incorporation of the con-

straints which allows one to compute a *set* of solutions by searching subsets of the $\phi(c)$ - c space.

Applicability of the method

It will be recalled that the proposed scheme is based on the theories proposed by Darken and by Howard and Lidiard, Kirkaldy and Manning which represent the interdiffusion coefficient as a product of functions. Hence, the algorithm implicitly assumes all of the assumptions that are common to both theories. The more important among these are the assumption of an isotropic lattice and the assumption that vacancies are in local equilibrium.

The proposed scheme will be applicable to those materials for which the interdiffusion coefficient can be represented in the functional form described by equation (1). Since no assumptions are made regarding the nature of the function $f(c)$ (other than the fact that it can be adequately represented by polynomials) the algorithm is not necessarily restricted to materials that obey Darken's treatment or the treatment by Howard and Lidiard, Manning and Kirkaldy. For other materials the mathematical models used to describe the quantity $f(c)$ and $\phi(c)$ may need to be replaced by other functions. In this context it should be noted that the mathematical models chosen to represent the quantities $f(c)$ and $\phi(c)$ can be modified as necessary. The choice was not based on physical arguments; these were merely the first set of functions, distinct from each other, that fitted the experimentally available data describing the quantities $f(c)$ and $\phi(c)$. It is quite possible that there exist other mathematical functions that are better suited to modelling these quantities. Thus the present investigation should be viewed as a preliminary attempt seeking to outline the methodology which one might pursue in attempting to obtain thermodynamic data from diffusion couples.

Modification of the modelling functions

It is clear from the computations that the modelling function $P_3[\exp(P_5)]$ cannot be universally applied and that the function $P_4[\exp(P_6)]$ may provide a better model. It is also evident that this function possesses sufficient degrees of freedom to adequately model the solution behavior of complex systems such as the Pd-Fe system for which the activity-composition curve crosses over from negative deviation to positive deviation. Hence, it is recommended that the more complex function, $P_4[\exp(P_6)]$ be used for any future calculations.

In addition, there may be physical reasons (from a thermodynamic standpoint) for altering the mathematical functions chosen to model $f(c)$ and $\phi(c)$ or for imposing additional constraints. In other words, the choice of the mathematical models selected to represent $\phi(c)$ [$\exp(P_5)$ or $\exp(P_6)$ in the present investigation] must not violate the laws of thermodynamics or contradict known solution behavior.

Errors in the computed activities

In the case of linear least squares fitting one can compute an upper bound on the errors associated with a particular solution to the least squares problem. Unfortunately it is not possible to do the same for the non-linear case. Thus, due to the non-linear nature of the fitting function ($P_4[\exp(P_6)]$), it is not possible to compute the error bounds for each solution. Hence, one can only outline the sources of error and the potential pitfalls that one must guard against.

Firstly, in non-linear least squares fitting, it is important to vary the start point at which the computations are initiated. In the present investigation, the starting point for the iterations was not changed. Such a solution scheme suffers from the drawback that a local minimum in $\phi(c)$ - c space located close to the starting point may "trap" the solution and prevent it from reaching other solutions in the space. This can prevent one from computing other feasible solutions that are located "far" from the starting point and thereby lead to errors. This may explain why the solution scheme was unable to compute a solution for the NiPt system in the region of interest. Hence in the general case, it is advisable to restart the computations from several different points.

Secondly, for some alloy systems, the activity-composition curves that comprise the set of feasible solutions lie very close to one another (e.g. Pd-Ni system). For such systems it is difficult to select the appropriate minimum. However, the various minima together depict a band within which the activity composition data is known to lie. This does not undermine the proposed scheme provided the differences between the various solutions are comparable to the errors associated with experimentally measuring the activity data.

Usefulness of the method

Despite some of the drawbacks described above, it is believed that the computational scheme will be useful in several applications. Firstly, it should be noted that the experimental activity data reported by Hultgren are usually representative of the system thermodynamics at lower homologous temperatures than the temperatures at which diffusivity data is measured. This implies that the experimental data reported in Hultgren could be used to pick the correct solution from sets of solutions representing the system thermodynamics at other temperatures. One could thereby generate activity data for higher temperatures. Secondly the technique will serve as an aid in checking the consistency of existing thermodynamic and diffusion data. Thirdly, for reactive metal systems such as the Nb-Ti system the proposed scheme may lead to a better estimate of the thermodynamic data. Finally it is hoped that this study will enhance the appreciation of the link between thermodynamic data and diffusion data.

EXTENSIONS TO BINARIES CONTAINING MISCIBILITY GAPS

The proposed algorithm may be extended to systems other than isomorphous binaries. In the case of systems exhibiting a miscibility gap this should be fairly straightforward since one knows that such systems exhibit a positive deviation from ideality. Over the composition range corresponding to the miscibility gap, the function $\phi(c)$ is negative, indicating that solutions of that composition are intrinsically unstable from a thermodynamic standpoint. Since the function $\phi(c)$ is known to be positive outside the miscibility gap, this implies that at the terminal compositions of the miscibility gap, the function $\phi(c)$ must be zero. As a result, one could split the computation into two halves. In the first half one would use the proposed scheme to compute the activity from the pure solvent to the composition corresponding to the miscibility gap. At either end of this compositional band the numerical value of the function $\phi(c)$ is known *a priori* to be zero. It is also known that the activities of the two compositions in equilibrium across the miscibility gap are identical. The value of the function $\phi(c)$ is also known at $c = 0$. Using all of this information, it should be straightforward to compute the activity-composition relationship for systems exhibiting positive deviations from ideality. For systems exhibiting negative deviations from ideality the situation is less clear, since one does not know the numerical value of $\phi(c)$ for intermetallic compounds.

CONCLUSIONS

The following conclusions may be drawn from this study:

(i) For isomorphous binary systems, given the $\tilde{D}$ - c relationship and one additional piece of information the entire activity-composition curve can be estimated. An algorithm has been developed that permits one to compute the system thermodynamics (which is implicitly contained in the variation of the chemical interdiffusion coefficient) by using a constrained nonlinear least squares approach that models the diffusivity as a product of two functions. The algorithm decomposes the interdiffusion coefficient into its two constituent terms: a thermodynamic term and a term representing the phenomenological coefficients.

(ii) Due to the inherent non uniqueness of the problem, the proposed scheme leads to multiple solutions. In order to select the correct solution it becomes necessary to use one additional piece of information. The additional piece of information may consist of the measured activity at a particular composition or the slope of the Henry's law line at infinite dilution.

(iii) The proposed computational scheme was applied to ten isomorphous binary systems. For eight of these systems the scheme was able to locate a solution

close to the experimentally measured data confirming the proposition that one can estimate activities from diffusivities. For four of these systems the correct solution was picked by using the theoretical predictions of the enthalpies of formation at infinite dilution. For one system there is no reliable experimental data available for comparison, but the computations provide fresh insight into the thermodynamics of the system. For another system the scheme led to results that were not consistent with the experimental data.

(iv) The algorithm can be easily extended to binary systems exhibiting a miscibility gap.

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APPENDIX

- $\tilde{D}$ = interdiffusion coefficient
 $f(c)$ = contribution of phenomenological coefficients to interdiffusion coefficient
 $\phi(c)$ = thermodynamic function representing the solution behavior
 τ_j = unknown variable constituting the model used for least squares analysis
 c_i = composition
 l_i = lower bound imposed on the thermodynamic function
 u_i = upper bound imposed on the thermodynamic function
 E^2 = Least squares error function
 w_i = weighing function used in the least squares analysis
 h_i = modelling function in least squares analysis
 D_i^* = tracer diffusivity of element i
 P_n = space of all n th order polynomials