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EXPERIMENTAL THERMOCHEMISTRY OF ALLOYS *

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ABSTRACT

The development of experimental thermochemistry is surveyed. The paper is divided into two parts. Foundations and Achievements, the year 1942 representing the arbitrary dividing line. It is shown that imagination was needed in the exploratory stages whilst new ideas in detail and improvements in materials, equipment and analytical methods dominated the second stage.

In both parts of the survey the subdivision is calorimetry in its various forms, electromotive force and vapour pressure methods. In particular, high-temperature methods are surveyed. The conclusions are that experimental alloy thermochemistry has reached a certain stage of finality, and interest might be concentrated on other substances such as ceramics, glasses and slags.

INTRODUCTION

Although investigators such as Person (1848), Döbereiner, Regnauld (1860) and Phipson (1866) had observed over 100 years ago that temperature changes may occur on mixing liquid metals, the systematic study of the thermochemistry of alloys was begun much later—long after W. Gibbs had established the thermodynamic background. Nevertheless, when the present author entered this field of investigation 44 years ago, the experimental foundations had already been laid. Virtually all the experimental methods employed at present were then known in principle as evidenced by the monograph by Weibke and Kubaschewski entitled Thermochemie der Legierungen, almost the whole edition of which fell victim to allied bombing soon after it appeared.

These methods entail the various forms of calorimetry and the Second-Law methods, i.e. the measurement of electromotive forces and of dissociation pressure. The state of affairs in 1943 will be outlined and discussed in the first part of this presentation. The second part will then deal with the advances made to date. Not to extend the story overmuch, the discussion will be confined to the determination of heats and Gibbs energies of formation and solution, excluding heat capacities. It will also include only a

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skeleton of references mainly concerned with novel methods, significant variants, and useful ideas. Even so, many pertinent contributions will be omitted. Reference may be made to a review article by Komarek [1].

FOUNDATIONS (1898–1942)

Calorimetry

Solution calorimetry

Naturally, among the first attempts to deal with alloy thermochemistry was the application of solution calorimetry employing aqueous solvents already in use in inorganic chemistry. Herschkowitsch [2], who was the first to employ this method as early as 1898, introduced a solvent suitable for the investigation of alloys, in particular of copper with baser metals such as tin. It consisted of two parts (by weight) of bromine, one part of potassium bromide and two parts of water. It is still called "Herschkowitsch's solvent".

Biltz and his coworkers used it, or hydrochloric acid in various dilutions, in the course of their systematic investigation of intermetallic compounds in the years 1923–1934 (e.g. refs. 3 and 4). The calorimeters were fairly simple, Weinhold or Dewar vessels, or a Bunsen-type ice calorimeter. For compounds difficult to dissolve, such as AuSn and $AuSb_2$, they constructed a calorimeter operated at 90 °C [5]. The calorimetric liquid consisted of paraffin oil.

Because with this type of work the heats of formation of intermetallic compounds are obtained as relatively small differences of relatively large heats of solution, great precision is required in their measurement. If uncontrolled side reactions occur in the solution, the results may be subject to excessively large errors. It is therefore much preferable, as elsewhere in solution calorimetry, to employ solvents similar in chemical nature to the solutes. Thus, Tayler [6] in 1900 used mercury as the solvent for the dissolution of alloys. See Richards and Forbes [7] for the study of heats of dilution of amalgams.

Combustion calorimetry

Heats of combustion in oxygen should not be used for the determination of heats of formation of alloys proper. The reason for this statement is that the results would again constitute small differences of large quantities, with the additional handicap that the reaction products are even less well under control than with aqueous solution calorimetry. In certain cases, where the desired heats of formation are strongly exothermic and alternative calorimetric methods difficult to envisage (e.g. metal silicides), combustion calorimetry may be employed.

However, there may be some future in Mixter's "combustion method" [8], which is the reaction of an alloy and the component metals with sodium superoxide (Na_2O_2).

Direct-reaction calorimetry

As has been mentioned above, early observers noted temperature changes on mixing liquid metals. Even in the solid state, metal/semimetal combinations can be made to react. A striking example was reported by Walter [9] in 1921. A mixture of lumps of iron and silicon reacted at 1250 °C, i.e. far below the melting points, the temperature increasing by 560 °C and the reaction product being molten. In the experience of the present speaker, one may consider the reaction mixture as a calorimeter, calculate the water equivalent additively from the heat capacities and add, for good measure, 20% to the observed heat effect to account for heat losses to the environment. In the example mentioned, the result turns out rather well in that $\Delta H_f = -8050$ cal g-atom^{-1} was calculated (or rather estimated) whereas $\Delta H_f = -8200$ cal g-atom^{-1} is the accepted value. Using a very primitive "calorimeter" we have even made use of this approach for the determination of the heats of formation of some exothermic intermetallic compounds [10] with reasonably good results: a lesson for thermochemists who think that only the most sophisticated apparatus would serve their needs.

Simple calorimeters for the determination of the heats of mixing of liquid metals were devised by Kawakami [11] in 1927. Again, fairly good results were obtained, but the water equivalents were rather low, thus detracting a little from the soundness of the experimental approach. The methods may in principle still be recommended for low-melting-point alloys.

Then in 1936, something exciting turned up—a calorimetric method that caused the late German master thermochemist W.A. Roth to exclaim benevolently: "Solch eine Frechheit ist mir noch nicht vorgekommen". The "Frechheit" was due to Oelsen [12] who took a bucket, filled it with 6.5 kg of water, inserted a Beckmann thermometer and called it the "Kuheimer-kalorimeter". Approximately 1 g-atom each of molten iron and molten aluminium, for instance, were poured simultaneously by two to three operators into a thick-walled steel cylinder lined with sintered sand, which was then sealed by a lid and placed in the calorimeter, the Beckmann recording the temperature increase. The heat content of the molten components must be subtracted from the measured heat effect, but the error involved is much smaller than that in computing the heats of formation from heats of solution or combustion using Hess's Law. This is the great advantage of these direct methods, in particular when the water equivalent is large. By repeating the experiments, pouring the liquid alloys rather than the component metals into the calorimeter and measuring their heat contents, the heats of mixing of the alloys were also obtained.

Enthusiastically, the present author took up the suggestion and, being in contrast to Oelsen on the staff of an institute for non-ferrous metallurgy, poured molten lead or bismuth onto alkali metals under argon in a calorimeter of water equivalent 1400 cal degree^{-1}—sometimes with disastrous results! However, most of the values then determined [13] are still valid.

The present author went on to look for alternative calorimetric methods to deal with intermetallica, not accessible to the Oelsen approach. From this, the first adiabatic high-temperature calorimeter for the investigation of reactions involving alloys originated [14]. Its operational temperature was ca. 700 °C, and spontaneous reactions such as the formation of Mg_3Bi_2 were investigated with it. However, the apparatus was not ideal for this purpose. Being relatively large in order to have the thermal capacity and space for dropping in metal powder compacts which reacted spontaneously at the experimental temperature, the calorimeter suffered from the disadvantage of maintaining a uniform temperature. To compensate the sudden changes in temperature, i.e. the initial fall in temperature and the subsequent rise due to the reaction, the observer was forced to anticipate the behaviour of the specimen. For future applications the calorimeter should be used for reactions rather slower than spontaneous.

Second-Law methods

Electromotive forces

With this method the chemical reaction to be investigated must be capable of being harnessed in a galvanic cell in such a way that its energy produces electromotive force. Simplified, the problem that faces the thermochemist is to measure the e.m.f. of a cell

$B/B\ \text{ions}/[B]_A$

where the baser metal B is in equilibrium with a solution, solid or liquid, of B in an alloy A_xB_y. Conditions for the application are that the cell reaction is reversible, that the electrolyte is a truly ionic conductor (with at most, say, 5% electronic conductivity), and that the amount of B transported during measurement is so small that virtually no change in concentration $[B]_A$ occurs. Diffusion rates in the electrodes must be so high that any amount of B deposited on, or dissolved from, the alloy electrode must be distributed or replaced quickly. This rules out the use of aqueous solvents for the electrolyte except for liquid alloy electrodes. Measurements by e.m.f. on liquid amalgams by Richards and Forbes [7] in 1907 were the first to give reliable thermochemical results. For other alloys, solid or liquid, higher temperatures had to be applied.

The natural choice for the electrolyte solvent were molten alkali halides. A simple H-shaped cell was introduced by Lewis and Kraus [15] in 1910 and subsequently frequently employed by various investigators. One leg contained the alloy, the other the baser metal, topped by the molten electrolyte so that the electrodes were in contact via the cross piece of the H. Popular solvents were eutectic mixtures of alkali metal chlorides in which a small amount of a salt of the transported metal is dissolved. They are still in use. Special attention must be paid to the dehydration of the electrolyte, otherwise secondary cells are set up. For the same reason, the affinity of the anion of the electrolyte to the more electropositive metal must be much less than its affinity to the constituent(s) of the alloy. Wagner and Werner [16] have estimated the magnitude of the error due to the displacement reactions in galvanic cells. Uniformity of temperature in the reaction zone is also an important condition to be strictly observed.

In order to eliminate, at least partly, the difficulties that arise by the use of molten salts, attention was quickly directed to the use of solid electrolytes. Wachter [17] employed solid silver chloride, a cationic conductor, for the investigation of silver–gold alloys. Hauffe [18] made use of the fact that in certain glasses sodium ions carry the electric current—Faraday's Law being obeyed—and determined the sodium activities in molten Na–Hg and Na–Cd alloys. Further development of solid electrolytes for e.m.f. measurements on high-melting-point alloys will be discussed below.

Dissociation pressure measurements

If one component of an alloy A_xB_y, say B, has a substantially higher vapour pressure than the other, its chemical activity may be determined by measuring the vapour pressure of pure B, p_B^0, and its dissociation pressure in the alloy, p_B. Then, $a_B = p_B/p_B^0$. For the investigation of vapour pressures, one distinguishes static, dynamic, and effusion methods.

The first systematic measurements were carried out on the metal with the highest vapour pressure, i.e. mercury. Hildebrand [19] in 1912 employed a simple manometric device to study liquid zinc amalgams. Later Biltz and Meyer [20] introduced the "isoteniscope" by which the substance (Au amalgams) was separated from the manometric arrangement by a sodium–potassium nitrate eutectic acting as a buffer.

Hirst and Olson [21] determined the concentration of mercury atoms in equilibrium with thallium amalgams by measuring the absorption of light corresponding to certain of the mercury reasonance wavelengths and were thus able to measure pressures of the order of 10^{-3} torr.

Next to mercury, zinc and cadmium are metals with relatively high vapour pressures and consequently drew the attention of early investigators of alloy stability. Hargreaves [22] employed the dew-point method originally devised by Lescoeur (1898) to determine the activity of zinc in zinc alloys. The principle is to hold a quartz tube in a temperature gradient, the alloy being placed in the hottest part of the tube and the condensation and evaporation of zinc being observed directly at the coolest spot, the temperature of which being varied. In this form the Hargreaves method has nearly exhausted its usefulness for alloy systems but continues to be employed in the form of the isopiestic method (see below). A corresponding method of Seith and Krauss [23] and that of Hargreaves have had many successors summarized under the name "isopiestic methods".

All the vapour pressure methods so far mentioned are static ones. To these may be added Biltz's investigations of metal sulphides and phosphides employing the sulphur and phosphorus valves (e.g. ref. 24). These substances are, however, outside the scope of the present survey.

A truly dynamic method is the so-called "transpiration method" which in principle is quite versatile and fairly reliable provided certain precautions are observed. In application, a steady, measured stream of inert gas is passed over the alloy at constant temperature. The gas carries along the volatile components of the alloy at a rate which is a function of the relative pressures and of the rate of gas flow. The vapour is condensed on a cool "finger" and the rate of removal and condensation of vapour measured at different rates of gas flow. Restrictions have to be built in, in front of and behind the specimen, to suppress back-diffusion. To find the true partial pressures, weight changes are extrapolated to low flow rates. The true pressures are not, as originally assumed, attained at zero flow rate but at moderate flow rates indicated by "plateaus" instructively demonstrated by Alcock and Hooper [25]. Originally applied by von Wartenberg to metals [26] in 1913, the method has been widely employed, for instance by Jellinek [27]. Apart from mass spectrometry (and potentially the use of radioactive tracers), it is the only method that permits the determination of the activity of all the constituents of an alloy by a single measurement, provided the pressures are of a similar order.

Another important source of error is the effect of thermal diffusion. This phenomenon always occurs when a mixture of gases of different molecular weight is enclosed in a space in which there is a temperature gradient. This was predicted fairly early, but disregarded by thermochemists whose results were thus largely frustrated. In 1936, Schmahl and Knepper [28] summarized and discussed the thermodiffusion effect for various gas mixtures. Hydrogen as the carrier gas should be avoided because of its lightness. Argon is preferable.

The most popular vapour pressure method to date is the Knudsen effusion method, the foundations of which were laid by Knudsen in 1909 [29]. Its potentialities, however, were not sufficiently recognized in this early stage of experimental alloy thermochemistry except by a few, such as Eucken [30]. Rough measurements by Egerton and Raleigh [31] of the cadmium pressures over Cd–Zn alloys in 1923 may, however, be mentioned here. The discussion of the method is transferred to the second part.

The survey of the "foundations" of experimental thermochemistry of alloys as reported in Thermochemie der Legierungen may thus end here.

ACHIEVEMENTS (1943–1979)

The subdivision of this survey into two parts is intentional and justifiable. As with any scientific subject, there are the pioneers who in turn depend on the knowledge of their contemporaries. As far as the experimental side of the subject is concerned the impetus began only in the twenties leading to the highlights of the thirties. That was the exploratory stage. However, if we are honest, little has been added in the later stages that requires much imagination. Analytical methods, it is true, have been greatly improved. Among these, the mass spectrometer deserves particular mention. Nothing of course is final in science. Even so, one may say that significant new ideas in experimental thermochemistry are unlikely to turn up in the next ten or twenty years. So, we may consider the following part as some sort of final assessment of the possible. This does not exclude the experience of the alloy thermochemists to other fields of chemistry, such as ceramics, slags, glasses, and halide systems, but it is fair to call this part "achievements". Let us deal in turn with the items mentioned in the first part.

Calorimetry

Solution calorimetry

In view of the objections mentioned earlier, it is not surprising that aqueous solution calorimetry has gone out of favour for alloys and that metallic solvents "are in". Liquid tin in particular has been used on a fairly wide scale, a suitable calorimeter being described by Ticknor and Bever [32] in 1952. The operational temperature of such calorimeters should be well above the melting point of the solvent metal so that the solubility of the solute metals, which mostly have higher melting points, may be relatively large. Other solvent metals of higher melting points than tin have been introduced: liquid aluminium for instance by Mathieu et al. [33]. Quite a commendable effort was made by John Elliott and his associates to employ liquid copper, nickel and iron, respectively, as calorimetric solvents. A special calorimeter, operated at 1000 and 1200 °C, was constructed [34] using liquid copper and copper alloys as solvents, and the design was then extended to even higher temperatures [35] to include nickel and iron. Thermochemical data, however, obtained in this way are small in number.

Combustion calorimetry

The Berthelot bomb is still being employed with some justification as a means of measuring heats of formation (as differences) of strongly exothermic compounds, such as transition metal silicides. However, a better application of the principle would be the use of the fluorine bomb [36] or alternatively the fluorination method proposed by Gross [37]. The reason for this preference is that metal fluorides show less deviation from stoichiometry than do oxides, thus reducing the error due to this source in "difference calorimetry".

Direct-reaction calorimetry

Actually, any calorimetric method to measure heats of formation is a difference method. Even with the determination of heats of formation of oxides in the bomb, some heat has to be supplied by ignition to start the reaction, and this is subtracted later. The point is that the difference in heat representing the final result should be as large a percentage of the measured values as possible.

With more resistant materials, increasing experience and more sophisticated equipment, it has now become possible to raise the operational temperature of reaction calorimeters to 1900 K and, in an exceptional case, even to 3000 K. However, the best operational temperature is not necessarily the highest attainable. It depends on the melting point of the alloy and the spontaneity of the reaction. Transition metal aluminides, for instance, form fairly exothermically, and reaction starts spontaneously just above the melting point of aluminium if compacts made up of mixed metal powders are heated. So we decided to build a calorimeter around this reaction [38]. The compact is suspended in a small furnace made of molybdenum wire surrounded by ten nickel-foil radiation shields, which in turn are enclosed in an aluminium block suspended in a brass vacuum container placed in a thermostat controlled at 25 ° C. Ten Cu-Eureka thermocouples have their hot junctions clamped on the surface of the aluminium block and the cold junctions to the brass block. The furnace is heated electrically until alloying takes place rapidly and the electrical energy supplied measured by an accurate watt-hour meter. When the calorimeter is again at 25 ° C, an amount of electrical energy is put into the furnace so that the calorimeter block is raised to the same maximum temperature as in the reaction run: the difference between the input electrical energy in the reaction and calibration runs is then the energy evolved by the reaction. Thus, the water equivalent need not be known, and the physical errors are restricted to the accuracy of the watt-hour meter.

Ferro and Capelli [39] have improved this "Öfchen-Kalorimeter" and used it for the investigation of Pd–Al and other alloy systems. Later, using the same principle, together with Borsese [40] they designed an aneroid isoperibol calorimetric apparatus containing four calorimeters. Since the temperature trend of each calorimeter is followed by 80 thermocouples in series, it is possible to carry out differential measurements. It has been applied to systems with one low-melting-point metal, the other metal being chosen so as to produce fairly exothermic heat effects. Examples are Au–Al, Mg–Bi, Y–Bi, Nd–Bi and other combinations with rare earth metals.

Mixing of molten metals in a calorimeter à la Kawakami [11] has been improved by Kleppa [41] and by Wittig [42]. These two isoperibol calorimeters appear to be quite precise provided they are applied to low-melting alloys.

An adiabatic calorimeter originally designed by Dench [43] at the request of the present author has proved its versatility and reliability for 18 years and has undergone quite a number of improvements, thanks to Grundmann [44], Hack [45] and Nüssler [46]. The principle of adiabatic calorimetry is too well known to be repeated here. The problem has always been one of materials. Initially it was believed that ceramic materials should be avoided, but now the "final" version has essential parts made of alumina [47]. We believe we have perfected the apparatus to such an extent that it is fool-proof, operational to 1900 K, and even ready for commercial duplication (which is now in fashion). When applying the method to the determination of heats of alloying, compacts of metal powder mixtures are heated adiabatically from a "safe temperature" to the "reaction temperature" and the heat effect recorded. Repeating the experiment with the reacted alloy, the difference in heat contents gives the heat of formation at the safe temperature; repeating it with unalloyed specimens of the same metal-to-metal ratio, the difference gives the heat of formation at the reaction temperature. To comprehend this, reference should be made to our Handbook [47].

The shape of the calorimeter proper is, as usual, cylindrical. Sale [48] constructed a duplicate of the apparatus with a spherical calorimeter. Whether this has advantages is as yet difficult to say.

In a successful attempt to circumvent the sophistications of the above adiabatic high-temperature calorimeter, Hoster [49] has devised a simplified version which he calls the "tandem calorimeter". Its principle is to measure temperature differences between two cylindrical specimens of similar heat capacity, the test and reference specimens, placed in the tube resistance furnace. A differential thermocouple has its two junctions in the middle of each specimen, the absolute temperature being also measured by a thermocouple. For calibration, a Pt coil with which an accurately known quantity of heat can be produced, is placed in a bore in the test specimen. In application, the heating current and time are chosen in such a way that the areas under the measurement and calibration curves are about equal.

Sophisticated calorimetry has at present reached its zenith in the form of the Tian–Calvet calorimeter. The original design could hardly be used at high temperatures, however. Laffitte [50] has indicated the improvements that were necessary. Kleppa [51] constructed a calorimeter based on this principle, which he first applied to heats of solution of alloys in liquid tin, reaching 800 °C. Essentially, Tian–Calvet calorimetry depends on the use of many thermocouples in series to achieve maximum sensitivity. In Kleppa's case the thermopile consisted of 176 chromel/alumel couples. The most extensive work on heats of formation of alloys employing the Tian–Calvet has for ten years (plus) been carried out at Marseille (e.g. ref. 52) up to

1200 °C, thus exceeding the operational temperature reached by Kleppa. One is inclined to think that simpler designs might be employed to accumulate such data, but the precision of the results enable one to extract fairly good partial heats of solution, provided always that the metals in question are not too sensitive to oxidation, etc.

Tian–Calvet calorimeters are now available on a commercial basis, but potential buyers should be warned to think carefully before they decide that the expenses are worth the desired results. As far as alloy thermochemistry is concerned, the ratio is unlikely to be favourable for the purchase.

The maximum temperature for the application of adiabatic and Tian–Calvet calorimetry is, let us say, 1600 °C, i.e. steel-making temperature. Thus, heats of mixing above this temperature must be obtained via the heat contents which can now be determined by drop calorimetry involving levitation melting. High-temperature data are of course desirable to assess the feasibility of certain industrial processes. A silver lining on the horizon has appeared. Betz [53] has succeeded in levitating separately two metals (or semimetals) to about 3000 K and alloying them, still levitated, observing the temperature changes by optical pyrometry. Examples are combinations of niobium with silicon and iron with copper. The accuracy of the results is claimed to be not better than ±20% of the heats of mixing; forty years ago our own claims when mixing molten metals in a calorimeter at considerably lower temperatures were not much less.

Second-Law methods

Electromotive forces

E.M.F. measurements on alloy systems have probably been the most reliable source of Gibbs energies. Either work relied heavily on molten alkali metal halides for the electrolytes, which must be predominantly ionic. Some attempts had then already been made to use solid electrolytes. This development has been greatly improved in the period of time now under consideration.

Kubaschewski and Huchler [54], having ascertained that silver dissolves in certain glasses as an ion, used this type of electrolyte to determine the Gibbs energy of a solution of silver in Ag–Au alloys. The experimental arrangement was simple. Early failures were remedied when the atmosphere of air was replaced by nitrogen. Otherwise there were no serious problems. Vierk [55], similarly, employed the Hauffe cell [18] to investigate liquid thallium alloys (e.g. Tl–Sn), thallium ions being dissolved in the glass electrolyte.

An important further step forward was the work of Kiukkola and Wagner [56], well known to those concerned. They introduced zirconia doped with calcia to determine the e.m.f. of simple cells of the type

$$\mathrm{Pt}\langle \mathrm{Co}, \mathrm{CoO}\rangle/\mathrm{ZrO_2}\text{–}\mathrm{CaO}/\langle \text{“FeO”}, \mathrm{Fe}\rangle \mathrm{Pt}$$

at temperatures above 1000 °C. Here the cell reaction is ⟨CoO⟩ + ⟨Fe⟩ = ⟨"FeO"⟩ + ⟨Co⟩. By replacing the one electrode by an alloy, say ⟨Co_xCu_y, CoO⟩, it is possible to deduce the Gibbs energies of the solution of Co in Co_xCu_y. In this particular case the alloy system is of a eutectic nature with limited mutual solubilities in the solid state. Dench and Kubaschewski [57] have selected this system as being suitable for testing the attainable precisions of measurements. It has been found that in the heterogeneous region Cu–Co reproducibility is within 0.2 mV, corresponding to 10 cal g-atom^{-1} of alloy. (Earlier statements claiming higher accuracies of e.m.f. results should be disregarded.) In the homogeneous region of the Co–Cu solid solutions, however, the reproducibility was much worse because of the difficulty in maintaining the concentration constant, or of analysing it.

The zirconia electrolyte may be used in the range of oxygen pressure from 1 to 10^{-18} atm at 1000 °C. This latter value corresponds roughly to the dissociation pressure of Cr_2O_3. Briggs et al. [58] have shown that by establishing an H_2O/H_2 equilibrium on the one side of the electrolyte, Cr_2O_3/Cr constituting the other electrode, and adjusting the former to a zero e.m.f., and additional power of ten in applicability could be achieved, owing to the fact that electronic conductivity in the electrolyte mattered less.

In order to further extend the range of applicability of the method in terms of oxygen pressure, other electrolytes had to be found. Thoria doped with yttria is such an alternative. It was applied to the investigation of the thermochemistry of WCo_3 for instance [59].

E.M.F. methods will continue to be useful in alloy thermochemistry. They are simpler in design than vapour pressure methods and, on the whole, more reliable and more accurate, provided always that all the pitfalls and sources of error are kept under control. There are several critical surveys that deal with these aspects. As for the imponderables of the application of the method, a paper by Worrell [60] may be consulted.

Of course, it is always desirable to have the results checked and supplemented by other Gibbs energy methods, for instance those that pertain to gas/alloy equilibria.

Dissociation pressures

No other method for the determination of thermochemical data of alloys has been so widely employed the past thirty years or so as that involving the measurement of vapour pressures. Most of the experimental principles were then already known, but novel variants have been introduced and analytical methods improved. Komarek, in his 1973 review [1], quotes nearly 300 references pertaining to vapour pressure measurements, although not all on alloy systems. Here we confine ourselves to some of the essential developments.

One word of warning, however! The reproducibility, not to speak of accuracy, of the results of all the different techniques are still rather low in view of the increasing demands made by practical application. Even for a relatively inert metal such as gold, vapour pressure results obtained in different laboratories may vary by as much as 40% [61]. Although this scatter may partly be compensated when activities are determined by a particular investigator, a substantial uncertainty always remains.

Dissociation pressure, static

Of the static methods optical absorption has found some application mostly with quartz cells which can be used up to 1100 °C. The advantage of the method is that mixtures of atomic and molecular species in the vapour above solids can be measured separately since the absorption line(s) corresponding to the excitation of a particular species is likely to be in another part of the spectrum. Thus, the results do not depend on the composition of the vapour. As examples, only some of the work of Pemsler and Rapperport [62] on zinc alloys may be mentioned here.

The isopiestic (constant pressure) method has found much wider application. Of the reported developments of the techniques of Hargreaves [22] (visual observation) and Seith and Krauss [23] (weight changes) the one of Hehenkamp and Wübbenhorst [63], who continuously measured the change in electrical resistance produced by the uptake of As and Sb by Ag and Cu wires, respectively, may be singled out.

Quite an enrichment of the isopiestic technique has been suggested by Herasymenko [64] who heated more than twenty specimens in a temperature gradient and thus greatly increased the yield of information provided by a single experiment, the volatile component being in this case cadmium. This method has been applied frequently, in particular by Komarek and coworkers to combinations of aluminium with transition metals (e.g. refs. 65 and 66). Measurements could be made down to 10^{-6} torr. At still lower aluminium pressure (10^{-8} torr), the rate of transport of aluminium from the reservoir via the vapour phase to the specimens was increased by adding NaCl, thus exploiting the transport reaction $NaCl + Al \rightarrow AlCl + Na$ [65]. The results of Komarek and coworkers show that the isopiestic technique compares well for precision with other vapour-pressure methods.

Dissociation pressure, dynamic

Apart from the so-called boiling point method, the transportation or transpiration method is a truly dynamic one. Many papers have dealt with the evaluation of the true pressures to be obtained by extrapolation of flow rates, for example when substantial diffusion effects occur [67]. As has been stated above, an advantage of the transportation technique is that in principle the dissociation pressures of all the constituents of an alloy can be determined in a single experiment. A disadvantage is that the molecular species in the vapour phase must be known. For many metals the monatomic species predominates, but in the case of substances which are evaporated as molecules it is usually necessary to establish the composition of the vapour species to obtain the vapour pressure.

A modification of the transpiration method devised by Gross et al. [68] permits vapour pressures above 1 torr to be measured and has been applied to a number of alloys. The substance of unknown activity placed in a vessel participates in a heterogeneous equilibrium in which it determines the pressure of one or more constituents in the vapour phase. Simultaneously, another known equilibrium is established which does not interfere with the former and has a well-defined partial pressure. Provided the flow through the affixed capillary is laminary, the unknown vapour pressure(s) can be obtained from the known pressure and an analysis of the condensed vapour.

Vapour transpiration has also been used in conjunction with levitation melting to measure vapour pressures of alloys at very high temperatures where the use of a container would be almost impossible because of severe chemical interaction. Mills et al. [69] have reported activity measurements on liquid titanium–vanadium alloys in the range 1800–2000 °C using the experience gained on similar measurements at 1900–2300 °C with iron–nickel alloys.

Effusion methods

With the well-known Knudsen effusion technique, the effusing vapour may be analysed, e.g. chemically, mass spectrometrically or by means of radioactive tracers. In simple cases the change of weight of the cell is determined as a function of time.

Radioactive ^{47}Cr was used by Kubaschewski and associates [70] to determine its activity in chromium alloys. In an improved form [71] of the technique, the vapour effusing from the orifice of the cell passed through a molybdenum funnel towards a molybdenum target. After the experiment, the Mo tube and target were burnt in oxygen together with the radioactive deposits. The molybdenum trioxide formed was compacted into pellets and their radioactivity compared with that of a pellet determined in the same way from an effusion experiment with pure chromium, the chemical activity being thus obtained as the quotient of two radioactivities.

Mass spectrometric analysis of vapours is indispensible whenever a reaction is involved, and various species appear in the vapour. Since mass spectrometry is costly, it is not whole-heartedly recommended for the investigation of alloys which predominantly vaporize in the form of simple metal atoms. However, there is a great advantage in the application of Knudsen-cell mass spectrometry to multicomponent alloys. Because the spectrometer analyses the gas, the relative concentrations of the components of, say, a Fe–Ni–Cr alloy are known in the form of intensities. These, related to the intensities obtained with the pure metals under equal conditions, give the chemical activities of all components in the condensed alloy. Better still, if an "inert" standard, such as silver, of known vapour pressure is added in the cell, the intensities pertaining to the metal components of the alloy investigated can be converted into vapour pressures. Whichever way is chosen, partial molar Gibbs energies of solution of all the components are obtained on a single alloy, and hence the integral Gibbs energy can be calculated. To the knowledge of the present author, the integral Gibbs energies of formation in the Fe–Ni–Cr system used by Probst et al. [72] are the first determined in this manner, thus avoiding a Gibbs–Duhem integration which requires many more measurements and still leads to unreliable results. The integral data are important because they are needed for the evaluation of phase boundaries in multicomponent systems. These first results still leave much to be desired in the way of accuracy, but a new road is opened.

If an "inert" standard cannot be found and chemical interaction seems unavoidable, a double cell system may be employed, one cell of which contains the calibrating substance. Such a device was developed by Büchler and Stauffer [73]. The twin cell in a resistance-heated block could be operated from outside and tilted in such a way that first one then the other orifice was brought into line of sight with the energy slit of the ion course. From the two measurements the activity could be obtained directly. De Maria and coworkers [74] used a similar apparatus for the determination of activities in the silver–copper system. Several such devices have been employed. However, the correct adjustment of the cells is a major difficulty and the impression remains that the multiple cell technique has not yet overcome its teething troubles.

A novel experimental technique has been developed by Hoch and coworkers [75] utilizing a triple Knudsen cell and a pure enriched isotope as the standard reference state. The alloy to be investigated is placed in one of the two effusion chambers of the triple cells and the isotopic standard in the other. The molecular beams from each chamber effuse into a third upper chamber and through a collimating hole into the ion source of a time-of-flight mass spectrometer. Since the recorded intensities are proportional to the vapour pressures within the chambers, a simple calculation gives the activity of the solute metal in the alloy. The method has been applied to the systems Ti–Cu and Ti–Al [75], for instance. Here again we have quite an ingenious device, the teething troubles of which may be overcome.

There are still more variants of the effusion method, but we must come to an end somewhere. Langmuir effusion, although it has its uses in inorganic thermochemistry, does not seem to offer much scope for alloy thermochemistry.

Finally, however, the torsion–effusion technique should at least be mentioned. It was originated by Volmer [77] who used a two-orifice cell, the orifices pointing in opposite directions on either side of a suspension fibre of known torsion constant. Vapour pressures are calculated from the distance of the two orifices, their areas, the torque and the torsion constant. Of the various applications to alloy systems, the work of Pratt and Aldred [78] deserves special mention. This type of technique does not require a knowledge of the vapour species and is valuable as a means for obtaining the total vapour pressure of a system in which a number of species are present to a significant extent in the equilibrium vapour.

CONCLUSIONS

When the present author set out to write this article, he believed he might cover most of the earlier and later experimental developments in alloy thermochemistry. Having come to the end of his story he finds that he had to omit more good ideas than he originally expected. What is still a little disappointing is the inadequate accuracy of the Gibbs energy methods—more for chemical than for physical reasons. Temperature measurement is usually a problem. More accurate data are in particular required for the calculation of multicomponent equilibrium diagrams—a new development of the greatest practical significance. The provisional answer to this problem is to employ several different methods for the same alloy system. In this respect calorimetric methods are indispensable, the temperature coefficients of the Gibbs energies being even less reliable than the absolute values. Accurate phase boundaries are also important for thermodynamic information.

This need to call on several experimental methods for mutual supplementation demands that in each case the simplest suitable method be selected. Some investigators seem to be so fascinated by the development of their particular method that they lose sight of the real objective, i.e. the provision of reliable data with the minimum effort.

Even so, to someone who has spent much of his working life on the development of experimental methods in alloy thermochemistry and the application of the results to practical problems involving chemical equilibrium, it appears that a certain stage of finality has been reached and that alloy thermochemists might turn their intelligence and their experience to other substances of similar importance such as ceramics, glasses, slags and salt systems.

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