

Thermodynamic Assessment of Platinum Group Metal Systems

THE OPTIMISATION OF BINARY PHASE DIAGRAMS

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Phase diagrams of alloy systems provide essential guidance for designers, metallurgists and engineers involved in the manufacture of metal products. This paper considers the use of computer-based methods of assessment of phase diagrams in two-component systems. Both thermodynamic and phase equilibrium data are used in the analysis to provide a final data set which is as consistent as possible with all the available experimental information. The treatment of the copper-platinum and copper-rhodium systems is described. While this optimisation method is often able to resolve problems within the binary system, the major advantage lies in allowing the estimation of properties in ternary and higher order systems.

On the basis of 70 metallic elements in the periodic table, there are 54,740 possible ternary systems and no less than 916,895 quaternary systems. Most industrial alloys have at least three components, and thus the probability of finding required data from published sources is quite small. Furthermore, the experimental determination of alloy properties, particularly long-term phase stability, is expensive and time consuming.

In recent years, and in line with the ready accessibility of computers, help has been sought in investigating higher order systems by calculating the phase relationships using thermodynamic data. Considering 70 elements once again, there are the comparatively modest number of 2415 possible binary systems, and the calculation approach is based on the use of critically assessed data from this limited number of systems. Binary data sets are "added together" to give an approximate representation of a higher order system which can then be refined to give a more accurate description using a few experimental measurements from the higher order system.

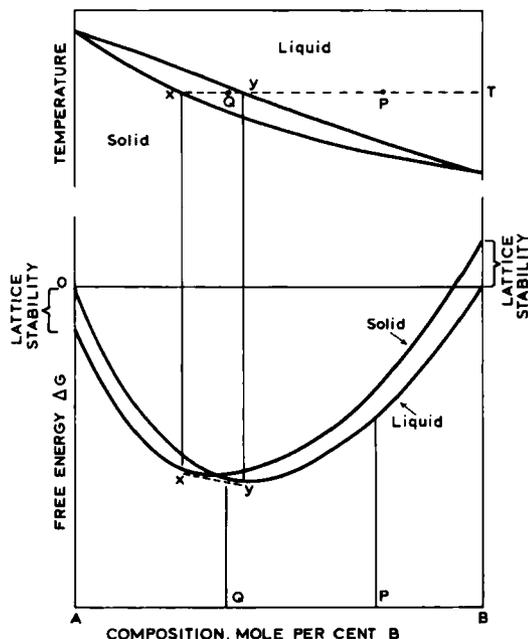
Experimental data for a binary system are

usually in two forms; thermodynamic data for the different phases, for instance activity measurements or heat of alloy formation, and phase diagram data which describe the equilibrium between the phases. In principle it is possible to calculate the phase diagram directly from experimental thermodynamic data, but it is unlikely that the calculated and measured diagram will show good agreement. In order to use the binary data as a basis for calculating higher order systems, a set of thermodynamic data which both represents the measured thermodynamic properties and reproduces the phase diagram is required.

Consider a binary metal system A-B. The phase boundaries between two phases, for instance liquid and solid, may be calculated from the free energy of formation of the two phases as a function of composition and temperature. This statement requires some elaboration.

The free energy of formation (ΔG) of the alloy is calculated from the **activities** of the components in the alloy, which are experimentally determinable properties. Activity is a measure of the effect of alloying on the

Fig. 1 Free energy curves for solid and liquid alloys at temperature T showing the derivation of phase boundaries. The alloy will adopt the state of lowest free energy, which is solid alloy up to point X and liquid alloy beyond point Y . Between X and Y a mixture of solid and liquid alloy will have a lower free energy than either liquid or solid alloy alone. X and Y are common tangent points to the two curves and define the solidus and liquidus phase boundaries



chemical properties of a component. It might be expected that the chemical reactivity of A in the alloy would be reduced compared with pure A. The activity is defined as the ratio of the vapour pressure of A in the alloy to the vapour pressure of pure A. In a so-called "ideal" alloy system, the activity is equal to the fraction of the element present, on a molar basis. In practice the activity may be greater or less than the mole fraction. The activity and mole fraction are related by the equation:

$$a_A = X_A \gamma_A$$

where γ_A is the activity coefficient, determined from the composition and experimental activity. The free energy of formation per mole of alloy is given by:

$$\Delta G = X_A RT \ln a_A + X_B RT \ln a_B \quad [i]$$

For those who do not welcome the prospect of a continued series of thermodynamic equations and relationships, it may be helpful to think of much of what follows as a purely mathematical exercise, involving the solution of mathematical rather than thermodynamic problems.

Free energy curves, based on equation [i], for both the solid and liquid phases of alloy A-B at one temperature are shown in Figure 1. One

further factor has been added, however. In order to calculate the equilibrium between the two phases it is necessary to refer the solid and liquid data to a common reference state. Pure liquids A and B have been chosen as the reference states, and a "lattice stability" term has been added to the solid curve. This represents simply the free energy difference between the pure solid and pure liquid components.

The alloy will adopt a state in which for a given overall composition the free energy is at a minimum. In Figure 1, an alloy of composition P will adopt a liquid state since at this point the liquid curve is lower than that of the solid. At Q, the liquid curve is also below the solid curve, but a system of coexisting solid and liquid would give an overall free energy on the line x-y, lower than either the solid or the liquid curve. A two-phase system represents the most stable state for any composition between x and y. The relationship between the free energy curves and a possible phase diagram is also shown in Figure 1.

In order to **calculate** the equilibrium composition in this system, or indeed in a more

complex system, a mathematical description of the free energy values is required. The problem then becomes one of finding the combination of phases and their compositions which will give the minimum overall free energy consistent with the mass balance of the alloy constituents. One method of solution has been developed and described by Eriksson (1).

The first stage in the representation of higher order systems is to evaluate ΔG for each phase in the binary systems from the available experimental data. Equation [i] may be re-written:

$$\Delta G = \Delta G_{\text{lattice stability}} + \Delta G_{\text{ideal}} (= X_A RT \ln X_A + X_B RT \ln X_B) + \Delta G_{\text{excess}} (= X_A RT \ln \gamma_A + X_B RT \ln \gamma_B) \quad [\text{ii}]$$

The first two terms are generally known. The third term is evaluated from the experimental data. The form of the equation used for the third term depends on the type and structure of the phase being considered, but solid and liquid solution phases are often represented by the Redlich-Kister polynomial:

$$\Delta G^{ss} = X_A X_B [C_0 + C_1(X_A - X_B) + C_2(X_A - X_B)^2 + C_3(X_A - X_B)^3 \dots] \quad [\text{iii}]$$

where $C_0, C_1, C_2 \dots$ etc. are temperature-dependent coefficients. Optimum values of the coefficients may be obtained by a computer-aided least-squares analysis of sets of equations representing the experimental data. In the work reported here, the optimisation program developed by Lukas, Henig and Zimmermann (2) was used.

A major feature of the regression analysis is that both thermodynamic and phase diagram data are treated simultaneously, and contribute to the final value of the coefficients. This is possible because both phase equilibria and thermodynamic properties can be written in terms of equations that involve the same unknown coefficients $C_0, C_1, C_2 \dots$ etc. In practice there are many combinations of coefficients that will give an acceptable mathematical fit to the data, particularly if the data are scattered, but some of the solutions will be highly improbable from the thermodynamic point of view. It is often necessary to control the analysis by subjective weighting of the data, by introducing fictitious but thermodynamically reasonable values for

some phases where data are sparse, and by limiting the number of coefficients chosen to represent each phase, in order to get a set of coefficients which experience says are reasonable.

An account of the assessment of two systems involving platinum group metals is given below.

Copper-Platinum

Experimental work on the copper-platinum system includes measurements of activities of copper in solid and liquid alloys (3-8), and calorimetric determinations of heat of alloy formation (3, 9, 10). The phase diagram itself is not well known, depending entirely on a set of measurements from 1907 covering less than half the composition range (11). While the available information is not extensive, there is very good agreement between the different authors. The raw data points input to the optimisation program are shown in Figures 2 to 5, although the activity data have been represented by $RT \ln \gamma$ rather than by $RT \ln a$ as required by the program since this is more convenient for graphical display. The final coefficients calculated by the optimisation program are given in Table I. Using these values, $RT \ln \gamma_{\text{Cu}}$, heats of formation and the phase diagram have been calculated and the results compared with the experimental values in Figures 2 to 5. The set of coefficients is able to provide a very good representation of both the thermodynamic data and the phase diagram. Moreover the coefficients provide a very economical form of data storage. Complete tables of thermodynamic values such as integral

Table I
Coefficients to Describe Excess Free Energy (ΔG^{xs} , joules) in the Copper-Platinum System

	Liquid phase	Solid phase
C_0	-32806 - 0.0044T	-42376 + 3.664T
C_1	-20378 + 1.60T	-16865 + 2.456T
C_2	-3858.0	-1531.3

Fig. 2 Experimental values of $RT \ln \gamma_{Cu}$ in solid copper-platinum alloys at various temperatures are plotted. The continuous line represents the calculated, assessed values at 1300K

○ 1300K, □ 1450K
 Myles and Darby, Ref. 3
 △ 1273K, ▲ 1473K
 Landolt and Muan, Ref. 4
 ◇ 923K, 1073K,
 Bidwell, Schulz and Saxer,
 Ref. 5
 + 1550K, ⊕ 1600K
 ⊞ 1700K
 McCormack, Myers and
 Saxer, Ref. 6
 ● 1273K,
 Schmah and Minzl, Ref. 7
 ■ 923K,
 Wiebke and Matthes, Ref. 8

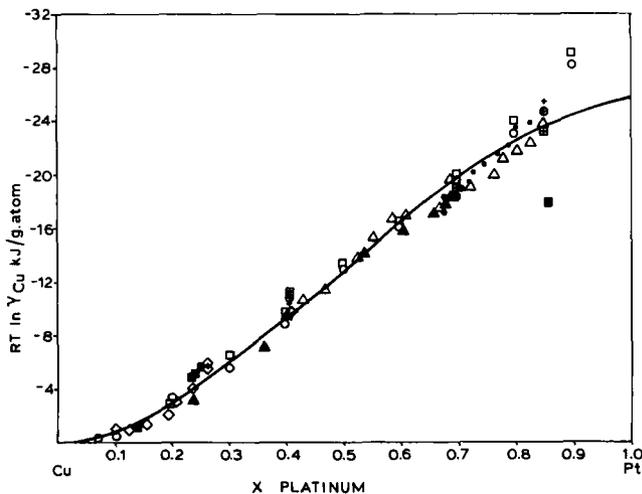


Fig. 3 Experimental and assessed values of $RT \ln \gamma_{Cu}$ in liquid copper-platinum alloys at 1600K

○ 1600K, McCormack, Myers and Saxer, Ref. 6

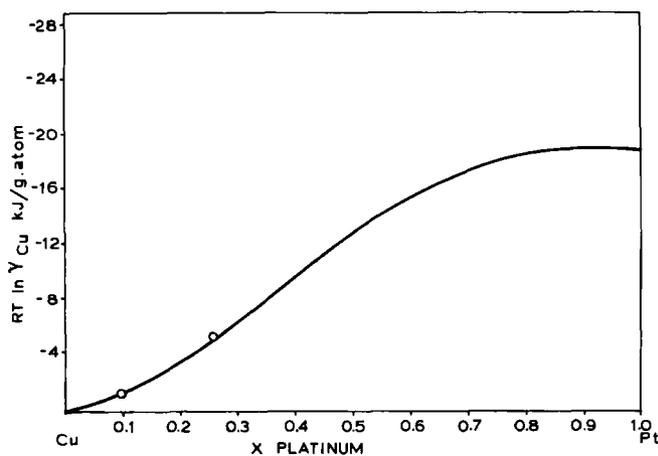
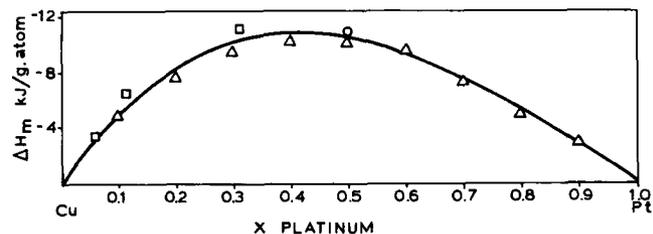


Fig. 4 Experimental and assessed values for solid copper-platinum alloys

△ Myles and Darby, Ref. 3
 □ Oriani and Murphy, Ref. 9
 ○ Geiken, Ref. 10



and partial free energies, enthalpies and entropies may readily be generated with the aid of a simple computer program.

A full description of the liquid thermodynamic properties has been obtained even though very few data points are available for the liquid phase. The liquid properties have in

effect been set by a combination of the liquidus and solidus compositions and the solid phase thermodynamic properties. At high platinum concentrations the liquid properties may not be very accurate since the phase diagram itself has been estimated in this composition range. However, the liquid thermodynamic data are

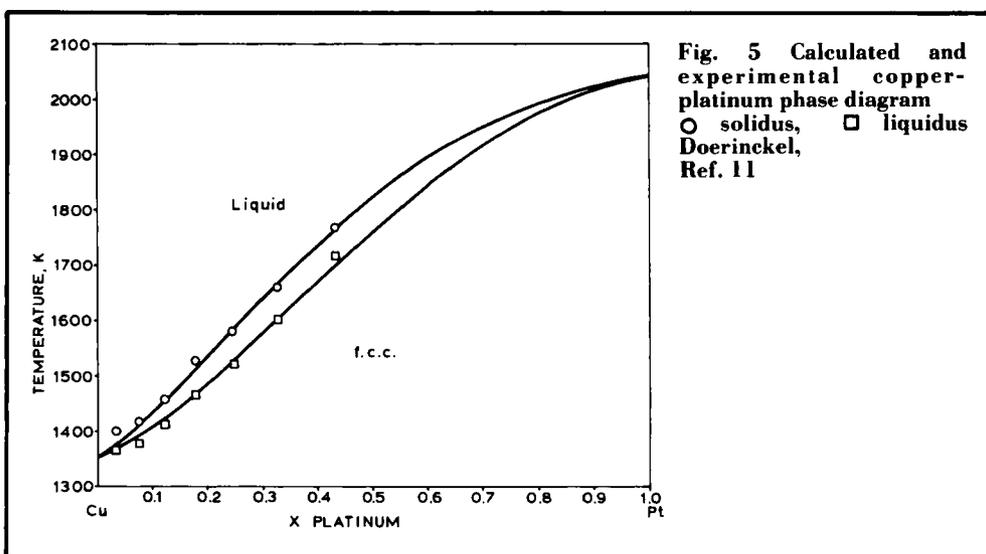


Fig. 5 Calculated and experimental copper-platinum phase diagram
 O solidus, □ liquidus
 Doerinckel, Ref. 11

consistent with a reasonable phase diagram and the measured solid data.

In the second example the form of the phase diagram alone has been used to estimate the solid and liquid thermodynamic properties.

Copper-Rhodium

There appears to be no experimental thermodynamic data available for this system. Phase analysis on a few alloys has been made, allowing a tentative outline of the phase diagram to be drawn (12, 13), showing a miscibility gap in the solid alloy, closing at about 1420K.

A simple one term expression for ΔG^{xs} ($\Delta G^{xs} = X_A X_B C_0$) was found by trial and error which gave the correct closing temperature for the miscibility gap. A corresponding value for the liquid phase was estimated based on the overall shape of the diagram (14). The optimisation program was run using the tentative phase boundaries, and with the rough estimates for the solid and liquid thermodynamic properties used to guide the final coefficients.

The results of the first computer run are shown in Figure 6 together with the experimental data points. Some adjustment to the solidus was required, and this was effected by changing the weighting of some of the input

data. The results of the second run are shown in Figure 7, which is considered to be satisfactory. The coefficients are given in Table II. It is interesting to see to what extent thermodynamic values have been changed by the adjustment of the diagram. The free energy curves corresponding to the diagrams in Figures 6 and 7 are shown in Figure 8. The change is in fact quite small, and suggests that the free energy values have been closely defined by the shape of the diagram. The thermodynamic quantities most likely to be in error are the dilute solution properties, that is the activities of copper in alloys with a high rhodium content and the activities of rhodium in high copper alloys. Clearly greater accuracy could be achieved if more data were available. It

Table II		
Excess Free Energy (ΔG^{xs} , joules) Coefficients for the Copper-Rhodium System		
	Liquid phase	Solid phase
C_0	16048 + 2.429T	17577 + 3.653T
C_1	8241.3 - 5.8187T	1299.4 - 2.994T

Fig. 6 The copper-rhodium phase diagram as initially calculated
 X 2-phase, solid + liquid, Raub, et al., Ref. 12
 ● single phase solid
 ○ 2-phase solid
 □ phase boundary, Luo and Duwez, Ref.13
 With the notation used below in Figure 7

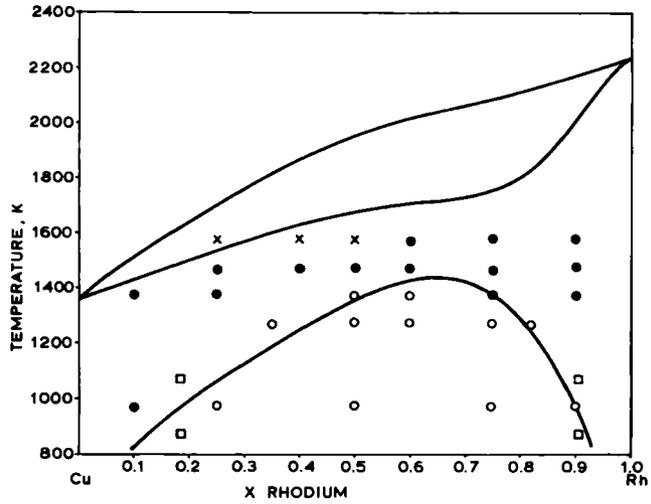


Fig. 7 The final form of the calculated copper-rhodium phase diagram

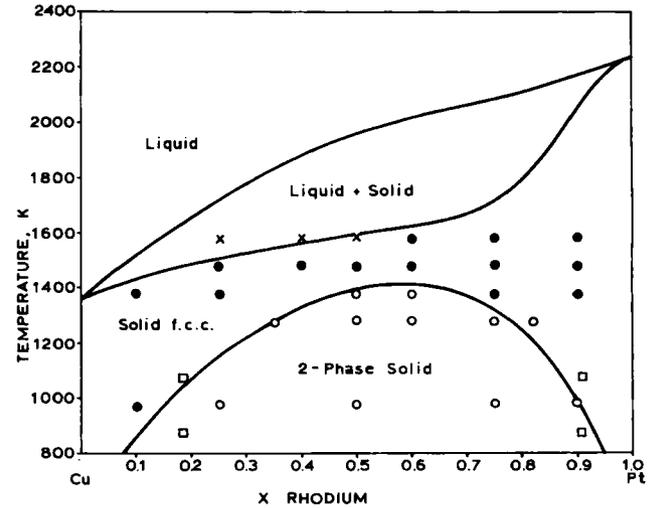
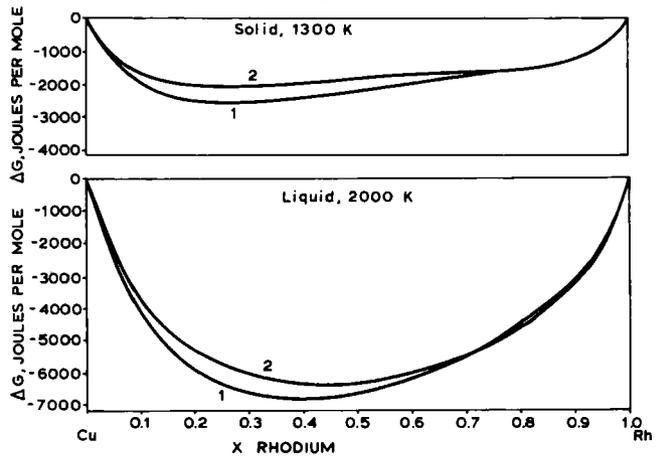


Fig. 8 Free energy of formation curves for solid and liquid copper-rhodium alloys, the phase diagrams corresponding to curves 1 and 2 are shown in Figures 6 and 7, respectively



must be pointed out that not all systems are amenable to derivation of thermodynamic properties in this way.

Higher Order Systems

From assessed binary data sets, thermodynamic properties of ternary systems may be estimated using the empirical relationship:

$$\Delta G_{ABC}^{\circ} = X_A X_B [A-B] + X_B X_C [B-C] + X_C X_A [C-A] + X_A X_B X_C K$$

where [A-B] represents the square-bracketed term in equation [iii], and [B-C] and [C-A] represent the equivalent terms for B-C and C-A binary systems. Where ternary data is available, the coefficient K may be adjusted to give the optimum fit. A small amount of ternary data in combination with the three sets of binary coefficients may give a good representation of the whole ternary system.

In summary, it has been shown that phase diagram measurements used in conjunction

with a few thermodynamic data points may be sufficient to allow a full thermodynamic description of a binary system to be achieved. Equally, uncertainties in phase diagrams, particularly at low temperatures where kinetics are slow, may be resolved by the use of thermodynamic data measured at a higher temperature. However, the advantages of self-consistent phase diagram and thermodynamic data sets are not so much that they resolve problems in the binary systems, but that the information may be used to investigate more complex, higher order systems, with a minimum of experimental work and, of course, expense.

Acknowledgement

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Protecting Steel Reinforcement Embedded in Concrete

The application of platinum in cathodic protection systems designed to inhibit the corrosion of ships and marine structures is now well established. In addition platinised electrodes are used for the protection of underground structures such as storage tanks, buried pipelines and oil well casings. Similar electrodes may also find use on surface structures, such as bridges and multi-storey car parks.

A recently published invention relates to the cathodic protection of steel in concrete (Taywood Engineering Limited, *British Appl.* 2,140,456A). Previously, asphalt/concrete

electrical ground beds could only be applied to surfaces that were, at least approximately, horizontal. Now it is claimed that an electrically conductive film, containing a suitable conducting pigment, enables a ground bed to be applied to undersurfaces or to the upright columns of a structure.

The primary anodes, which are stuck to the concrete structure and subsequently covered with the conductive paint, consist of titanium or niobium coated with platinum. These anodes are connected to the positive terminal of a DC system while the steel reinforcement is joined to the negative terminal, to constitute the cathode.