

PHASE EQUILIBRIA IN CONDENSED SYSTEMS

O. KUBASCHEWSKI and I. BARIN

*Lehrstuhl für Metallurgie der Kernbrennstoffe und Theoretische Hüttenkunde
der Rheinisch-Westfälischen Technischen Hochschule Aachen, GFR*

ABSTRACT

The evaluation of metallurgical equilibrium diagrams from thermochemical data in contrast to the use of conventional methods is demonstrated with a number of examples: first with binary alloy systems, i.e. eutectic systems (Ga-Zn, Ga-In), solidus-liquidus gaps (Mg-Cd, Ni-Co, Ni-Cu, Fe-Cr, Nb-Ta), miscibility gaps (Cr-Mo, Ni-Cu, Bi-Zn) and systems exhibiting intermediary phases (Fe-U, Fe-V, Fe-Cr), and then with ternary and quaternary systems, i.e. solution-forming systems (Fe-Co-Ni, Fe-Cr-Ni, Fe-Cr-V, Au-Pd-Pt, Pb-Sn-Cd, Pb-Cd-Zn-Sn) and compound-forming systems (Mg-O-S, Fe-O-Cl). The practical significance of this new development is discussed.

Although much of this paper is devoted to metallurgical equilibria, the underlying principles are equally applicable to other substances, such as oxide, salt or even organic systems. The emphasis is on relatively high temperatures at which kinetic checks are less predominant and the knowledge of chemical equilibrium is thus more important.

Metallurgical equilibria are commonly described by temperature versus concentration plots at normal pressure, known as phase diagrams or equilibrium diagrams*, which provide fundamental information for the metallurgist, whether he be chemically, physically or mechanically oriented. Good equilibrium diagrams are equally important in other fields, such as those of oxide-oxide systems for the ceramist.

The standard of conventional phase diagram work in metallurgy was set in the years 1897-1905 by Heycock and Neville, whose degree of accuracy has seldom been surpassed in the temperature range 20-1000°C. In Germany, the evolution of this field is inextricably connected with the name of Gustav Tammann.

The principles of the derivation of phase boundaries from Gibbs energies were clearly indicated in papers published by van Laar around 1908. On the other hand, since phase boundaries in chemical systems represent equilibria, chemical activities may be evaluated from phase diagrams. One example of many is Rey's calculation¹ of the activity of silica and metal oxides in silicate

*The author makes a distinction between 'phase diagrams' obtained by conventional experimental methods and 'equilibrium diagrams' calculated from thermochemical data.

melts. The use of independently determined thermochemical data for the evaluation of equilibrium diagrams is more recent. Using estimated entropies of fusion, Hauffe and Wagner² calculated liquidus curves in metallic systems exhibiting compound formation as early as 1940, but truly the first evaluation of phase boundaries based on the experimental thermochemical data is Wagner's calculation³ of the solidus-liquidus gap in the system silver-gold. Much of the recent work of the present author and his associates has been devoted to the systematic development of this field.

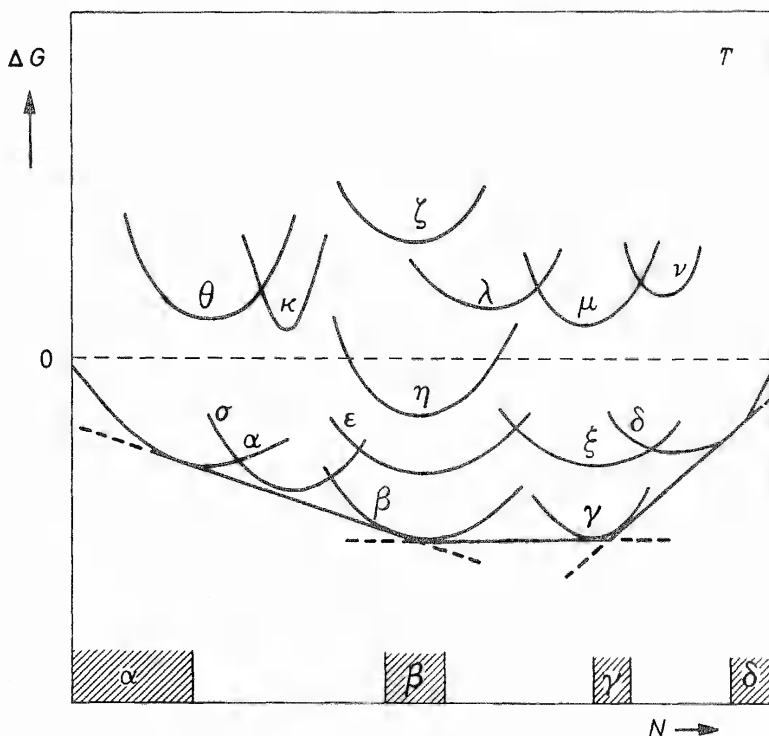


Figure 1. Gibbs energy versus concentration for a hypothetical binary system at a given temperature and pressure.

There are two major aspects of the evaluation of phase boundaries from thermochemical data in contrast to the conventional methods. Thermochemical measurements may be carried out at kinetically favourable temperatures and the results used to calculate phase boundaries at any temperature including those at which equilibration may take months or years. The knowledge of the exact position of such phase boundaries is, of course, of the greatest practical significance because the use of certain alloys in plant may extend over years at these temperatures and success or premature failure depends on whether the alloy was originally in a stable or metastable state.

The second advantage of the thermochemical over the conventional method is only now becoming apparent, namely the possibility of extrapolating the

PHASE EQUILIBRIA IN CONDENSED SYSTEMS

thermochemical properties of binary systems into multi-component ranges with sufficient accuracy to permit calculation of the phase boundaries in ternary, quaternary and more involved systems. This does not yet eliminate the need for the application of conventional methods but substantially reduces the number of such tests.

Systematic experimental studies of the thermochemical properties of alloys were first carried out for the sheer pleasure of breaking new ground, as so often in fundamental science. This attitude still prevails in some laboratories concerned with the measurement of such data. All too often is the most important aspect, the exact relationship of the results with the equilibrium diagram, neglected. It may be repeated that good phase boundaries are vital thermochemical information. Investigators of thermochemical data are to be requested to assess their results critically together with all the available information on phase diagrams⁴ and earlier thermochemical work⁵. If this is done conscientiously, much unnecessary duplication of work may be avoided.

The principle of the evaluation of phase boundaries from Gibbs energies may be seen from *Figure 1*, in which the Gibbs energies of formation of

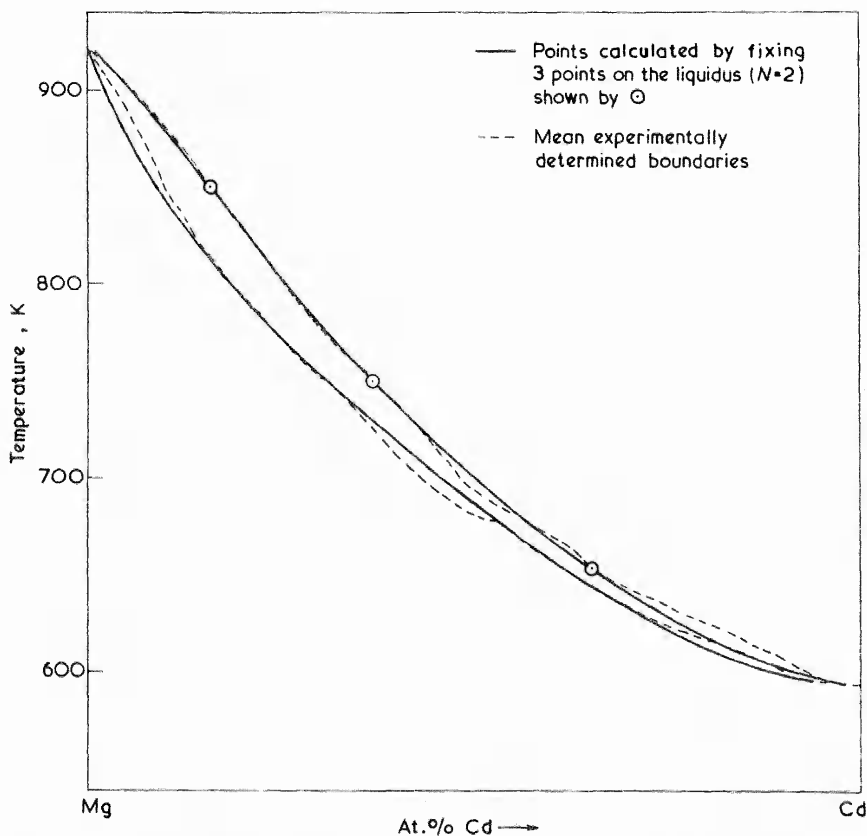


Figure 2. Calculated and experimental solidus and liquidus curves in the system magnesium-cadmium.

various phases are plotted against concentration at a given temperature and pressure in a hypothetical binary system. Since it is always the phase or mixture of phases with the lowest Gibbs energy that is stable, tangents to the lowest $\Delta G-T$ curves have been drawn in *Figure 1*, the points of contact giving the phase boundaries at that temperature and pressure. Thus, *Figure 1* illustrates the graphical method of evaluation. Alternatively, the Gibbs energy curves may be expressed by polynomials and the tangents obtained by calculation invoking the help of a computer. The latter method is not necessarily superior, as it may be difficult to describe the refinements in the thermochemical data by polynomials, as has been demonstrated with the solidus-liquidus gap in the system magnesium-cadmium by Gale and Davis⁶, as shown in *Figure 2*.

By now, quite a large number of equilibrium diagrams of binary systems have been evaluated and consistent sets of thermochemical data produced.

EUTECTIC SYSTEMS

If, in a simple eutectic system, the mutual solid solubilities are sufficiently small to be disregarded, the liquidus temperatures (T_{liq}) may be calculated from the partial heats ($\Delta\bar{H}_i$) and entropies ($\Delta\bar{S}_i$) of solution of the component i at mole fraction N_i ,

$$T_{liq} = (\Delta\bar{H}_i + L_i)/(\Delta\bar{S}_i + \sigma_i) \quad (1)$$

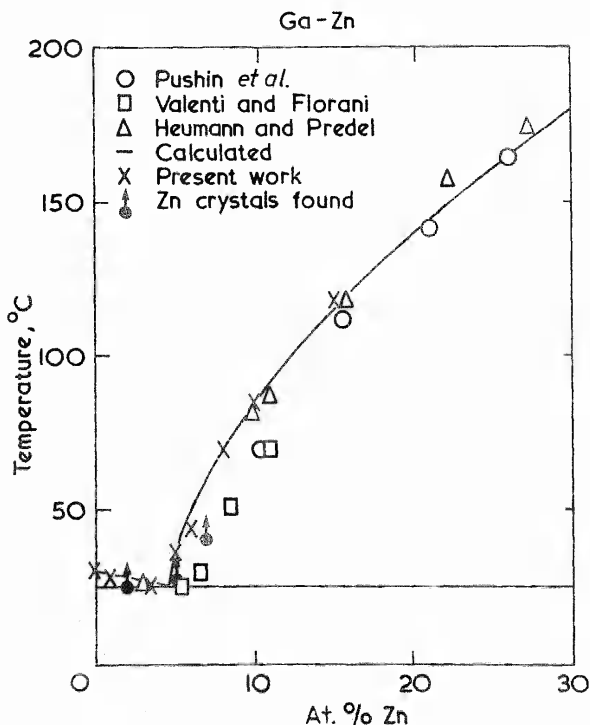


Figure 3. Calculated liquidus curve in the system gallium-zinc and experimental liquidus points.

PHASE EQUILIBRIA IN CONDENSED SYSTEMS

where L_i and σ_i are respectively the heat and entropy of fusion of component i . Experience has shown that liquidus curves thus calculated from good thermochemical data mostly agree very well with those measured by thermal analysis. This observation is important because it means that experimental liquidus curves may be incorporated in the thermodynamic evaluation of a metallic system including other than just eutectic systems.

However, there are exceptions, namely systems with semi-metals having a pronounced tendency to supercooling and therefore to diffusional delays.

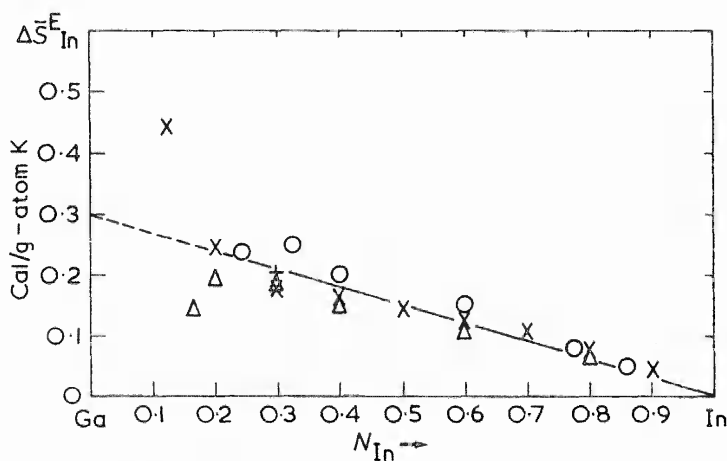


Figure 4. Partial excess entropies of solution of liquid indium in liquid indium-gallium alloys calculated from the heats of mixing and liquidus points obtained by thermal analysis.

In such cases the thermochemical method has proved to be superior to the conventional methods. An example is the system gallium-zinc where the calculated liquidus temperatures at high gallium contents had been found by Kubaschewski and Chart⁷ to be up to 20°C higher than those obtained by normal thermal analysis, as may be seen from Figure 3. Only after prolonged annealing (7 days) above the liquidus and the application of particularly slow cooling rates was the calculated curve confirmed (crosses in Figure 3).

In similar cases it is advisable to obtain the eutectic composition by combining partial heats of mixing and thermal liquidus points and extrapolating the resulting excess entropies of solution into the concentration range rich in semi-metal, as has been demonstrated by Hayes and Kubaschewski⁸ with gallium-indium alloys. Figure 4 shows how faulty thermal liquidus points lead to increasing deviations of the partial excess entropies from the mean curve as the gallium side is approached.

SOLIDUS-LIQUIDUS GAPS

If two metals are mutually completely soluble in the solid and liquid states, the solutions are separated by a solidus-liquidus gap. Making a number of simplifying assumptions, namely that both the solid and liquid solutions are regular and have the same heat of mixing and that the width of the gap in

terms of temperature ($\Delta\theta$) is required only for approximately equiatomic compositions, Wagner³ derived the following equation:

$$\Delta\theta = \frac{N_1^s L_1 + N_2^s L_2}{RT^2/N_1^l N_2^l + T\Delta H_0'} \left(\frac{\delta T}{\delta N_2^l} \right)^2 \quad \text{if } N_2^l \approx N_2^s \quad (2)$$

where the superscripts, s and l, refer to the solid and liquid phases, respectively, and the subscripts, 1 and 2, to the two component metals. $\Delta H_0'$ is the second derivative of the excess Gibbs energy with respect to the mole fraction of the liquid phase and $(\delta T/\delta N_2^l)$ the slope of the liquidus curve.

Where the solidus-liquidus gap is small, equation (2) despite its limitations is quite useful. In the system cobalt-nickel, all the thermodynamic excess functions were found to be zero within the experimental errors⁹. In equation (2), the $T\Delta H_0'$ term is therefore zero and $(\delta T/\delta N_2^l)$ obtained from the difference in melting points of the component metals. Near-ideal behaviour in the system Co-Ni is compatible with a calculated solidus-liquidus gap of $\Delta\theta = 0.26^\circ\text{C}$ for the equiatomic alloy. Another metallic system likely to exhibit near-ideality is the system Nb-Ta. Using equation (2), the known melting points and estimated heats of fusion ($\sigma_f = 1.95 \text{ cal g-atom}^{-1} \text{ K}$), one finds $\Delta\theta \approx 21^\circ\text{C}$ for the equiatomic alloy. Naturally, this result will be difficult to verify experimentally because of the very high melting points.

Where the solidus-liquidus gaps are wider and are required for the whole range of compositions, Wagner's equation is obviously inadequate. An adequate equation to account for deviations from regularity, differences in

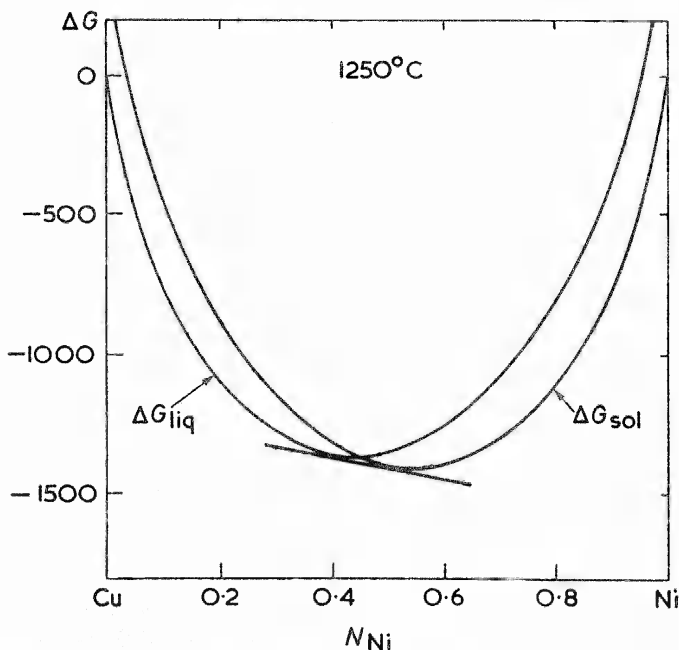


Figure 5. Gibbs energies of mixing of, respectively, liquid and solid copper-nickel alloys from liquid copper and solid nickel.

PHASE EQUILIBRIA IN CONDENSED SYSTEMS

excess functions of solid and liquid and compositions other than equiatomic would be very complex. The mode of evaluation frequently employed in such a case is to assess the thermochemical properties of the solid and liquid solutions across the whole range of compositions, to calculate the integral Gibbs energies at intervals of, say, 5 at.% for a series of temperatures with due regard to the standard states of the components, to plot the Gibbs energies against composition and to draw the tangent to the two curves at temperature T , as exemplified by *Figure 5* for the system copper-nickel¹⁰ at a selected temperature of 1250°C. The tangent touches the two curves at the solidus and liquidus compositions. In the interval, the solid-liquid mixture has a lower Gibbs energy than either of the homogeneous solutions.

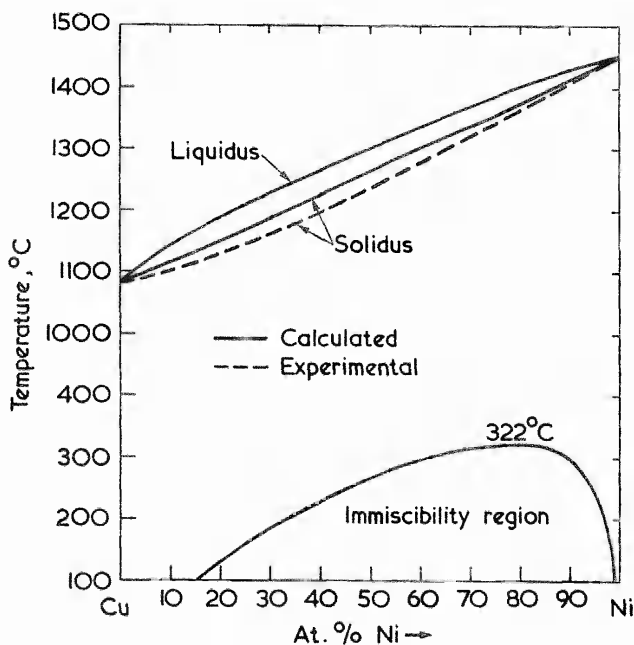


Figure 6. Equilibrium diagram of the system copper-nickel.

In *Figure 6*, the calculated solidus and liquidus curves are represented by the full lines whereas the dotted solidus curve represents the results of thermal analyses. Meanwhile the calculated solidus temperatures have been confirmed by differential analyses of thoroughly annealed alloys by Predel and Mohs¹¹. This example illustrates the point made earlier: calculated solidus curves often lie substantially higher than the experimental ones owing mostly to the shortage of time allowed for equilibration during thermal analysis. This shortcoming of conventional methods is likely to be found to apply to many more 'established' solidus curves than is generally appreciated. An earlier example where this was found to be true is the chromium-iron system^{10a}.

In view of the greater reliability of the experimental liquidus in contrast to the solidus temperatures, it is recommended to adjust the thermochemical

data for the solid and liquid solutions within the experimental tolerance so as to represent the liquidus curves obtained by conventional methods exactly rather than to rely entirely on the thermochemical results which are often so scattered as to prohibit an accurate assessment. The chromium-iron system is a case in point. For illustration, the numerous measurements of the partial Gibbs energy of chromium in liquid alloys by different investigators have been converted with an estimated heat of solution into excess entropies.

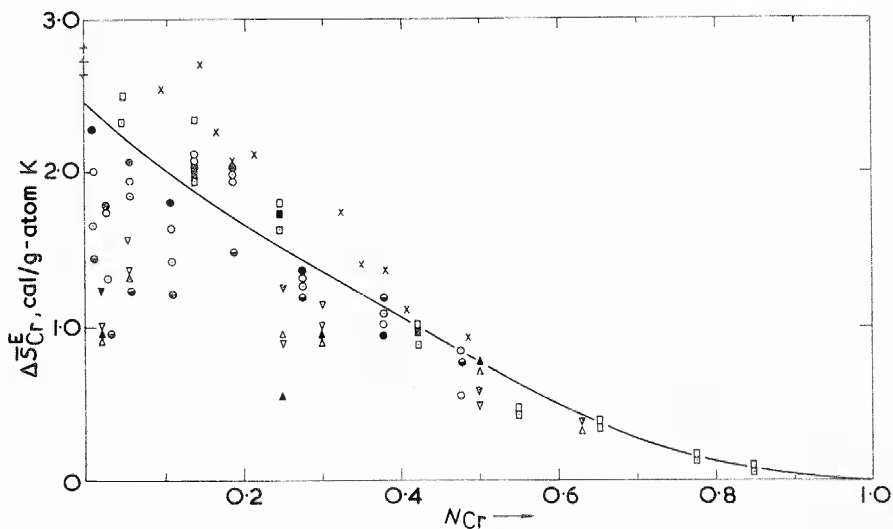


Figure 7. Partial excess entropies of solution of liquid chromium in liquid chromium-iron alloys. (The full line represents the results of a calculation from other pertinent thermochemical data, which is compared with the experimental results of various authors after combination with the accepted heat of mixing.)

Figure 7 shows the scatter of the experimental thermochemical results from five different sources whereas the full line is compatible with the liquidus curve and the thermochemical properties of the solid solutions. Actually, none of the results of the Gibbs energy measurements has been used in the evaluation of $\Delta\bar{S}_{Cr}^E$ by Müller and Kubaschewski^{10a}.

MISCIBILITY GAPS

If two metals form solid solutions with a positive heat of mixing, the occurrence of a miscibility gap at some lower temperature is to be expected, the mutual solubilities approaching zero as 0 K is approached. The reason for this behaviour follows from the Gibbs-Helmholtz equation and the characteristic shapes of the ΔH versus N and $T\Delta S$ versus N curves. Whereas the ΔH versus N curves tend towards a parabolic shape, the $T\Delta S$ versus N curves approach $N = 0$ and $N = 1$ asymptotically. Figure 8 shows the resulting ΔG versus N curve for the chromium-molybdenum system at 800°C taking the shape of an inverted camel-back⁶. The tangent touches the ΔG versus N curve at the compositions of the phase boundary at 800°C. This example also demonstrates the superiority of the thermochemical method of phase boundary determination because a 60% Cr alloy had to be

PHASE EQUILIBRIA IN CONDENSED SYSTEMS

annealed at 800°C for over a year to prove incontrovertibly that it decomposed into a Mo-rich and a Cr-rich solution¹², whereas technical alloys may have to withstand high temperatures for longer periods than that.

At lower temperatures, the progress of alloy deterioration may become so slow that a calculated miscibility gap would be meaningless from the technological point of view. The miscibility gap in the system copper-nickel which

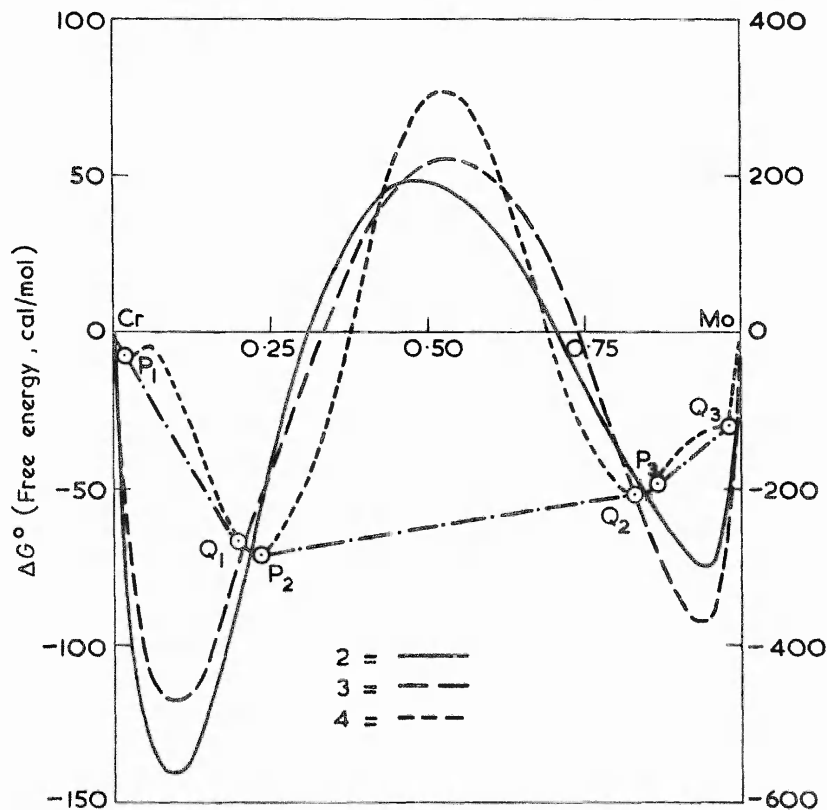


Figure 8. Calculated Gibbs energies of chromium-molybdenum alloys at 1073 K using different analytical approximations (2, 3, 4: upper limits of the summation index in the relationships for the calculation of the Gibbs energy versus atomic fraction).

closes at 322°C (Figure 5) is such a hypothetical example because the period after which decomposition would become noticeable may be estimated to be very far in excess of the life-time of any technical Cu-Ni alloy.

The investigation by thermal analysis of the phase boundary of a miscibility gap even in the liquid state seems to be subject, on occasion, to considerable errors owing to the small differences in Gibbs energy, that is, small 'driving forces', as exemplified by the system Bi-Zn (Figure 9) where admittedly one of the components is a semi-metal. In this case again, the thermochemical properties obtained at higher, i.e. kinetically more favourable, temperatures allow a definite decision to be made on which of the controversial results to accept.

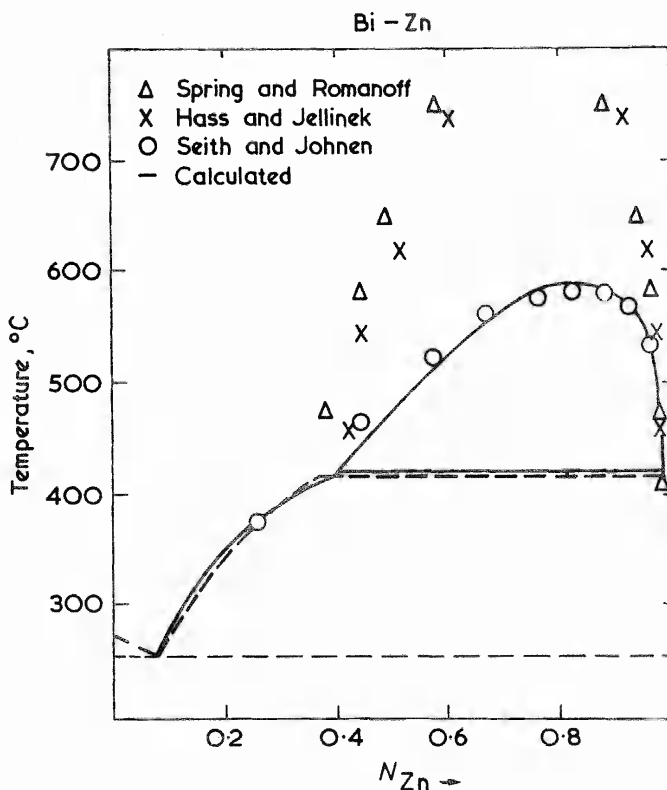


Figure 9. Calculated equilibrium diagram of the system bismuth-zinc and experimental points.

SYSTEMS EXHIBITING INTERMEDIARY PHASES

Systems forming intermetallic compounds of narrow composition ranges can be fairly easily treated by the thermochemical method because it is mostly the liquidus temperatures and the eutectic or peritectic temperatures and compositions that are required. The shape of the liquidus curves depends mainly on the heats and entropies of fusion of the compounds and the component metals. If necessary, entropies of fusion can be fairly well estimated and if the melting points are known, the heats of fusion are also obtained. An early approach to the problem by Hauffe and Wagner² has already been mentioned.

Figure 10 illustrates, for a selected temperature, the graphical evaluation of the phase boundaries in the uranium-iron system. The entropies of fusion of UFe_2 and U_6Fe were estimated by Kubaschewski¹³ and their melting points adopted from the work of Grogan and Clews¹⁴. The resulting equilibrium diagram (Figure 11) is in good agreement with the otherwise independent investigation of Grogan and Clews.

As an example of a system of a more involved nature and requiring more experimental thermochemical effort, the ferrovanadium alloys have been

PHASE EQUILIBRIA IN CONDENSED SYSTEMS

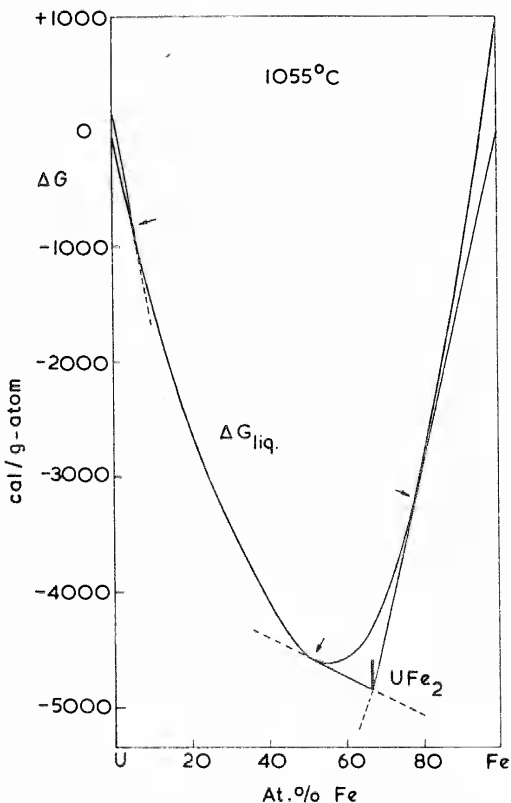


Figure 10. Gibbs energies of formation of liquid uranium-iron alloys and of the phase UFe_2 from the solid metals at 1328 K.

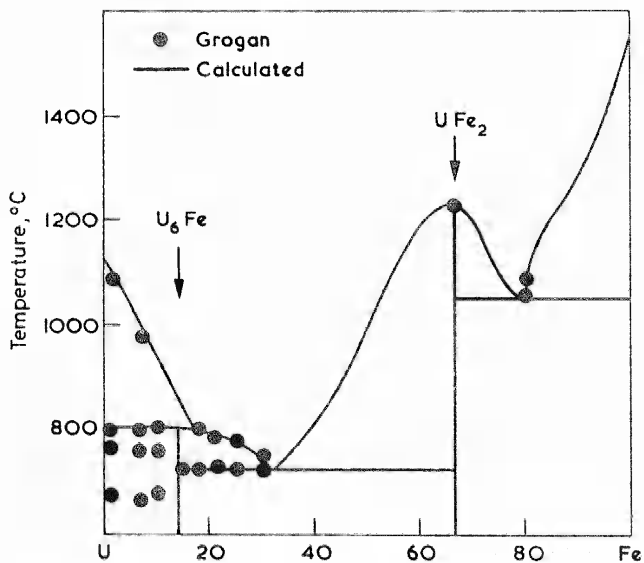


Figure 11. Calculated equilibrium diagram and experimental points for the system uranium-iron.

selected. It has been mentioned earlier that systems of complete mutual solubility below the melting points but a positive heat of mixing are likely to form a miscibility gap at lower temperature. If on the other hand the heat of mixing is negative, one would expect formation of some type of superstructure at lower temperature. This is the case in the system Fe-V which forms a σ

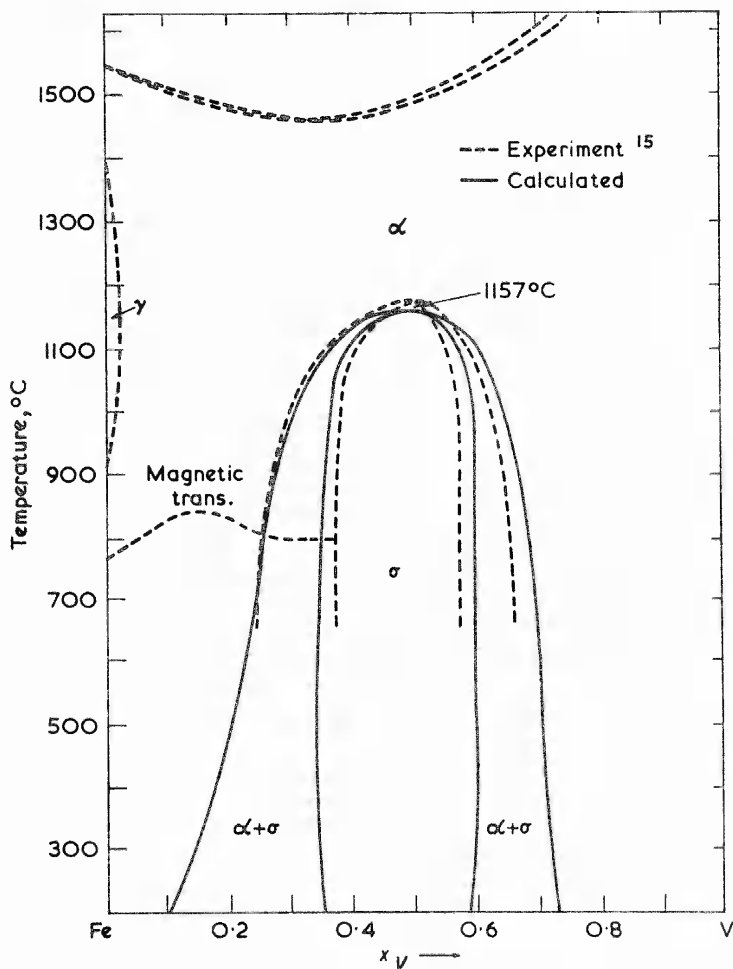


Figure 12. Calculated and experimental phase boundaries for the α and σ phases in the system iron-vanadium.

phase of fairly wide extension below about 1160°C. Spencer and Putland¹⁵ measured the heat of mixing of disordered α alloys and heats and temperatures of the transformation $\sigma \rightarrow \alpha$ and adopted Gibbs energies of formation for the α alloys from torsion-effusion measurements of Myles and Aldred¹⁶. With this information they calculated the $\alpha/\alpha + \sigma/\sigma$ boundaries which are shown as full lines in Figure 12. Agreement with the experimental phase boundaries (dotted lines) is quite good in this case. This is by no means always so: in particular does one often find solid solubilities at the lower temperatures

PHASE EQUILIBRIA IN CONDENSED SYSTEMS

smaller than with conventional methods and some indication of this may be seen in *Figure 12* on the vanadium-rich side. The discrepancies are again due to diffusional delays in equilibration to which the thermochemical method is much less prone.

The system chromium-iron presents a somewhat special case in that it exhibits positive heats of mixing in the disordered state but forms a σ phase

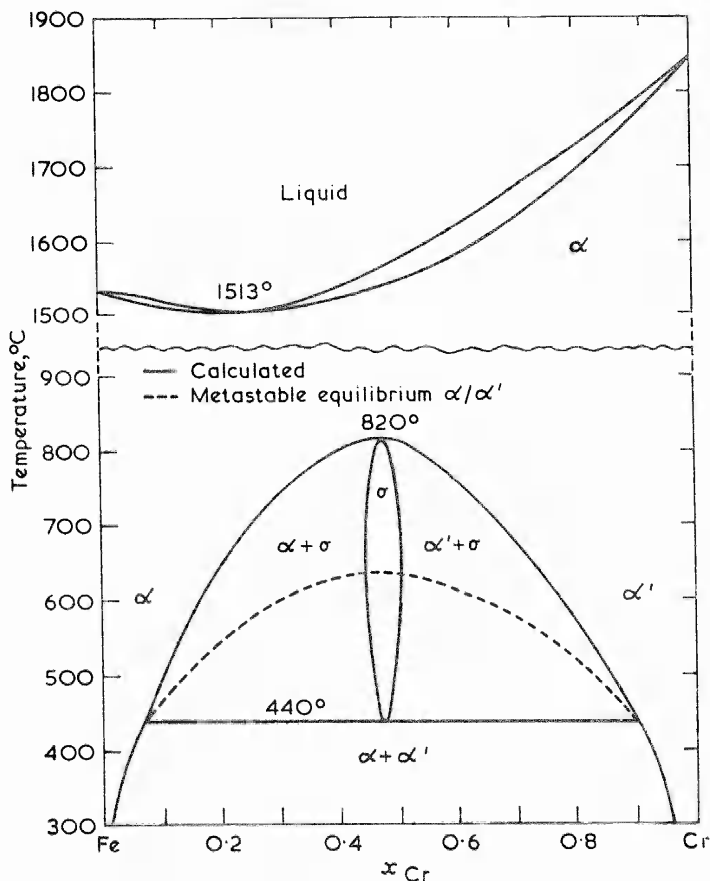


Figure 13. Calculated equilibrium diagram of the system chromium-iron.

which is also endothermic. In such a case one must expect the ordered structure to exist only over a limited temperature range below which a miscibility gap appears. This was indeed found to be the case in the Cr-Fe system^{10a} with practical consequences that will not be elaborated here (*Figure 13*).

KAUFMAN'S APPROACH

Kaufman in Cambridge, Mass., has also concerned himself with the derivation of equilibrium diagrams by thermochemical reasoning for many

years. An earlier approach is particularly interesting. He quite rightly argued that it would take a long time to provide the experimental thermochemical data needed for the full and accurate elaboration of the important metallurgical equilibrium diagrams and that short-cuts accepting a loss of accuracy were desirable. Kaufman first showed (1959) that the difference in Gibbs energy between crystallographic forms of a metal made an important contribution in controlling alloying behaviour, phase transformations and stacking fault

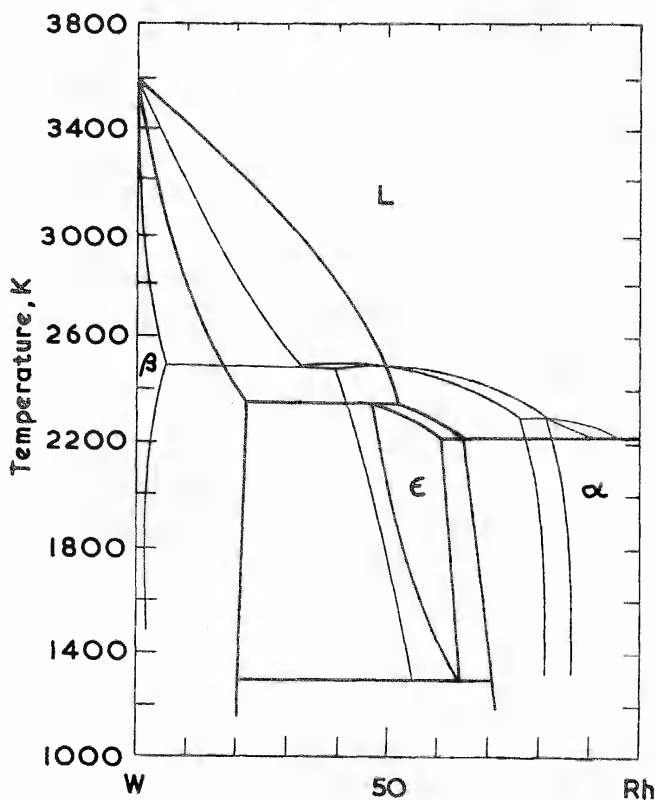


Figure 14. Experimental phase diagram of the system tungsten-rhenium (thin lines) and tentative calculation of the phase boundaries by a simplified method after Kaufman (thick lines).

energy of the metal over a wide range of temperature and pressure. He then set out to obtain relative lattice stability information concerning the body-centred cubic, hexagonal close-packed and face-centred cubic configurations of metals in various ways.

In certain cases the energy differences are known because the metals are stable in different modifications at some temperature and/or pressure and can be determined directly. In other cases, the energy differences can be obtained by extrapolation from binary systems. The missing data were estimated. In a review paper by Kaufman¹⁷, the relative phase stabilities of the transition metals were surveyed and numerous binary equilibrium

diagrams computed, considering only the b.c.c., f.c.c., h.c.p. and liquid phases. This was done by assuming that similar modifications formed ideal solutions thermochemically. As one example of many, the experimental and computed phase diagram of the system tungsten-rhodium is shown in *Figure 14*. Naturally, deviations are substantial since the approach deliberately disregards other contributions to the energy of mixing, such as the strain energy (size factor), vibrational, magnetic and electronic terms, but then (as Dr. Kaufman pointed out to the present authors) 'a start has to be made somewhere'.

Meanwhile, as anticipated, Kaufman has been using more sophisticated methods of approach including experimental thermochemical evidence. His review paper¹⁸ contributed to the Metallurgical Chemistry Symposium at Brunel University is recommended for perusal.

TERNARY AND QUATERNARY SOLUTIONS

The second advantage of the thermochemical method of phase boundary evaluation pointed out earlier is the potential application to the extrapolation of the binary data into multi-component ranges. When the thermochemical properties of ternary systems are available, the mode of evaluation of phase boundaries is in principle the same as that indicated by *Figure 1*, only that the tangents become tangent planes. For quaternary systems, the evaluation can no longer be envisaged geometrically but offers no great problem to a mathematical treatment provided a computer is available.

A number of equations have been proposed for deriving ternary properties from binary data for single-phase systems. Since the bond mechanism of metallic solutions is complicated, these equations are essentially empirical, based on the regular solution model or the quasi-chemical approximation. They have been surveyed by Ansara¹⁹ whose group under Professor Bonnier at the University of Grenoble has also made substantial contributions in the field under review. Spencer and Hayes²⁰ have examined four of these equations and compared the heats and excess Gibbs energies, respectively, calculated by these methods with experimental ternary data.

Kohler²¹ suggested that excess Gibbs energies in a ternary solution A-B-C, in which the atomic fractions are N_A , N_B and N_C , may be expressed in binary terms by the equation:

$$\Delta G^E = (1 - N_A)^2 [\Delta G_{B-C}^E]_{N_B/N_C} + (1 - N_B)^2 [\Delta G_{A-C}^E]_{N_A/N_C} + (1 - N_C)^2 [\Delta G_{A-B}^E]_{N_A/N_B} \quad (3)$$

the binary compositions, at which the binary ΔG^E terms are taken, being shown in *Figure 15*.

Toop²² proposed the following equation:

$$\Delta G^E = \left[\frac{N_A}{1 - N_B} \Delta G_{A-B}^E + \frac{N_C}{1 - N_B} \Delta G_{B-C}^E \right]_{N_B} + (1 - N_B)^2 [\Delta G_{A-C}^E]_{N_A/N_C} \quad (4)$$

The binary terms are shown in *Figure 16*. Both the Kohler and Toop equations may be derived from a rigorous equation given by Darken²³ provided the ternary system and its constituent binaries exhibit regular solution behaviour.

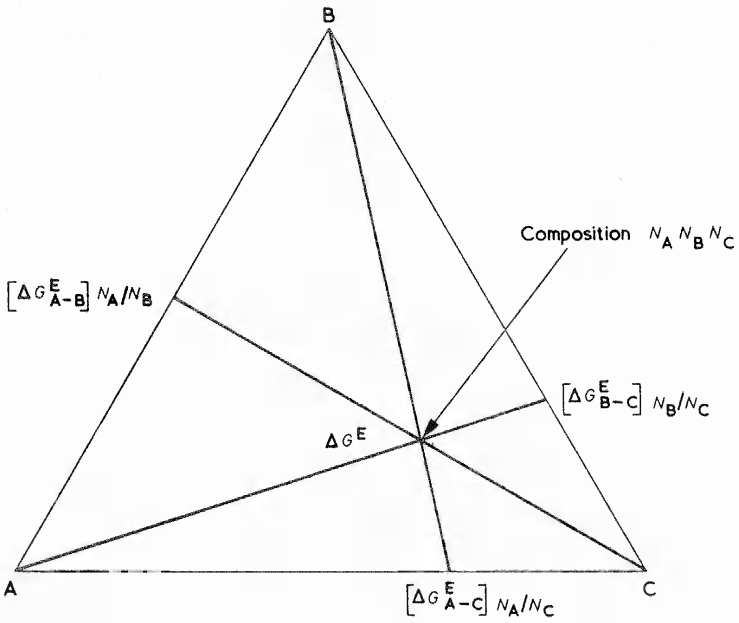


Figure 15. Illustration of the binary terms used in the application of the Kohler equation.

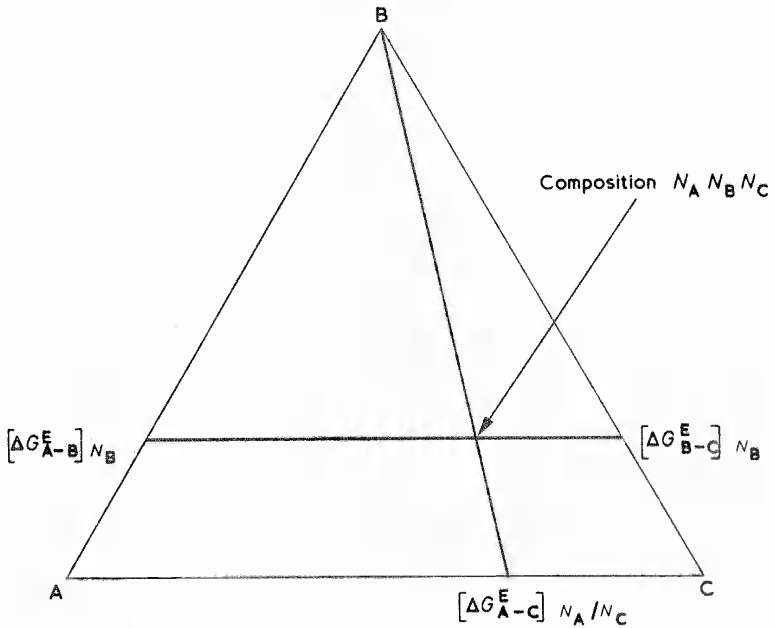


Figure 16. Illustration of the binary terms used in the application of the Toop and Bonnier equations.

Bonnier and Caboz's equation²⁴ takes the form

$$\Delta G^E = \left[\frac{N_A}{1 - N_B} \Delta G_{A-B}^E + \frac{N_C}{1 - N_B} \Delta G_{B-C}^E \right] N_B + (1 - N_B) [\Delta G_{A-C}^E]_{N_A/N_C} \quad (5)$$

where the binary Gibbs energy terms are the same as those in the Toop equation (Figure 16).

The Margules equation²⁵ differs from the previous three in that it contains a ternary term whereas the others contain only binary terms. There are seven constants: two for each constituent binary plus one for the ternary:

$$\Delta G^E = N_A N_B [N_A K_{BA} + N_B K_{AB}] + N_A N_C [N_A K_{CA} + N_C K_{AC}] \\ + N_B N_C [N_B K_{CB} + N_C K_{BC}] + N_A N_B N_C K_{ABC} \quad (6)$$

For low-affinity solutions, these methods mostly give similar values and agree quite well with the experimental ones, often within the experimental accuracy. For high-affinity systems deviations are larger. Figure 17 shows

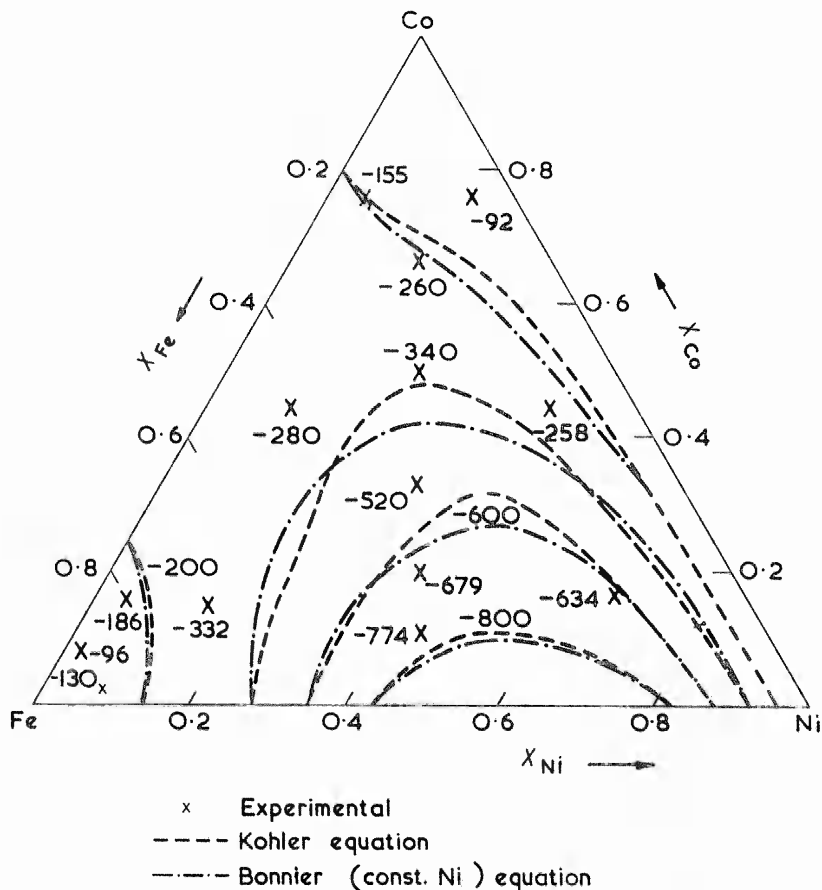


Figure 17. Iso-enthalpies of formation of solid iron-cobalt-nickel alloys at 1473 K.

as an example the experimental heats of formation (in place of the excess Gibbs energies) of iron-cobalt-nickel alloys in comparison with the values calculated by means of the Kohler and Bonnier equations²⁶. However, it is difficult at the present stage to decide about the relative merits of the various modes of extrapolation and further experimental values must be obtained for a systematic survey. Ansara¹⁹ who has made a thorough study of the subject seems to give precedence to the Kohler equation. The calculated and measured excess Gibbs energies of the system Pb-Cd-Sn are shown in Figure 18.

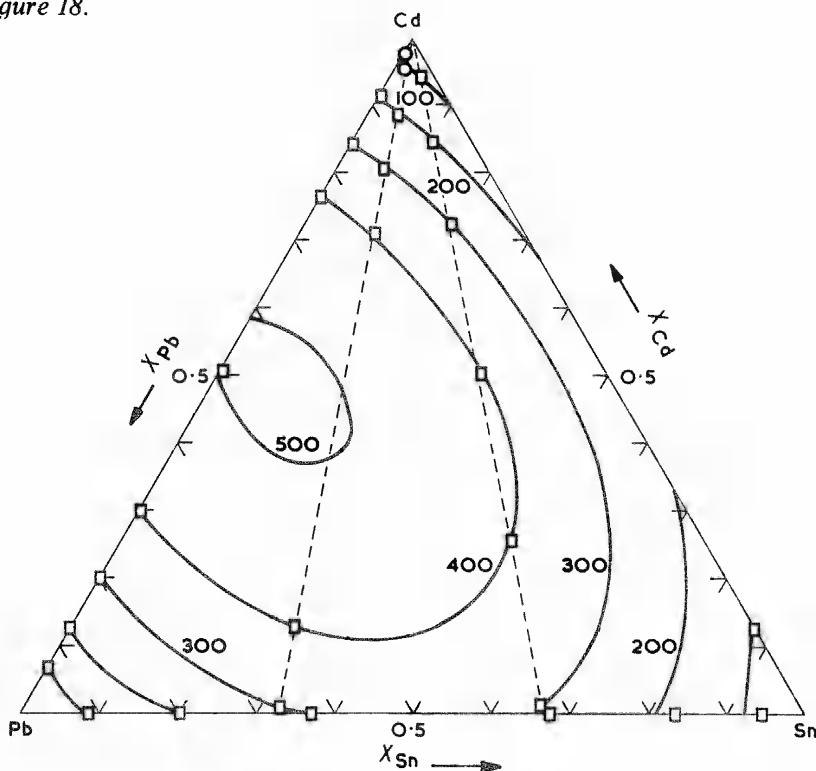


Figure 18. Calculated and experimental excess Gibbs energies for liquid lead-tin-cadmium alloys.

As mentioned earlier, some thermochemical information is required for the ternary alloys in addition to complete sets of values for the binary border systems, when the Margules equation is applied. An example of its use is the calculation of the thermochemical properties of, and the extent of the miscibility gap in, the system gold-palladium-platinum by Kubaschewski and Counsell²⁷. From measured values, the excess entropy and heat of mixing were expressed by the following equations:

$$\begin{aligned} \Delta H^E/\text{cal}(\text{g-atom})^{-1} = & N_{\text{Au}}N_{\text{Pd}}(-11141N_{\text{Au}} - 3065N_{\text{Pd}}) \\ & + N_{\text{Pd}}N_{\text{Pt}}(-5234N_{\text{Pd}} - 3021N_{\text{Pt}}) + N_{\text{Pt}}N_{\text{Au}}(5691N_{\text{Pt}} - 634N_{\text{Au}}) \\ & + 3036N_{\text{Au}}N_{\text{Pd}}N_{\text{Pt}} \quad (7) \end{aligned}$$

PHASE EQUILIBRIA IN CONDENSED SYSTEMS

$$\begin{aligned} \Delta S^E/\text{cal}(\text{K g-atom})^{-1} = & -3N_{\text{Au}}N_{\text{Pd}} - 2.9 N_{\text{Pd}}^2N_{\text{Pt}} - 1.7 N_{\text{Pd}}N_{\text{Pt}}^2 \\ & - 0.9 N_{\text{Pt}}^2N_{\text{Au}} - 3.5 N_{\text{Pt}}N_{\text{Au}}^2 + 9 N_{\text{Au}}N_{\text{Pd}}N_{\text{Pt}} \end{aligned} \quad (8)$$

The resulting boundaries of the ternary miscibility gap are compared at two temperatures with the experimental boundaries after Raub and Wörwag²⁸ in Figure 19.

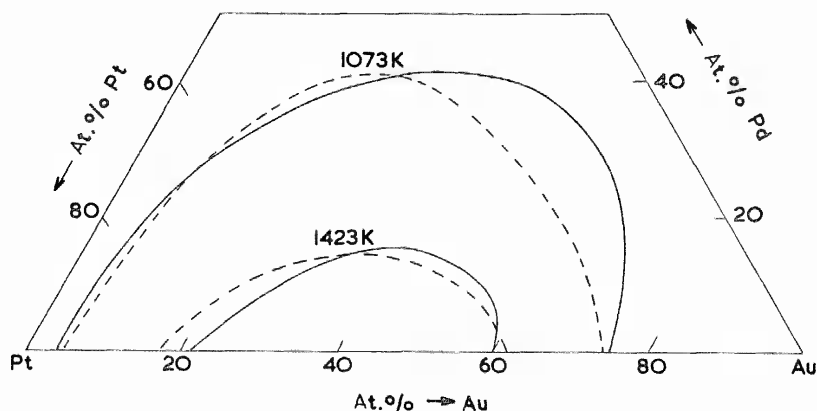


Figure 19. Calculated (dashed) and experimental (full) phase boundaries of the miscibility gap in the system gold-palladium-platinum at two temperatures.

From the practical point of view perhaps the most important ternary system in metallurgy is that of the iron-chromium-nickel alloys. Figure 20 shows the calculated and experimental austenite-ferrite equilibria²⁹ at 1277°C, that is, above the stability range of the σ phase. Phase boundaries in the latter range may be computed if estimates of the thermochemical properties in the Fe-Ni and Ni-Cr systems can be provided, those for the Fe-Cr system being well known. Kubaschewski has indeed made an earlier attempt to estimate the phase boundaries at 1277°C by assuming that the σ phase in the Ni-Cr system is just stable below 700°C at 75 at.% Ni. Kaufman, in some other context, assumed σ -Ni-Cr to be just metastable, but the effect on phase boundary calculations in the ternary system should not be great and further experimental evidence is to be awaited.

However, Spencer and Counsell³⁰ have calculated the α/σ relations in a similar system, Fe-Cr-V, at temperatures of 427, 700 and 900°C from assessed thermochemical data for the binaries. Only the values for σ -Cr-V had to be estimated since this phase has never been observed and must therefore be metastable. First, the heats and entropies of the α - σ transformation in pure chromium and vanadium were estimated from data in the Fe-V and Fe-Cr systems. (This is of course plain formalism because the pure metals do not and cannot exist in the σ form.) The phase boundary calculations were then carried out using the method described by Counsell, Lees and Spencer²⁹. As an example the phase relationships at 700°C are reproduced in Figure 21. There are certain discrepancies compared with the experimental results of Martens and Duwez³¹, in particular with regard to

the relative positions of the tie-lines. Errors in the calculated equilibria could arise from the method used to fit the experimental data and to sum the three binary expressions for calculations of ternary Gibbs energies. However, Martens and Duwez experienced difficulties in locating the phase boundaries and tie-lines, which is not surprising considering the relatively low temperatures; moreover, in the binary Fe-Cr system their $\alpha + \sigma$ region is not in good

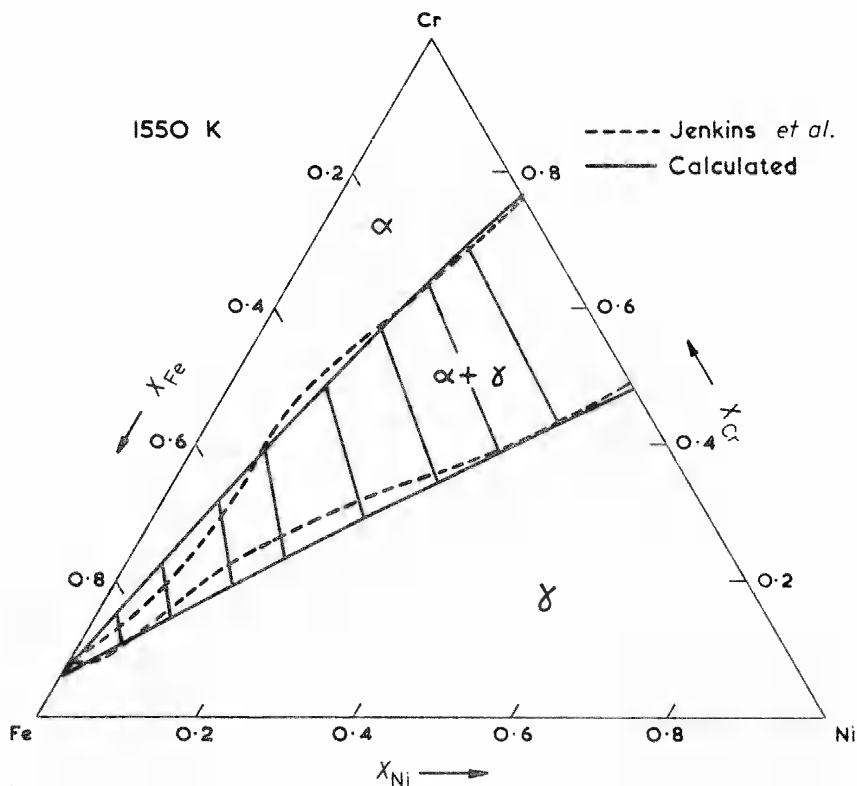


Figure 20. Calculated and experimental phase boundaries of the austenite-ferrite equilibrium in the system iron-chromium-nickel at 1550 K.

agreement with the assessed boundaries. Considering all this, the agreement between the two sets of results is fair and provides a further illustration of the potential of thermochemical calculations of phase boundaries in ternary systems using only binary alloy data.

Next the method should be extended to quaternary systems. An industrially important problem of this kind would be the effect of fourth elements on the austenite-ferrite equilibrium in iron-nickel-chromium alloys mentioned above, but only one attempt to calculate phase boundaries in a fourth order system has been made, namely those of the miscibility gap in liquid Pb-Cd-Zn-Sn alloys by Counsell, Lees and Spencer²⁹. The method has been described by the authors as 'the minimization of the Gibbs energy', the computational method chosen being that described by Nelder and Mead³².

PHASE EQUILIBRIA IN CONDENSED SYSTEMS

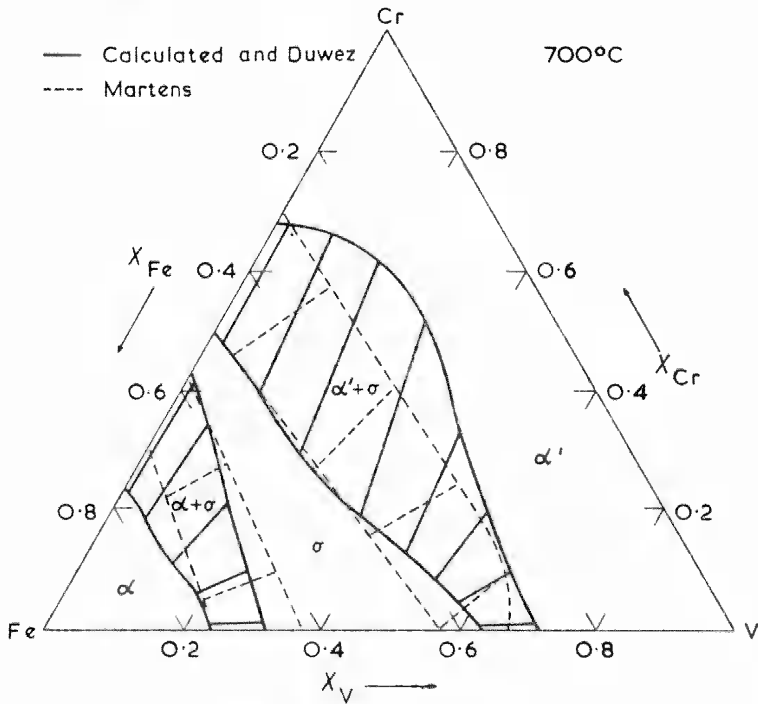


Figure 21. Calculated and experimental phase boundaries of the α - σ equilibrium in the system iron-chromium-vanadium at 973 K.

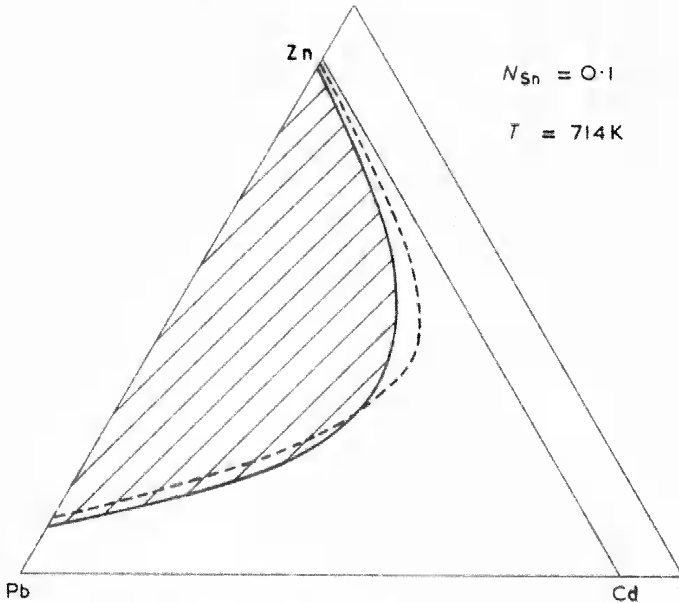


Figure 22. Section of the quaternary system lead-cadmium-zinc-tin at 10 at.% Sn. (The full curve and the tie-lines show the calculated, and the dashed curve the experimental two-phase region at 714 K.)

In *Figure 22*, the computed and experimental phase boundary of the miscibility gap at 441°C and 10 at. % Sn are shown for the sake of illustration.

This also raises the question of data representation in higher order systems, which is actually much older than the present approach. No satisfactory answer has as yet been found, but the problem is under consideration, as may be seen from the discussion about it at the Metallurgical Chemistry Symposium 1971³³.

From the same source, information may be gathered on the activities of other laboratories in the field under review, in particular at the Carnegie-Mellon University, Pittsburgh (C. H. P. Lupis) and the Royal Institute of Technology, Stockholm (M. Hillert, G. Kirchner and others), which cannot all be elaborated here. Actually, there are few fields in metallurgy where scientific interest has been growing recently at so fast a rate as in the application of chemical thermodynamics to the calculation of equilibrium diagrams.

A severe restriction on the accuracy of the calculated phase boundaries is imposed by their great sensitivity to small errors in the thermochemical data, the required accuracy for which is as yet rarely achieved in experimental thermochemistry. Use should therefore be made of existing, *reliable* phase boundary information or additional phase diagram work performed by means of conventional methods, and the basic data thus gradually adjusted. Alloys melting below 1000°C, it is true, are quite well covered, but these are of less practical interest. The present author is directing his attention to metallurgical systems of greater industrial significance (say, to alloyed steels and Nimonic alloys which incorporate quite a proportion of the Periodic Table) and experimental thermochemists are needed to join this effort because the task is huge.

COMPOUND-FORMING SYSTEMS

The previous sections have dealt with the equilibrium diagrams of systems involving solid and liquid solutions. However, in process metallurgy numerous problems are encountered where the formation of solutions is only of minor significance whereas equilibrium with a gaseous phase must be taken into account. The question then arises which solid and liquid compounds are stable under given conditions of temperature and composition of the gas. Quite a number of such equilibria have been studied experimentally and discussed on the basis of available thermochemical data at the Institut für Theoretische Hüttenkunde at Aachen, where calculation and plotting of the diagrams is performed by a computer³⁴.

For the graphical representation of the stability ranges either the temperature and one of the partial pressures of the gaseous components or two of the partial pressures at constant temperature are chosen. The systems studied include Pb-S-O³⁵, Cu-S-O³⁶, Fe-S-O³⁷, U-O-F³⁸, U-O-Cl³⁹ and Mg-O-S⁴⁰.

The systems alkaline earth metal-oxygen-sulphur are of considerable practical interest because of the potential use of the oxides for the removal of sulphur dioxide from industrial gases by sulphate formation. *Figure 23* shows the equilibrium diagram of the system magnesium-oxygen-sulphur

PHASE EQUILIBRIA IN CONDENSED SYSTEMS

in terms of temperature and oxygen pressure at a sulphur dioxide pressure of 10^{-4} atm which is the tolerable maximum with regard to air pollution. For the construction of the diagram, the thermochemical data of the condensed phases MgS , MgSO_3 , MgSO_4 and MgO and the gaseous species SO_2 and O_2 after Barin and Knacke⁴⁵ have been perused. The phase boundaries intersect at a quadruple point $\text{MgO-MgS-MgSO}_4\text{-SO}_2$ which shifts with increasing SO_2 pressure to higher temperatures.

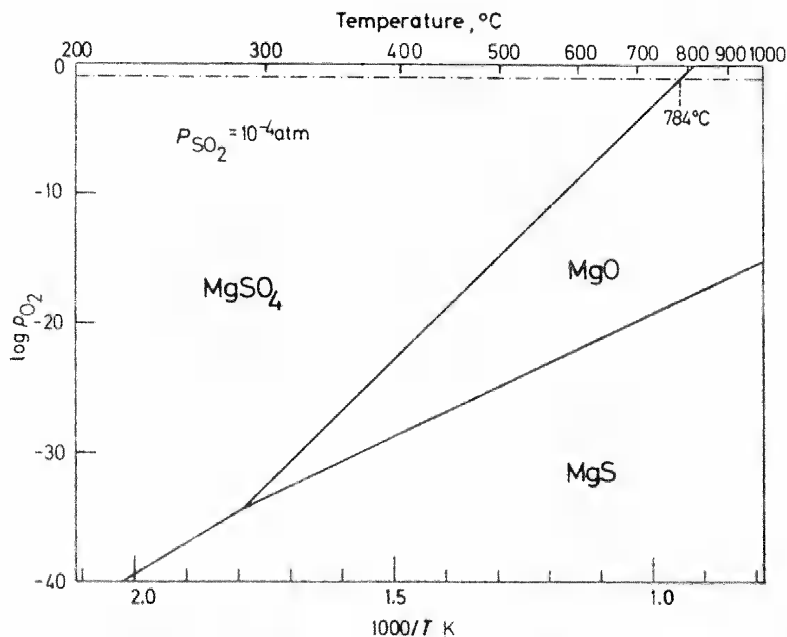


Figure 23. Stability areas in terms of oxygen pressure and temperature in the system magnesium-oxygen-sulphur at constant sulphur dioxide pressure (10^{-4} atm).

Sulphur-containing exhaust gases generally have a content of, say, 0.1 atm of free oxygen. Thus, the matter of interest is the intersection of the $(-2 \log p_{\text{SO}_2})$ line with the indicated $(\log p_{\text{O}_2} = -1)$ horizontal representing the maximum temperature at which the SO_2 content of the exhaust gas is reduced to the required limit. More revealing for practical purposes would be a plot of $\log p_{\text{SO}_2}$ versus $1/T$ at $p_{\text{O}_2} = 1$ atm including similar plots for other MO/MSO_4 equilibria. This shows the increasing stability of the alkaline earth sulphates with atomic number⁴⁰, so that the temperature of reaction may be increased to kinetically more favourable temperatures. However, this aspect is not quite relevant in the context of the present paper.

Another example has been selected from the field of process metallurgy, namely the system iron-oxygen-chlorine, important for the chlorination of ores containing ferric oxides which are to be either concentrated or selectively vaporized. In this case a graphical representation is chosen in the form of isothermal sections at 427 and 927°C (Figures 24 and 25) based on the

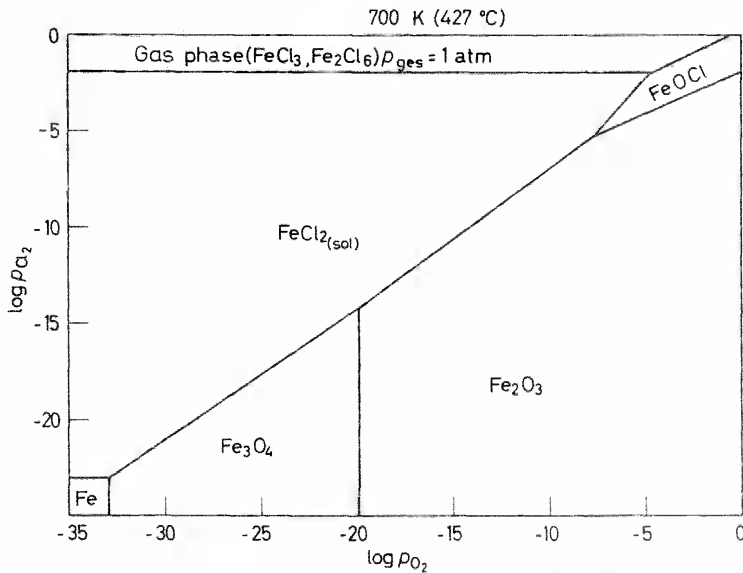


Figure 24. Isothermal section of the system iron–oxygen–chlorine at 700 K. ($P_{\text{ges}} = p_{\text{FeCl}_3} + p_{\text{Fe}_2\text{Cl}_6}$ is the total pressure of volatile chlorides.)

thermochemical properties of the gaseous compounds FeCl_2 , FeCl_3 and FeCl_6 , and those of the condensed phases: iron, wüstite, magnetite, hematite, FeOCl and FeCl_2 .

It may be seen from Figure 24 that chlorination of the iron oxides at lower temperatures produces surface coatings consisting of FeCl_2 or at higher oxygen pressures, FeOCl . Such surface coatings are of course undesirable

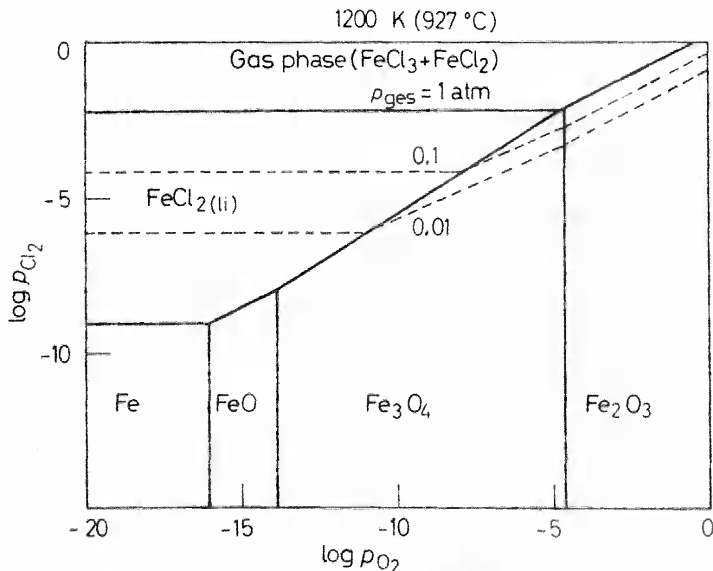


Figure 25. Isothermal section of the system iron–oxygen–chlorine at 1200 K for $p_{\text{FeCl}_3} + p_{\text{Fe}_2\text{Cl}_6} = 1, 0.1$ and 0.01 atm.

because they represent kinetic obstacles. At the higher temperature (*Figure 25*), FeOCl is no longer stable and chlorination of hematite proceeds directly, forming gaseous iron chlorides. A reduction of the oxygen pressure would be technologically sensible.

Figure 25 also shows that gaseous iron chlorides may easily be transformed with oxygen to Fe₂O₃ producing chlorine. The conversion of the chlorides at 700 K takes place via the formation of FeOCl, as has been confirmed experimentally⁴¹.

It has been mentioned earlier that thermochemical considerations alone rarely describe technical processes fully. Kinetic conditions may play an important role. During the chlorination of wüstite and magnetite under the appropriate conditions, for instance, it has been observed by Mann⁴² that it is not liquid dichloride that is formed but gaseous trichloride whilst the lower oxides are being oxidized to Fe₂O₃. This kinetic effect was first observed by Gat⁴³ in the chlorination of UO₂ and interpreted as being due to a preferential chemisorption of chlorine from a Cl₂-CO mixture leading to an assimilation of the liberated oxygen ions by the oxide lattice⁴⁴.

Whereas the thermochemical conditions can normally be evaluated from existing data, the kinetic interactions have to be investigated experimentally from case to case. Nevertheless, their thermochemical background, i.e. the equilibrium diagrams, should be known first and it is to be expected that the thermochemical approach will increasingly find its practical application.

ACKNOWLEDGEMENTS

The authors are grateful to Dr P. J. Spencer of the National Physical Laboratory, who assisted with the preparation of this paper, and to Professor O. Knacke of the Technische Hochschule, Aachen, who discussed and criticized its contents.

REFERENCES

- ¹ M. Rey, *Faraday Soc. Disc.* **4**, 257 (1948).
- ² K. Hauffe and C. Wagner, *Z. Elektrochemie*, **46**, 160 (1940).
- ³ C. Wagner, *Acta Met.* **2**, 242 (1954).
- ⁴ M. Hansen, *Constitution of Binary Alloys*, McGraw-Hill, New York (1958); 1st Splmt. (1965), R. P. Elliott: 2nd Splmt. (1969), F. A. Shunk.
- ⁵ R. Hultgren *et al.*, *Selected Values of the Thermodynamic Properties of Metals and Alloys*, Wiley, New York (1963).
- ⁶ B. Gale and J. M. Davis, *Metal Sci. J.* **5**, 25 (1971).
- ⁷ O. Kubaschewski and T. G. Chart, *J. Inst. Metals* **93**, 329 (1965).
- ⁸ F. H. Hayes and O. Kubaschewski, *J. Inst. Metals*, **97**, 381 (1969).
- ⁹ F. H. Hayes, F. Müller and O. Kubaschewski, *J. Inst. Metals*, **98**, 20 (1970).
- ¹⁰ L. Elford, F. Müller and O. Kubaschewski, *Ber. Bunsenges. Phys. Chem.* **73**, 601 (1969).
- ^{10^a} F. Müller and O. Kubaschewski, *High Temp.-High Press.* **1**, 543 (1969).
- ¹¹ B. Predel and R. Mohs, *Arch. Eisenhüttenwes.* **42**, 575 (1971).
- ¹² O. Kubaschewski, *Refractory Metals*, AGARD Conf., Oslo, Pergamon, Oxford, p. 191 (1964).
- ¹³ O. Kubaschewski, *Thermodynamics of Nuclear Materials*, Proc. I.A.E.A. Sympos., Vienna, p. 219 (1962).
- ¹⁴ J. D. Grogan and C. J. G. Clews, *J. Inst. Metals*, **77**, 571 (1950).
- ¹⁵ P. J. Spencer and F. H. Putland, *J. Iron and Steel Inst.* **211**, 293 (1973).
- ¹⁶ K. M. Myles and A. T. Aldred, *J. Phys. Chem.* **68**, 64 (1964).
- ¹⁷ L. Kaufman, *Phase Stability in Metals & Alloys*, Proc. Battelle Colloquium, Geneva & Villars, p. 125 (1967).

- ¹⁸ L. Kaufman, *Metallurgical Chemistry*, Proc. Sympos., Brunel Univ. & NPL, HMSO, p. 373 (1972).
- ¹⁹ I. Ansara, *Metallurgical Chemistry*, Proc. Sympos., Brunel Univ. & NPL, HMSO, p. 403 (1972).
- ²⁰ P. J. Spencer, F. H. Hayes and O. Kubaschewski. *Rev. Chim. Minér.* **9**, 13 (1972).
- ²¹ F. Kohler, *Monatsh. Chemie*, **91**, 738 (1960).
- ²² G. W. Toop, *Trans. Met. Soc. AIME*, **233**, 850 (1965).
- ²³ L. S. Darken, *J. Amer. Chem. Soc.* **72**, 2909 (1950).
- ²⁴ E. Bonnier and R. Caboz, *Compt. rend.* **250**, 527 (1960).
- ²⁵ K. Wohl, *Trans. A.I.C.E.* **42**, 215 (1946).
- ²⁶ F. H. Hayes, P. J. Spencer and L. Elford, *Chemical Metallurgy of Iron & Steel*, Iron & Steel Institute: London (1973).
- ²⁷ O. Kubaschewski and J. F. Counsell. *Monatsh. Chemie*, **102**, 1724 (1971).
- ²⁸ E. Raub and G. Wörwag, *Z. Metallkunde*, **46**, 513 (1955).
- ²⁹ J. F. Counsell, E. B. Lees and P. J. Spencer, *Metal Sci. J.* **5**, 210 (1971).
- ³⁰ P. J. Spencer and J. F. Counsell, *Z. Metallkunde*, **64**, 662 (1973).
- ³¹ H. Martens and P. Duwez, *Trans. Amer. Soc. Met.* **44**, 484 (1952).
- ³² J. A. Nelder and R. Mead, *Computer J.* **7**, 308 (1965).
- ³³ O. Kubaschewski (Ed.), *Metallurgical Chemistry*, Proc. Sympos., Brunel Univ. & NPL, HMSO: London, pp. 483 *et seq.* (1972).
- ³⁴ U. Gat and R. Hörbe, *Berichte der Kernforschungsanlage Jülich Nr. 596*, Zentralbibliothek KFA Jülich (1969).
- ³⁵ O. Knacke and W. Neumann, *Erzmetall*, **9**, 261 (1956).
- ³⁶ O. Knacke, W. Hirschwald and P. Reinitzer, *Erzmetall*, **10**, 123 (1957).
- ³⁷ O. Knacke, J. Gaube, H. Lydtin and H. Pohl, *Arch. Eisenhüttenwes.* **28**, 109 (1963).
- ³⁸ O. Knacke, G. Lossmann and F. Müller, *Z. anorg. u. allg. Chem.* **370**, 91 (1969).
- ³⁹ O. Knacke, F. Müller and E. van Rensen, *Z. Physik. Chem. Neue Folge*, **80**, 91 (1972).
- ⁴⁰ H. A. Friedrichs, O. Knacke and W. Schultze, *Arch. Eisenhüttenwes.* **44**, 125 (1973).
- ⁴¹ A. W. Henderson, T. T. Campbell and F. E. Block, *Met. Trans.* **3**, 2579 (1972).
- ⁴² E. Mann, *Dissertation*, Technische Hochschule Aachen (1972).
- ⁴³ U. Gat, *Dissertation*, Technische Hochschule Aachen (1968).
- ⁴⁴ O. Knacke, *Metallurgical Chemistry*, Proc. Sympos., Brunel Univ. and NPL, HMSO, p. 549 (1971).
- ⁴⁵ I. Barin and O. Knacke, *Thermochemical Properties of Inorganic Compounds*, Springer: Berlin (1973).