

MEASUREMENT AND APPLICATIONS OF HIGH-TEMPERATURE METALLURGICAL THERMODYNAMIC DATA

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Abstract—The high-temperature measurement of thermodynamic data for substances of metallurgical interest is reviewed and some specific applications of the data are described. Emphasis is placed on experimental techniques which have been designed to overcome particular problems associated either with the very high temperatures of the studies concerned or with the refractory nature of the materials under investigation. Examples of the practical use of thermodynamic data in phase diagram calculations, studies of precipitation reactions in steel, and vapour deposition processes, illustrate the important role that thermodynamic calculations can play in assisting in the optimum design of metallurgical processes. Some substances for which thermodynamic values are currently required are defined and suggestions are made as to areas where thermodynamic measurements and calculations will be required in the future.

1. INTRODUCTION

The metallurgical industry is faced by a number of major problems in the coming years, both in regard to the cost and availability of its fuels and in regard to the decreasing quantities and quality of the raw materials and ores that it uses. It would thus seem more important now than at any other time that attention should be given to the application of thermodynamic data and calculations to consideration of such problems as increasing the efficiency of existing processes, determining the feasibility and optimum yield of potential new processes, establishing how the most economic use can be made of fuels and other raw materials and ensuring that a product of satisfactory purity and long-term stability is achieved.

To support the evident interest of the metallurgical industry in solving such problems, and to avoid unnecessary, time-consuming and costly experimentation in process development, it is essential that good thermodynamic data are readily available and that rapid and reliable calculation procedures are developed for the practical application of the data. Moreover, the present energy and resources problems make it imperative that in all metallurgical research, whether it be carried out in university, government or industrial laboratories, great care should be taken to avoid unnecessary repetition of previously-performed experiments, and very careful consideration should be given to the practical utility of the planned programme of work.

In the field of metallurgy, many processes (e.g. extraction, refining, heat-treatment, etc.) are carried out at quite elevated temperatures, where diffusion rates are sufficiently rapid to allow thermodynamic equilibrium to be approached. The provision of thermodynamic data relevant to metallurgical processes thus frequently involves high-temperature measurements. In the present paper, fairly brief descriptions will be given of developments in experimental techniques for measurements on substances important in metallurgy, with emphasis on ways in which the experimental problems associated either with the very high temperatures of the studies or the refractory nature of the materials under investigation, have been overcome. A few examples will also be given of important areas of application of the measured data. It is noted that sub-

stances of metallurgical interest include many inorganic compounds as well as metals and alloys.

2. MEASUREMENT

Recent comprehensive reviews of experimental methods used in metallurgical thermodynamic research have been written by Kubaschewski *et al.*¹ and by Komarek.² In the present paper, a few of these methods have been selected for discussion and these are classified according to the particular development which they incorporate, either as an experimental improvement or in terms of extending the scope of the method.

2.1. Avoidance of specimen-container reactions at high temperatures by use of refined experimental techniques

2.1.1. *Partial Gibbs energy determinations using levitated specimens.* The problem of the occurrence of interfering reactions between specimens and their containing vessels becomes serious at high temperatures, and with reactive substances can prohibit the determination of reliable thermodynamic values. An experimental technique which enables this problem to be avoided employs electromagnetic levitation of the specimen. The technique has the further advantage of enabling experimental temperatures in excess of 2200°K to be attained readily. The method has been used successfully, for example by Mills *et al.*^{3a,b} in studies of liquid Fe-Ni and liquid Ti-V alloys, for which the high melting-temperatures and reactive nature of the metals make levitation-melting a particularly attractive technique.

Activities of both components in the melt are determined by analysing the vapour composition as a function of the liquid alloy composition according to the method described by Speiser *et al.*⁴ Since vapour analysis is carried out, studies can be made of alloys formed by metals of similar volatility.

The basic simplicity of the experimental set-up is illustrated in Fig. 1. In the experiments carried out by Mills *et al.*,^{3a} the specimen, of approximately 1 g mass, was lowered directly into the electromagnetic field and reached thermal equilibrium in a few seconds. Levitation was maintained for about 5 min during which time specimen temperatures were measured using a two-colour optical pyrometer, and experimental temperatures were controlled to $\pm 10^\circ\text{K}$. Mechanical stability of the levitated specimen was improved during the measurements by introducing purified helium at atmospheric pressure into the quartz vaporisation cell. This also had the effect of

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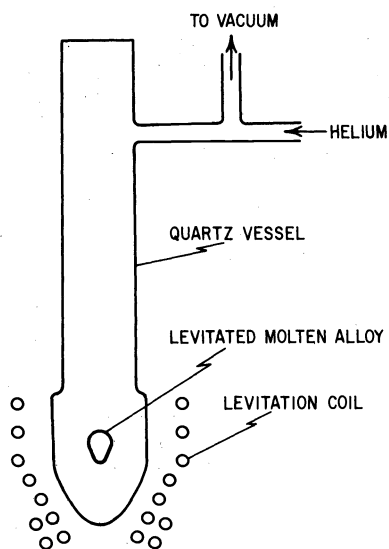


Fig. 1. Levitation apparatus for activity determinations at high temperatures. (From *J. Chem. Thermo.* 4, 581 (1972).)

reducing the evaporation rate. The condensed vapour was dissolved in a nitric + hydrochloric acid mixture and made up to a known volume after the removal of nitrous oxide. Nickel was determined by precipitation as nickel dimethylglyoxime, and iron was determined by a titration method.

2.1.2. *Heat capacity measurements using pulse calorimetry.* The experimental method of high-speed pulse calorimetry has been developed specifically to overcome problems which arise at high temperatures due not only to specimen-container reaction, but also to increased heat transfer, evaporation, loss of mechanical strength, etc. Whereas most experimental methods for the determination of heat capacities require relatively long periods of time (minutes or even hours) for the measurements to be performed, pulse calorimetry can be carried out in a fraction of a second and is thus ideally suited to high-temperature studies. The method is applied particularly to the determination of heat capacities of metals at high temperatures, and work performed using the technique has been reviewed by Cezairliyan.⁵

The apparatus used by Cezairliyan⁶ is shown in Fig. 2. Most high-speed methods used for heat capacity meas-

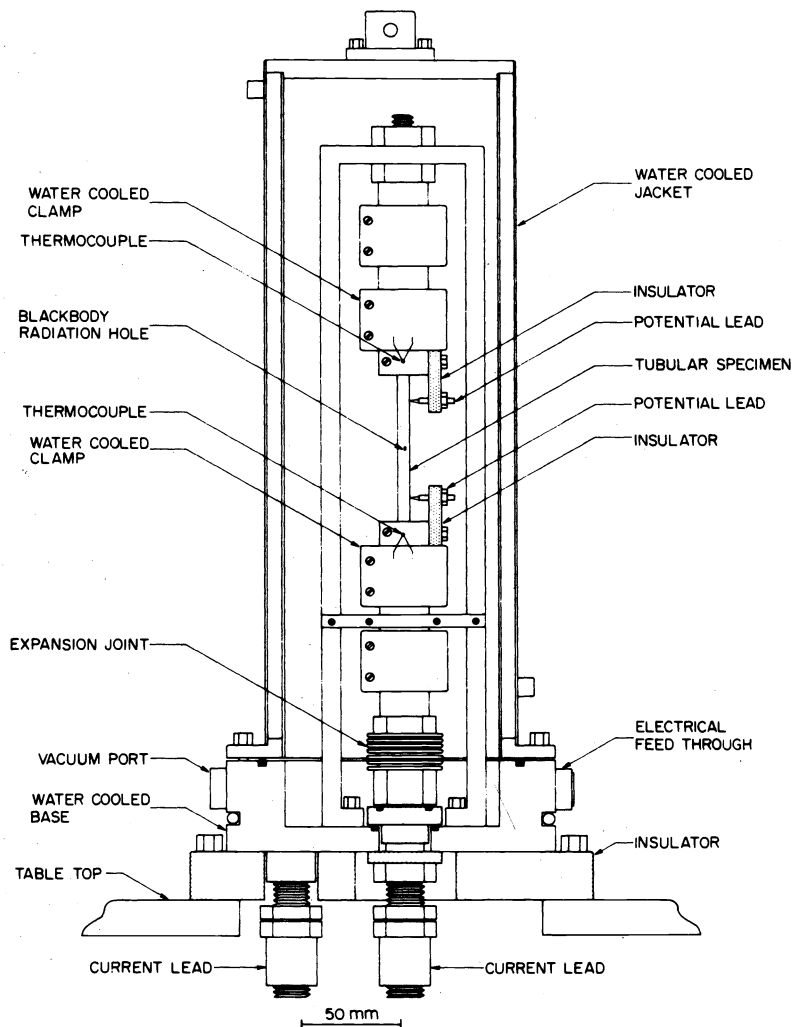


Fig. 2. Pulse calorimetry apparatus of Cezairliyan. (From *J. Res. Nat. Bureau Stds* 75C, 7(1971).)

urements are based upon rapid resistive heating of the specimen by the passage of large currents. The power imparted to the specimen and the specimen temperature are both recorded as a function of time. The power is determined by measurement of the current flowing through the specimen and of the potential difference across the effective specimen as a function of time, while temperature measurements are made using thermocouples or optical pyrometry. Power losses are usually estimated or obtained from data taken during the period immediately following the heating of the specimen. The duration of a high-speed measurement is generally of the order of 0.001–1 sec. The problem of measuring the specimen temperature accurately during a measurement has been coped with by Cezairliyan *et al.*⁷ using a high-speed pyrometer designed by Foley,⁸ which permits 1200 specimen temperature evaluations per second. This pyrometer has the advantage that it is capable of comparing the radiances from the specimen with that of a reference lamp during the pulse experiment. Problems arising from photomultiplier fatigue, drift, and changing environmental conditions are thereby eliminated.

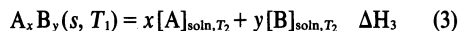
Due to recent improvements in high-speed digital recording techniques, it is claimed that the accuracy of the best high-speed pulse calorimetric measurements is as good as can be obtained by conventional methods at temperatures up to 2000°K, and above 2500°K the accuracy of pulse calorimetry is superior. Typical error limits for the measurements are given as 2% at 2000°K and 3% at 3000°K with a precision of 0.5% between these temperatures.

The ability of the method to be used at temperatures beyond the scope of other calorimetric techniques is demonstrated by the work of Affortit and Lallement⁹ in their studies of the heat capacity of Nb and W at temperatures up to 3600°K, while Cezairliyan¹⁰ has determined the melting point and electrical resistivity (above 3600°K) of tungsten by the pulse heating method.

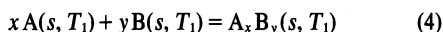
2.2. Extension of established experimental methods to higher temperatures to study specific liquid alloys or more refractory materials

2.2.1. High-temperature solution calorimetry. The method has been discussed in some detail, for example by Leach¹¹ and by Laffitte.¹²

In the most common application of this method, the enthalpy of formation, ΔH_f , of an alloy or intermetallic compound is obtained as the difference of the heat effects associated with dissolution firstly of the pure components of the alloy and then of the alloyed specimen, in a suitable liquid solvent metal, as shown by the following equations:



whence for the reaction



$\Delta H_f = x\Delta H_1 + y\Delta H_2 - \Delta H_3$, where x and y are the atom fractions of components A and B respectively ($x + y = 1$), T_1 is the initial temperature of the specimens and T_2 is the solvent temperature. T_2 may be less than or greater than T_1 .

The best experimental conditions are obtained if the

solvent metal has a low vapour pressure, a low melting point, a low affinity for oxygen, and is compatible with the container. These requirements are met very well by tin which has consequently found wide use as a solvent. Unfortunately, many of the transition and refractory metals do not readily dissolve in liquid tin, and it is for alloys of these metals, which are of greatest technological importance, that data are most urgently needed. With this fact in mind, Vieth and Pool¹³ have constructed a liquid metal solution calorimeter, based on the design of Tian and Calvet,¹⁴ for use at temperatures up to 1573°K in a vacuum environment of 2.6×10^{-4} Pa. The apparatus is illustrated in Fig. 3. The liquid uranium solvent is contained in a beryllium oxide crucible, and heat effects obtained on solution of the specimens are detected by a thermopile consisting of 120 W–W/25 Re thermocouple junctions mounted on a boron nitride support structure around the reaction tube containing the solvent bath. The isothermal block containing the thermopile and reaction well is constructed from boron nitride. A sample chamber, capable of holding 24 specimens, is used to introduce specimens into a preheat furnace and thence into the solvent bath.

The calorimeter has been used to measure partial enthalpies of solution of V, Cr, Fe and Ni in uranium at 1423°K, and appears to offer prospects for determining enthalpies of formation of refractory alloys and compounds which have previously been inaccessible to calorimetric studies.

Numerous solution calorimeters based on the design of Tian and Calvet¹⁴ are in use in laboratories around the world, and in particular, at the Centre de Recherches de Microcalorimétrie et de Thermochimie at Marseille, a

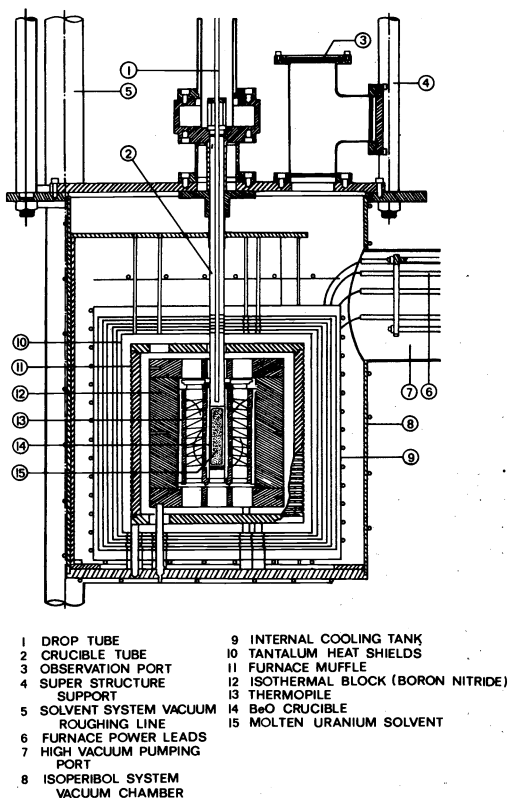


Fig. 3. Liquid metal solution calorimeter for use at temperatures up to 1573°K (Vieth and Pool, ref. 13).

number of such calorimeters have been constructed for use at temperatures up to 1473°K. Important studies of molten oxide systems have been made by Kleppa and co-workers using this calorimetric technique, more recent examples being measurements of enthalpies of formation of chromite spinels¹⁵ and of liquid PbO-GeO₂ melts¹⁶ at 1173°K. The method has also recently been used by Xuan, Castanet and Laffitte to measure the partial molar enthalpy of solution of α -alumina and CaF₂ in cryolite at 1290°K.¹⁷

The Calvet calorimeter has found another important application in its use by Gerdanian to study partial enthalpies of solution of oxygen in a number of non-stoichiometric metal oxides, e.g. Fe_{1-x}O¹⁸ and PuO_{2-x}.¹⁹ The measurements in this case are carried out by making successive additions of small quantities of oxygen to an oxide of known composition and determining the enthalpy change associated with each addition.

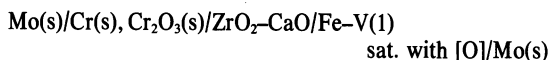
2.2.2. High-temperature differential thermal analysis. Predel and Mohs²⁰ have described a calorimeter which is based on the principle of quantitative differential thermal analysis and which operates at temperatures up to 1873°K in a vacuum of 1.3×10^{-3} Pa or in an inert gas. Because of its high operating temperature, the calorimeter allows studies to be made of liquid transition metal alloys, for which calorimetric data are badly needed. The apparatus has been used to measure, for example, the enthalpies of mixing of liquid Fe-Ni,²¹ Fe-Co²¹ and Co-Ni²⁰ alloys, and the enthalpies of fusion of Fe, Co and Ni.²⁰ The calorimeter (Fig. 4) is situated in a water-cooled jacket and employs two independently-controlled heating systems. The main heater is a molybdenum cylinder which permits temperatures up to 1673°K to be reached using a 5.5 kW power supply. The secondary heater is

situated in the molybdenum calorimeter block, and with a power supply of 1.5 kW, the temperature can be increased to 1873°K. Use of the dual heating system enables small temperature changes to be effected quite simply.

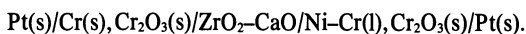
The central molybdenum block contains the alumina specimen crucible, and to measure the enthalpy of mixing of an alloy, the second molten component is allowed to flow into the first from a crucible situated just above the main crucible. Any difference in the initial temperatures of the first and second components of the alloy can be corrected for from a knowledge of the heat contents of the two metals. The thermal effect on alloying is recorded by a photo-electrically controlled recorder.

Calibration is effected by means of a Pt-Rh heater sintered into alumina and protected from the molten metal by a thin-walled alumina tube. The platinum leads to the heater have a resistance less than 0.1% of the heating spiral itself in order to reduce generation of energy in the leads. Calibration measurements are carried out frequently and at different temperatures in the course of the experiments, using different amounts of electrical energy. At the higher temperatures, however, only relatively small increases in temperature of the calibration heater can be used because of the danger of melting the platinum leads. Consequently the estimated accuracy of high-temperature calibration is 3%.

2.2.3. High-temperature electro-motive force studies. The use of solid oxide electrolytes in the determination of Gibbs energy values for metal systems is well established. The method relies on ionic conductivity being maintained at very low oxygen pressures, and many investigations have been carried out at high temperatures using the popular calcia-stabilized zirconia electrolyte. Typical examples of the high-temperature application of the electrolyte are studies made by Kay and Kantopoulos²² of the deoxidation thermodynamics in the Fe-V-O system at temperatures in the range 1823-1973°K using the cell



and investigations made by Fruehan²³ of molten Cr-Ni alloys at temperatures around 1873°K using the cell

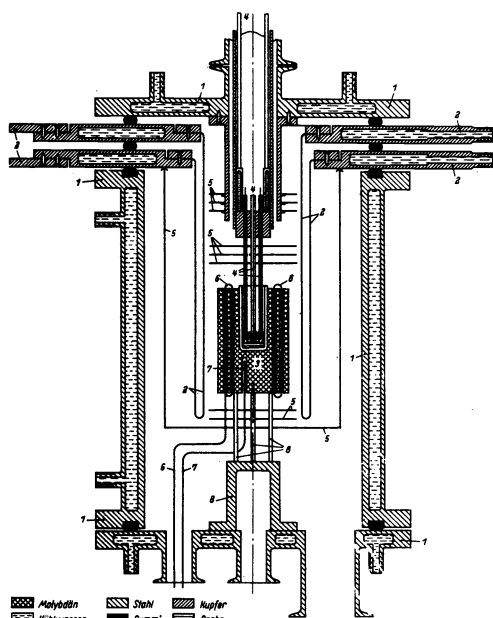


At 1873°K, the dissociation pressure of Cr₂O₃ is about 10^{-7} Pa whereas Fruehan demonstrated that ZrO₂+CaO exhibits insignificant electronic conductivity down to about 3×10^{-8} Pa at that temperature.

An important practical application of solid oxide galvanic cells at high temperatures is in the determination of the oxygen concentration of molten metals. In the form of probes consisting of standard electrodes encased in solid oxide electrolyte, the cells enable measurement to be made of oxygen levels in, for example, molten steel and copper.²⁴

2.3. Adaptations of existing experimental techniques to overcome problems associated with usual methods of operation

2.3.1. An adapted Knudsen method for studies of silicides. The application of the Knudsen-effusion vapour-pressure method to thermodynamic studies of alloy systems usually requires that one component of the alloy is considerably more volatile than the other(s).



- | | |
|----------------------|-----------------------------|
| 1 Chamber | 5 Radiation shields |
| 2 Main heater | 6 Secondary heater |
| 3 Calorimeter block | 7 Reference thermocouple |
| 4 Measuring 'finger' | 8 Calorimeter block support |

Fig. 4. DTA apparatus for measurement of enthalpies of fusion and of mixing for alloys at temperatures up to 1873°K. (From *Archiv für das Eisenhüttenwesen* 41, 1 (1970).)

However, a variation of the method has recently been described by Kubaschewski and Chari²⁵ by means of which it has been possible to obtain Gibbs energy data for certain refractory transition metal silicides, while avoiding the very high temperatures which would be required to produce silicon vapour at measurable pressures in a direct dissociation process. Experimental problems associated with specimen-container reactions and temperature measurement and control have thereby been reduced.

The method makes use of the reaction between Si in the silicides and SiO₂ to produce gaseous SiO at pressures which can be measured by the Knudsen effusion method at temperatures of the order of 700°K below those required for direct dissociation of the silicides.

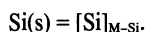
If the reference reaction



is first studied, followed by measurements for the metal-silicon alloy concerned, as shown below



it can be seen that subtraction of equation β from equation α corresponds to the reaction



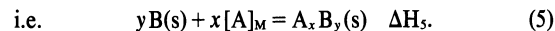
Hence the partial Gibbs energy of solution of silicon in the alloy is related to the silicon monoxide pressures for the two reactions by the equation

$$\Delta G_{\text{Si}} = RT \ln (P_{\text{SiO}}^2 \beta / P_{\text{SiO}}^2 \alpha).$$

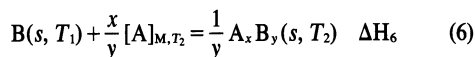
Measurements have been made for the Mo-Si system²⁶ at temperatures between 1410 and 1675°K using this method and the results have been integrated to obtain Gibbs energies of formation for the silicides Mo₃Si, Mo₅Si₃ and MoSi₂.

2.3.2. Precipitation calorimetry. One of the problems associated with liquid metal solution calorimetry studies of alloys is the poor solution characteristics sometimes encountered with certain intermetallic compounds. Such behaviour was observed by Bryant and Pratt²⁷ in the course of measurements on palladium and platinum aluminides, using liquid tin as the solvent metal. While pure Pd, Pt and Al were found to dissolve satisfactorily in tin, the aluminides did not. These authors consequently devised the precipitation method as a means of obtaining the required data.

The method relies on the ability to induce precipitation of the phase under investigation by addition of one of its components to a dilute solution of the other component in a liquid metal solvent M.



The heat effect accompanying this reaction may be measured in the usual way and is then combined with the enthalpy of solution of pure A in liquid M to give ΔH_f of A_xB_y(s) according to the reactions shown below:



whence by multiplying eqn (6) by y and eqn (7) by x , and

adding,



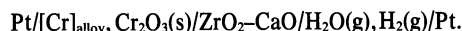
Combination of the enthalpies of pure A and B between T_1 and T_2 with the above value of ΔH_8 enables $\Delta H_f(T_2)$ to be determined.

It can be seen from the above sequence of steps that the precipitation technique is based on the synthesis of the phase under investigation, whereas the usual solution method involves a de-alloying process.

Bryant and Pratt have defined the conditions²⁷ under which the precipitation method can be used with an accuracy of about 1% where the extent of precipitation is in excess of 99%. They conclude that the method is useful for phases with solubilities less than 0.1 at%, but point out that a limitation of the method is that it is usually possible to study only the most stable phase in the precipitating system. This phase must also be of definable composition (ideally a line compound) and have a low solid solubility for the solvent metal.

Examples of the application of the method are to measurements of ΔH_f for PdAl²⁷ giving results in excellent agreement with those obtained by Ferro and Capelli²⁸ using a direct reaction method, and to studies of ΔH_f values for IIB-VB compounds.²⁹ Bryant and Pratt suggest that even if the solvent were restricted to liquid tin, many compounds of type IIB-VIB, IIA-VB and VIII-Al would be suitable for study by the precipitation method.

2.3.3. A "null" e.m.f. method. The calcia stabilized zirconia electrolyte is predominantly an ionic conductor at oxygen pressures as low as 10⁻¹² Pa. At lower pressures however, the increase in electrical conductivity limits the usefulness of this electrolyte. In practical terms, this means that the electrolyte cannot be used in the usual cell arrangement with metals whose affinity for oxygen is greater than that of, say, molybdenum or tungsten. To try to overcome this limitation, Briggs *et al.*³⁰ set up the following cell:



The experimental arrangement is shown in Fig. 5. The

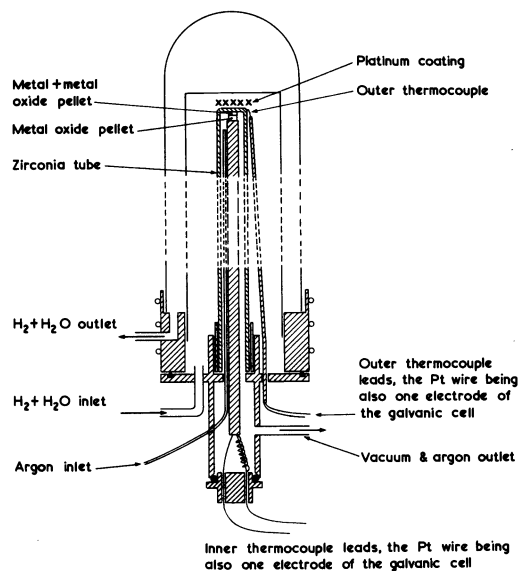


Fig. 5. Arrangement of cell for "null" e.m.f. method. (From *J. Chem. Thermo.* 3, 43 (1971).)

composition of the H_2 + water vapour mixture was adjusted until the cell produced zero e.m.f., i.e. until the same oxygen partial pressure existed at both electrodes. This oxygen pressure was calculated from the equilibrium constant and the known partial pressures of hydrogen and water vapour. The accuracy of the method was confirmed using a mixture of $Cr + Cr_2O_3$ at 1273°K corresponding to an oxygen dissociation pressure of $10^{-16.8}$ Pa; further tests of the method were made by measurement of the chromium activity in three ternary Fe–Cr–Ni alloys.³¹

By making the technique a null-point method in this way, interference from electronic conduction is made as small as possible and the range of utility of calcia stabilized zirconia as an electrolyte is extended.

The limit of application of this null method is defined by the minimum mole fraction of H_2O which can be maintained in the vapour mixture (say 10^{-5}). Below this level, water vapour present as an impurity from various sources, begins to interfere. It is therefore preferable for studies of reactions involving the more stable metal oxides to use electrolytes which are ionic conductors at very low oxygen partial pressures, e.g. thoria with yttria or lanthana as solutes.

3. APPLICATIONS

Metallurgical thermodynamic data and calculations have a very important role to play in investigating the feasibility, optimum operating conditions, and yield of proposed metallurgical processes. Thermodynamic calculations will also provide information on the phase equilibria to be expected in a given alloy, oxide or gas system at different temperatures, pressures and compositions. Applied thermodynamics is consequently used as a powerful analytical technique in many areas of the metallurgical industry.

Because there is frequently a need to maintain confidentiality in considering industrial problems, many important successes of applied metallurgical thermodynamics remain unpublicised for some time. However, examples of the successful application of thermodynamic calculations *are* available and a number of such examples were considered at a symposium held in England in 1971.³² Descriptions were given of the practical use of thermodynamic data in the extraction³³ and refining³⁴ of copper, in the development of the zinc blast furnace,³⁵ in the chlorination of metal oxides,³⁶ in the definition of vapour-deposition conditions for Ti–Zr alloys using the iodide process,³⁷ in the calculation of "chill factors" for addition of master alloys to liquid iron,³⁸ in the investigation of improved support metals for the Float Glass Process,³⁹ and in the definition of suitable gas atmospheres for carburisation treatments.⁴⁰ The subject matter of the examples quoted indicates the scope of thermodynamic calculations. Further examples of the application of such calculations to practical metallurgical problems have been discussed by Kubaschewski.⁴¹

In the present review, just three examples have been chosen for more detailed discussion and these are considered to be representative of many others.

3.1. Calculation of metallurgical phase diagrams

It is difficult to exaggerate the importance to the metallurgist of reliable phase diagram information, since the phases and structures which form in an alloy system at different compositions, temperatures and pressures, determine the mechanical and physical properties of the alloys concerned. If the phase diagram for a particular

alloy system is available prior to manufacture of the alloys, then the necessary information is at hand to avoid wasted time and expense in the preparation of alloys with inferior properties. Consequently the phase diagram compilations of Hansen, Elliott and Shunk⁴² occupy an important place in any metallurgical library.

Metals, alloys and refractory compounds are being used increasingly for extended periods at elevated temperatures and it is therefore of considerable importance that information should be available on the high-temperature stability of the various phases that can occur in a given material. It is possible to use thermodynamic calculations, either in conjunction with conventional metallographic studies or independently, to determine the phase equilibria of interest.

An important advantage of thermodynamic calculations of equilibrium phase boundaries is that the necessary thermodynamic data can be measured at temperatures which are sufficiently high to ensure that equilibrium is established in the alloys, then used to calculate phase equilibria at lower temperatures where diffusional delays frequently reduce the accuracy of phase boundaries determined by conventional metallographic methods. Despite such slow diffusion rates, an alloy may show a tendency to two-phase separation after use for extended periods at moderate temperatures, and such behaviour could lead to failure of an important component. The importance of establishing *equilibrium* phase boundaries is therefore apparent, and is demonstrated by the formation of embrittling σ phase and resulting failure of certain turbine blades which has occurred after use at 1033–1200°K for some thousands of hours.⁴³ Formation of a σ phase could have been predicted by thermodynamic calculation of the *equilibrium* diagram for the alloys concerned, even though conventional metallographic studies of the blade materials indicated an apparently satisfactory structure at the required operating temperatures. Kubaschewski⁴⁴ has given examples of alloy systems for which thermodynamic calculations have defined phase separations previously undetected in metallographic investigations.

Several important review papers have been published which deal specifically with the calculation of phase equilibria in binary alloy systems, for example those by Kubaschewski and Chart,⁴⁵ by Kubaschewski⁴⁶ and by Kaufman.⁴⁷ However, it is in the calculation of phase equilibria in ternary and higher order systems, using continually-improved computer techniques, that considerable advances have been made in the application of thermodynamic calculation methods. Although most alloy systems of technological interest contain more than two constituents, conventional metallographic studies of the phase equilibria in the alloys concerned would be much too time-consuming and costly to be carried out in any detailed sense. It is for such systems that thermodynamic calculations are likely to play an important role in future alloy development.

Calculations of ternary phase diagrams are made from the basis of assessed thermodynamic data for the three related binary systems, together with thermodynamic data for the ternary alloys when these are available. However, since ternary data are scarce, optimum use must be made of any reliable phase boundary information that is available to assist in establishing the best set of thermodynamic data for the calculations. When neither ternary thermodynamic properties nor ternary phase diagram information exist, it becomes necessary to carry out calcula-

tions using assessed data for the binaries only. In such cases it is preferable, when possible, to supplement the calculations by metallographic examination of specimens taken at selected alloy compositions. Such work has been performed for example by Kirchner *et al.*⁴⁸ and by Carmio and Meijering⁴⁹ in studies of the Fe–Mo–W and Au–Ni–Pt systems respectively.

A major problem in calculating ternary thermodynamic values, and hence phase equilibria, from data for the related binaries, is the choice of a suitable equation to relate the binary and ternary properties. Many equations have been proposed for this purpose and these have been discussed in some detail in reviews by Ansara,⁵⁰ and by Ansara and Bonnier,⁵¹ while Spencer *et al.*⁵² have tested a number of the available equations for systems for which ternary thermodynamic data are available.

When suitable expressions have been obtained to represent the Gibbs energy surfaces for the various phases in a ternary system, the equilibrium phase boundaries are calculated by computer, for example by a series of calculations involving the minimisation of the Gibbs energy of alloys of defined composition. This method has been described by Gaye and Lupis⁵³ and by Counsell *et al.*⁵⁴ while Kaufman and Bernstein⁵⁵ have published detailed computer programs for calculating phase boundaries in ternary systems. In simple terms, the computer calculations provide phase compositions corresponding to the points of contact of the tangent plane to the ternary Gibbs energy surface. An excellent example of the application of computer methods to the thermodynamic calculation of phase diagrams is the recent work by Kaufman and Nesor,⁵⁶ who have calculated phase diagrams for a large number of superalloy systems (e.g. Fig. 6). At NPL we have recently studied the ranges of appearance of σ phase in the Fe–Cr–V,⁵⁷ Fe–Co–Cr⁵⁸ and Ni–Co–Cr⁵⁸ systems (e.g. Figs. 7 and 8). Such calculations can be performed in a fraction of the time and at a fraction of the cost of metallographic studies of the alloys concerned and, as shown by the examples given, are already providing successful in predicting the phase equilibria in complex systems. Moreover, once the necessary thermodynamic data have been established, the calculations can be made for any specified temperature. The methods used in the calculations are also applicable to oxide and salt systems for example, and thermodynamic data and calculations are thus likely to play a large role in materials development for a wide cross-section of technologies.

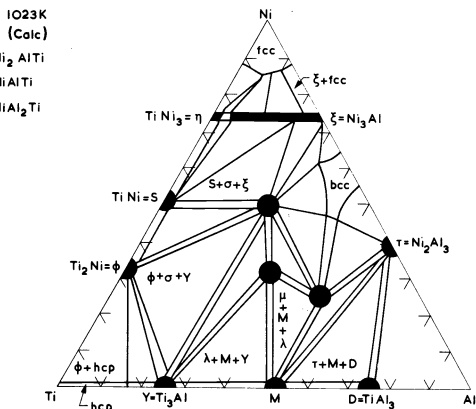


Fig. 6. Calculated isothermal section of the Al–Ni–Ti phase diagram at 1023 K. (From *Met. Trans.* 5, 1623 (1974).)

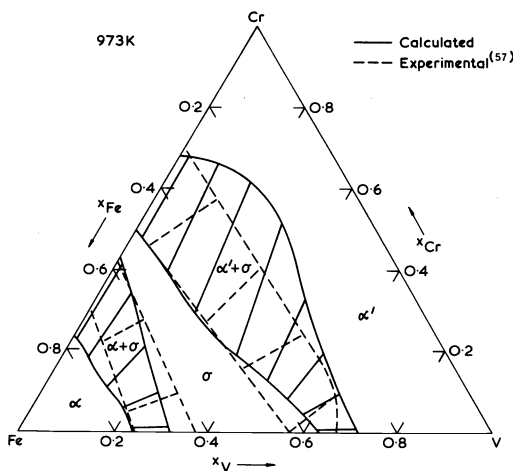


Fig. 7. A comparison of the calculated and experimental isothermal section of the Fe–Cr–V phase diagram at 973 K.

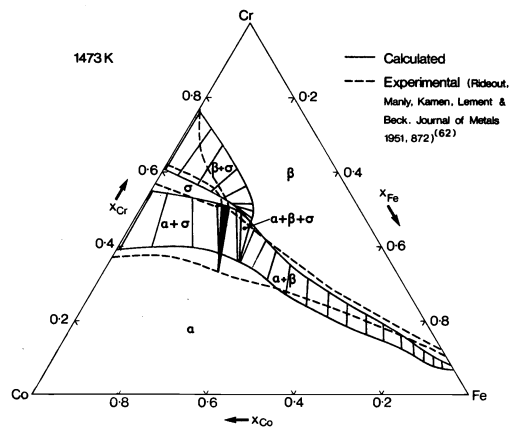


Fig. 8. A comparison of the calculated and experimental isothermal section of the Fe–Co–Cr phase diagram at 1473 K.

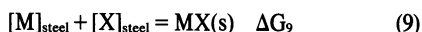
3.2. Precipitation reactions in steels

The controlled precipitation of, for example, carbides and nitrides in steel, is a well-known example of a method of producing increased toughness and strength. For a steel containing several different solutes, it is possible to carry out a thermodynamic analysis, prior to manufacture, to determine the variations in precipitate stability and solution temperature brought about by changing the steel composition. Hence optimum solute concentrations and heat treatment temperatures can be calculated so as to give the required sequence of precipitation in the production process. Kinetic factors may of course also play a part in determining the processes which take place, but since the temperatures at which precipitation occurs in the steel are often high, calculations based on the assumption of thermodynamic equilibrium may give a fairly reliable representation of the actual precipitation sequence.

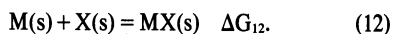
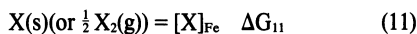
For a particular steel, which contains a total of 2–3% by mass of solute elements, in the absence of any previous knowledge the assumption must be made that it is possible, in principle, for any one constituent to react with any other constituent to form a precipitate. However, due to the large excess of iron and the very dilute nature of each of the solutes, the likelihood of many of these precipitation reactions occurring is negligible. For example, inter-

metallic compounds and the phosphides and aluminides of such solutes as Mn, V and Nb are not expected to form according to thermodynamic calculations. On the other hand, the carbides, nitrides and sulphides of these metals require more detailed investigation.

The basic reaction to be considered in calculating the Gibbs energy of formation of a precipitate from dilute solution in the steel is represented by:



where M and X are solutes and MX is the precipitated compound. This equation is built up by consideration of the following reactions:



Since the concentration of each of the solutes is very low, it is reasonable to make the assumption that the partial Gibbs energies of solution ΔG_{10} and ΔG_{11} are those applicable to dilute solutions in the various binary Fe-M and Fe-X systems and are not significantly affected by the presence of the other solutes. The further assumption, that Henrian behaviour of the solutes obtains, may also be made. Hence the required Gibbs energy change, ΔG_9 , for the reaction of interest is given by $\Delta G_{12} - \Delta G_{10} - \Delta G_{11}$. When ΔG_9 is equal to zero, the precipitated compound MX is in equilibrium with M and X in solution in the steel, and the temperature for which $\Delta G_9 = 0$ for the given concentrations of M and X represents the solution temperature for the compound concerned (or the temperature at which the compound first forms on cooling the steel).

Figure 9 shows plots of calculated Gibbs energies of formation as a function of temperature for various compounds in an austenitic steel. On cooling the steel, the

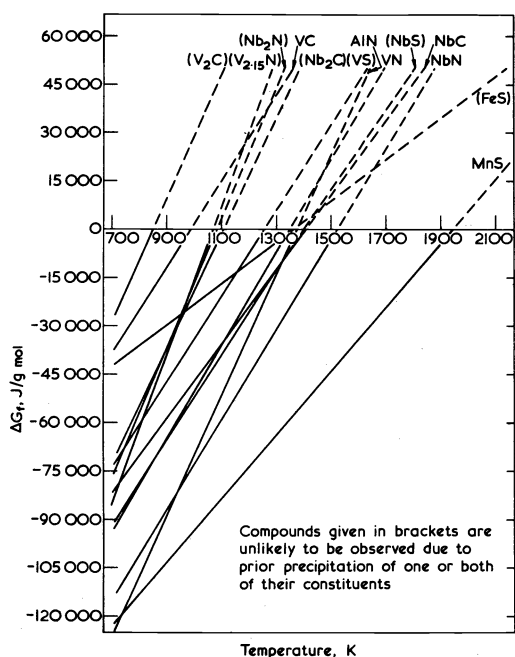


Fig. 9. Calculated Gibbs energies of formation of compounds from solution in austenitic steel.

sequence of stability of the compounds, represented by their temperatures of formation, (using the *initial* steel composition in each case) is calculated to be MnS, followed by NbN, NbC and so on. Of course, the lowering of concentration of a constituent in solution by its precipitation in a compound reduces the probability of formation at lower temperatures of less stable compounds containing that constituent. Plots such as those given provide very useful qualitative, and less reliable quantitative, information on the compounds which are expected to form in a steel of given composition, on their likely sequence of precipitation and on the maximum temperatures of stability of the compounds formed.

3.3. Vapour deposition processes

The preparation of materials of high purity by controlled deposition from the vapour is a widely used and well-established process. Vapour deposition is an area of metallurgy in which thermodynamic calculations can play a large part in establishing optimum operating conditions for the processes concerned.

A recent sophisticated example of the development of a computer method to calculate the equilibrium compositions in multicomponent systems containing an ideal gas phase and several stoichiometric condensed phases, using a Gibbs energy minimization technique, is that due to Bernard *et al.*⁵⁹ These authors have described the background theory to a computer program which enables the user to calculate for the deposition process of interest the effect of varying the temperature, pressure and initial composition of the gas mixture. The calculation method has been applied to the determination of deposition conditions for the production of TiC in the system Ti-C-H-Cl using a cold wall process.⁶⁰ Results were produced which yielded analyses of the conditions under which the phases TiC, TiC + Ti and TiC + C were formed for differing initial concentrations of the gas mixture $TiCl_4-CH_4-H_2$, (Fig. 10). The composition of the gas phase at equilibrium and the yield of TiC were also obtained. Thus it was shown that, starting with an equi-molar mixture of $TiCl_4$ and CH_4 ($TiCl_4 = CH_4 = 10^{-4}$), the yield of TiC is a maximum between 1200 and 1800°K and the amount of gaseous species is a minimum. On the other hand, for methane-rich mixtures ($TiCl_4 = 10^{-4}$ mol, $CH_4 =$

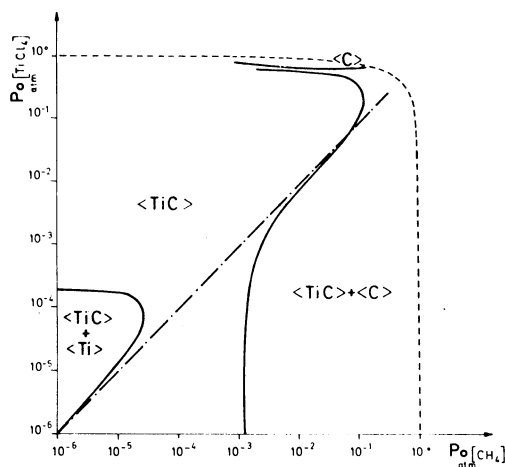


Fig. 10. Calculated deposition ranges for TiC at 1800°K for various initial gas phase compositions and pressures. (From *J. Less-Common Metals* 40, 173 (1975).)

10^{-1} mol), it is necessary to keep the temperature below 1000°K in order to obtain pure solid TiC.

Experimental investigations confirmed the calculated theoretical boundaries between the TiC and TiC + C phase regions at 1800°K , and thereby demonstrated the time and expense that can be saved by carrying out thermodynamic calculations of the best operating conditions for vapour deposition processes prior to practical tests.

4. FUTURE REQUIREMENTS FOR METALLURGICAL THERMODYNAMIC DATA

It has been pointed out in the introduction that the energy and resources problems faced by the metallurgical industry demand of the research worker a much greater awareness of the ultimate practical usefulness of his investigations. It is essential that greater effort be expended, before performing experiments, in carrying out literature surveys and, if necessary, in making critical assessments of published information, to ensure that planned measurements are really required.

From the point of view of the industrial user of thermodynamic data, literature surveys and data assessments are often too time-consuming to be worthwhile, and it is for this reason that computer storage of metallurgical thermodynamic data has been undertaken in a number of countries⁵⁸ to cope with the vast amount of information now available in the literature. These data banks contain the assessed values required by industry for application to specific problems; they can be updated to keep pace with new values which become available, and programs can be written to perform calculations using the stored data and having as output the particular graph or tabulated values required by the user.

Thermodynamic data are still lacking in a number of important areas however. In the case of alloy systems, information is needed for alloys of transition metals which are important constituents of steels and high-temperature alloys. For example, data are scarce for alloys of chromium, vanadium, titanium, zirconium, niobium, molybdenum, tantalum and tungsten. In some cases, although Gibbs energies of formation have been determined, a need exists for corresponding calorimetric measurements to be performed so that complete thermodynamic assessments of the systems concerned can be carried out. The refractory nature of the metals involved gives rise to difficulties in regard to experimental measurements, but in view of the technological importance of alloys containing these metals, it is of prime concern that experimental methods be developed to enable thermodynamic data to be obtained for both solid and liquid alloys. Some of the methods available have been described in this paper. The acquisition of the necessary data will enable calculations to be made of phase stability in alloy steels and superalloys for different compositions and temperatures and will thereby provide important information with regard to the production and final high-temperature use of the alloys concerned. Such calculations are also important in relation to carbide formation in alloys containing transition metals. The available data on transition metal carbides is not complete at the present time, however, and in some cases reported values may be inaccurate because of the non-stoichiometric nature of the carbides involved. Similar comments apply to the published thermodynamic data for transition metal nitrides. Only a very limited amount of data exist for mixed carbides and carbonitrides, although such compounds

appear frequently in alloy steels, and thermodynamic values, if available, would assist considerably in determining optimum compositions and heat-treatment temperatures for the steels concerned.

Also in connection with steel production, there is a need for accurate partial thermodynamic values for tramp elements such as Sn, P, As and Sb in both solid and liquid iron. It has been observed that recycling of scrap is leading to a build up of impurity levels in some steels and this can have a markedly adverse effect on the properties of the steel produced. Thermodynamic data can assist in finding a solution to this problem.

Accurate thermodynamic values are needed for the dilute solutions of gases in many metals in connection with corrosion and casting problems and the control of the gas content of metals.

Borides are of importance for example in regard to oxidation resistance of refractory metals and wear resistance of transition metal alloys. Titanium boride also has an important role in the grain refining of aluminium. Thermodynamic data for borides are still very incomplete however and would find important practical application in areas such as those mentioned.

Much useful thermodynamic information is still to be obtained for slag systems; reliable enthalpies of formation for molten oxide systems are very scarce and would provide valuable information with regard to the temperature dependence of Gibbs energy values and calculations of slag-metal equilibria. There is an important field, as yet virtually unexplored, in the area of phase equilibrium calculations for multicomponent oxide systems.

In summary, the present paper has attempted to demonstrate important applications of metallurgical thermodynamic data, to define areas where thermodynamic information is still needed, and to describe some of the experimental methods which have been developed to obtain the required values. The challenging situation facing the metallurgical industry is one in which the thermochemist has a valuable role to play.

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