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HIGH TEMPERATURE REACTION CALORIMETRY*

POTENTIALITIES, LIMITATIONS AND APPLICATION OF RESULTS

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ABSTRACT

Various calorimeters devised by the author and his associates during the last forty years are briefly surveyed. The type of calorimeter to be developed depends on the type of reaction to be studied. A rough distinction is between spontaneous and slow reactions, the latter requiring high-temperature or solution methods, or both. Critical remarks on the performance of the various calorimeters are made and the restrictions on their application to high temperatures are outlined. The potentialities of the Tian-Calvet calorimeter are noted.

In the second part of the paper, examples for the practical applications of thermochemical data are given. These pertain to aluminothermic types of reaction, "chill factors", thermal production of magnesium, deoxidation of iron and the calculation of phase boundaries in binary and ternary systems (Cu–Ni, Fe–Ni–Co, Fe–Ni–Cr, Fe–Ni–Cu and Fe–Co–Cr).

INTRODUCTION

The present speaker is very interested in a Kalorimetrietagung since he has dealt with calorimeters for nearly forty years. However, from the beginnning, calorimetric methods have for him not been an end in themselves but a means for the solution of practical problems involving chemical equilibrium.

The present paper will therefore be divided into two parts. Firstly, the calorimetric variants devised by the author and his co-workers will be briefly reviewed. No details will be given because many of these may be obtained from refs. 1 and 2. Secondly, practical examples, mostly of industrial interest, will be described in order to illustrate the importance of the experimental background without which such problems could not be solved.

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Originally, the present contributor started calorimetric work for sheer enjoyment of the subject. Stimulated by Oelsen's ingenious Kuheimercalorimeter, which gave good results because the water equivalent was 7 kcal, the contributor poured liquid metals, such as lead, bismuth or tin, onto alkali metals stored under rather impure argon in a graphite container within an ordinary isoperibol calorimeter. If something went wrong with the transfer of the liquid metal to the calorimeter, spectacular effects developed on the floor which may be described as inverse "Leidenfrost phenomena". Nevertheless, even today Oelsen's as well as the author's heats of formation obtained in this manner[3] are still correct to within ± 12%.

Similarly, spectacular effects occurred a little later when (as a contribution to the German scientific war effort) the present contributor was supplied with several litres of 87% H_2O_2. Rather more academic research was then devoted to it than was envisaged by the then authorities. In particular, a simple method was devised[4] to determine partial heats of solution of water in hydrogen peroxide. Unfortunately, the calorimeter (essentially a Dewar vessel) with its contents regularly exploded at an H_2O_2 concentration of 67%, a phenomenon later confirmed by the British counterpart of the present author. We are glad to say that the results obtained by so risking our lives are still valid within a few percent.

A method involving the formation and condensation of low-boiling-point chlorides (such as VCl_4) in a platinum tube within a room temperature calorimeter was developed by Von Goldbeck[5].

To understand metallurgical thermochemistry proper, one must turn to the type of reaction involved. The first rough distinction is between spontaneous, i.e., fairly to highly exothermic reactions on the one hand and slow reactions on the other. The earliest known calorimeter to deal with spontaneous reactions is Berthelot's bomb which is still an important apparatus in organic thermochemistry. As for the metallurgist, its results are to be taken *cum granum salis* because the final state of the products is difficult to analyse and side-reactions with the container material difficult to eliminate.

The heats of formation of metal halides can also be best determined by direct reaction calorimetry, as exemplified by the work of Gross (e.g., ref. 6) or the bomb calorimetry of the Argonne National Laboratory[7].

These methods have in common the small input energy required to start the reaction, that is, the quantity of heat actually measured represents most of the heat of reaction sought for. There are a few other less violent reactions suitable for direct-reaction calorimetry. The combination of iron and sulphur to form "iron sulphide" is well known to students who attend their first course in inorganic chemistry. The similar readiness of, say, BaO and MoO_3 to react harmlessly but efficiently to form barium molybdate[8] is less well known.

Other spontaneous reactions require more energy to be started. These are the strongly exothermic metal–metal or oxide–oxide reactions. When these are partly ionic, the heats of formation can be quite substantial. For Ca_3Sb_2, for instance, the value is 174 kcal mol^{-1}.

Therefore, the present contributor developed an adiabatic calorimeter operating[9] at 700°C. However, whatever its merits, it was not suitable for even moderately spontaneous reactions. Only the skill of his co-workers made it possible to obtain reasonably reliable results for the type of intermetallic compound just indicated.

Better suited for the purpose was the later developed Öfchencalorimeter[10] used to determine the heats of formation of fairly exothermic alloys, in particular the aluminides of transition metals. An intimate mixture of the component metal powders is compacted and reaction initiated by heating the mixture to reaction temperature in the calorimeter, the reaction temperature in the case of aluminides being somewhat above the melting point of aluminium. The compact is heated by a small furnace within the calorimeter until alloying takes place rapidly, the electrical energy supplied being measured and subtracted from the total heat effect observed. The method has been improved upon and systematically applied to alloys of the rare earth metals with low-melting-point metals, such as lead and thallium, by Ferro et al.[11].

However, most alloys of industrial interest do not form spontaneously from the component metals but only more or less slowly depending on temperature. A first attempt to study this type of reaction, such as the formation of iron–chromium alloys, was made by devising a forerunner of the so-called DTA method[4].

A calorimeter was then constructed in the author's laboratory to improve accuracy[12]. Still dissatisfied on this last point, an adiabatic high-temperature calorimeter was developed which has proved its value for nearly fifteen years. First built at the National Physical Laboratory, it has been rebuilt and newly equipped at the Technische Hochschule Aachen[13].

For the determination of heats of alloying, the specimen, a compacted powder mixture of two metals or more (e.g., Fe, Ni, Cr) is enclosed in an insulating box which is enclosed in a furnace. Heat is supplied to the specimen by means of an internal resistance heater, the input energy being measured by means of a precise watt-hour meter. Measurements are made of the energy required to heat the specimen adiabatically from one steady temperature (say, 700°C) to another (maximum, 1550°C). Measurements of the change in heat content of the component metals are then made over the same temperature interval in runs similar to the reaction runs. The physical accuracy is of the order of $\pm$ 50 cal g-at.$^{-1}$ of alloy. It might be slightly improved upon by using, instead of the cylindrical shape of this calorimeter, a spherical[14] or a conical one[15].

However, in high-temperature calorimetry, the errors stemming from chemical reactions are far more serious than the physical errors. Chemical interaction is bound to occur between the specimen and the container and/or the radiation shields, between the impurities and the component substances and, owing to the increased vapour pressures, with the insulations. Electronic conduction in the insulators also increases. Because of all this, the present speaker would limit the application of reaction calorimetry to little more than 1600°C, that is, steelmaking temperatures. Levitation melting to avoid contact of the specimen with its environment would be of little help, but "calorimetry in space", as suggested by Dr. Lukas at the present meeting would be a possible though very expensive solution of the problem.

The alternative is of course (dis)solution calorimetry. Aqueous solution calorimetry is of long standing and well known since the days of Thomsen and Berthelot. For the metallurgist, its application is somewhat exhausted, but the application of the principle to higher temperatures is still pregnant with future use. In this case, it is of paramount importance to keep the heats of solution small. In other words, alloys should be dissolved in liquid metals (e.g., tin), double oxides in liquid oxides (e.g., lead borate[16]) and halides in molten chlorides[17].

PRACTICAL APPLICATION OF RESULTS

The real importance of thermochemical results lies in their application to industrial problems. Heats of reaction obtained from calorimetric measurements serve to calculate heat balances. Examples are the calculation of the temperature increases in aluminothermic reactions, of the so-called "chill-factors", etc. The reason for calculating the former is to gain knowledge of the temperatures attainable, which must be above the melting points of the products so that metal and slag may separate. The classic example is the aluminothermic production of chromium,

$$Cr_2O_3 + 2Al \rightarrow Al_2O_3 + 2Cr$$

Also a long time ago, the production of uranium from its tetrafluoride by reaction with alkaline earth metals,

$$UF_4 + 2Me \rightarrow 2MeF_2 + U,$$

had to be considered. It could be shown[18] that, when Me = Ca, the desired temperature rise can be attained by starting from room temperature, whereas Me = Mg required preheating or the application of a booster.

Normally, the reactions to be considered are not as simple as indicated above because the ores to be aluminothermically reduced are composed of many more oxides, etc., than just one. However, this fact offers no difficulty to the applied thermochemist.

Chillfactors also have been calculated on a fairly wide scale[19], for the benefit of the steelmakers.

However, practical applications of chemical thermodynamics mostly require knowledge of the Gibbs energy of reaction. Where the reactants and the products of the reaction are essentially ionic, that is, to which the Third Law is applicable, the necessary data may be obtained entirely from calorimetric measurements. The information required are the heats and entropies because

$$\Delta G_T = \Delta H_T - T\Delta S_T$$

and the heat capacities, because

$$\Delta H_T = \Delta H_{298} + \int_{298}^{T} \Delta C_p \cdot \mathrm{d}T$$

and

$$\Delta S_T = \Delta S_0 + \int_{0}^{T} \frac{\Delta C_p}{T} \cdot \mathrm{d}T$$

where the 3rd Law implies ΔS_0 = zero.

If the substances involved in the reaction are in liquid or gaseous states, the heats and entropies of transformation, fusion and/or evaporation must be incorporated in these equations.

Thus, alternative thermal reactions to the electrolytic production of magnesium, for example, may be considered thermodynamically entirely on the basis of calorimetric results. Potential processes are the reduction of magnesium oxide by carbon or by silicon, represented by the equations:

$$\mathrm{MgO} + \mathrm{C} = (\mathrm{Mg}) + (\mathrm{CO}) \qquad (\alpha)$$
$$4\,\mathrm{MgO} + \mathrm{Si} = 2(\mathrm{Mg}) + \mathrm{Mg_2SiO_4} \qquad (\beta)$$
$$2\mathrm{MgO} \cdot \mathrm{CaO} + \mathrm{Si} = 2(\mathrm{Mg}) + \mathrm{Ca_2SiO_4} \qquad (\gamma).$$

where round brackets denote the gaseous state. The reactants would have to be briquetted and reacted at temperatures controlled by thermochemical equilibrium.

Reaction (α) was tested in a pilot plant at the calculated temperature of about 1900°C some forty years ago in Austria but led to severe explosions of the magnesium powder which had to be obtained by quenching and was consequently very fine.

Reaction (γ), using calcined dolomite instead of magnesia, is thermochemically superior to reaction (β). The process was suggested by Moschel and Pistor at the I. G. Farbenindustrie, also some forty years ago, and is being employed on a small scale in France and, presumably, in Canada. In Anglo-American countries it is known under the name of "Pidgeon process".

However, most problems arising in applied thermochemistry require independent information of Gibbs energies via e.m.f., dissociation pressure or similar measurements. This is why in the speakers laboratory as many Gibbs energy methods have been devised as calorimetric ones. It may be suggested that the *Kalorimetrietagung* should in future take note of such experimental developments.

It is, for instance, difficult, nay, not possible, to obtain complete thermodynamic information about dilute solutions in metals from calorimetry alone. Solubility data, e.m.f. and dissociation pressure results have to be incorporated. The application of the results is multifold.

The classic and also typical example is the de-oxidation of iron by aluminium (or other de-oxydants), represented by the chemical equation:

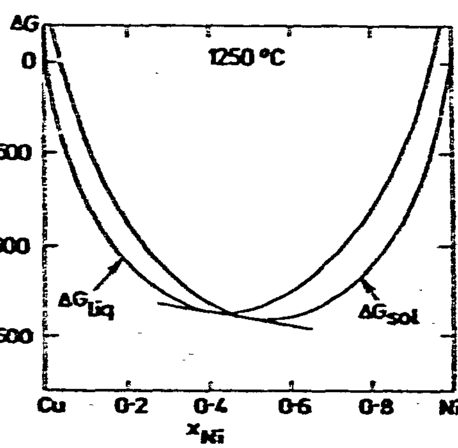
$$\mathrm{Al_2O_3} = 2[\mathrm{Al}]_{\mathrm{Me}} + 3[\mathrm{O}]_{\mathrm{Me}} \qquad (\delta)$$

where the square brackets indicate [dissolved]$_{\text{solvent}}$. Any high-melting metal may be introduced for Me, mostly of course for metals that might be refined by aluminium. Apart from oxygen, sulphur may be an important contaminant. Aluminium may have to be replaced by the rare earth metals, for instance. The number of applications of this thermochemical approach is increasing.

In the case of the de-oxidation of iron by aluminium, the thermochemists and the industrialists have disagreed for fifty years, or so, about the de-oxidation constant, $c_{\text{Al}}^2 c_{\text{O}}^3$. In terms of weight percentages the calculated figure for reaction (δ) has always been around 10^{-13}, whereas the figure found in practice has been of the order of 10^{-9}. Repeated research has shown that the calculated figure has been almost correct, but sound reasons of a kinetic nature have been put forward to account for the deviations.

These short remarks should have served to indicate another application of chemical thermodynamics to important practical problems pertaining mostly to the refining of metals or, inversely, to their interaction with their environment, container materials for instance.

Finally, the present speaker's interest in the thermochemistry of concentrated solutions may briefly be reviewed. Originally, the intention was to calculate more accurate phase boundaries in binary systems than provided by the conventional phase diagrams. Later, it was discovered that the thermochemical method offered a means to calculate phase boundaries in multi-component systems more quickly than the conventional methods could ever hope to achieve.



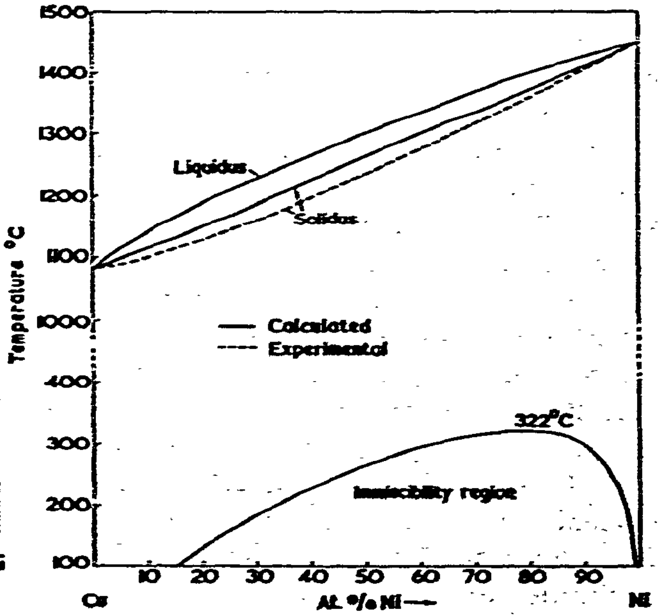


Fig. 1. Gibbs energies of formation of, respectively, liquid and solid copper–nickel alloys from liquid copper and solid nickel in cal g-at.$^{-1}$ at 1250 °C.

Fig. 2. Equilibrium diagram of the system copper–nickel.

As an example of the former, the calculation of the solidus–liquidus gap in the system copper–nickel[20] is shown in Fig. 1, which also indicates the graphical method of phase boundary determination from thermochemical data. Heats and Gibbs energies of mixing are determined for the solid and liquid alloys, Gibbs energies calculated for various temperatures between the melting points of the metals and related to solid nickel and liquid copper. Figure 1 depicts the ΔG (formation) vs. concentration curves at a selected temperature and shows how, by drawing the tangent to the curves, one may obtain the concentration of the phase boundaries at that temperature, because it is always the phase or the mixture of phases with the lowest chemical potential (the lowest Gibbs energy of formation) that is stable. The procedure is repeated at other temperatures and the thermochemical data adjusted so that the experimental liquidus curve, which is usually the more accurate, is reproduced. Figure 2 shows the calculated solidus curve together with the experimental one. It may be seen that the experimental curve is too low owing to the difficulties in obtaining equilibrium on thermal cooling curves—an observation first pointed out by Wagner[21] with respect to the silver–gold system.

Also drawn in Fig. 2 is the boundary of the miscibility gap. Such miscibility gaps are not easily determined by conventional methods because of the length of time of equilibration. In the case of Cu–Ni, the immiscibility region is, however, hypothetical because the rate of separation into two solid solutions is estimated to be of the order of millions of years, but, where it is in the order of the life of plant, the thermochemical method is indispensable.

Other examples of calculated binary equilibrium diagrams may be seen from a survey paper[22].

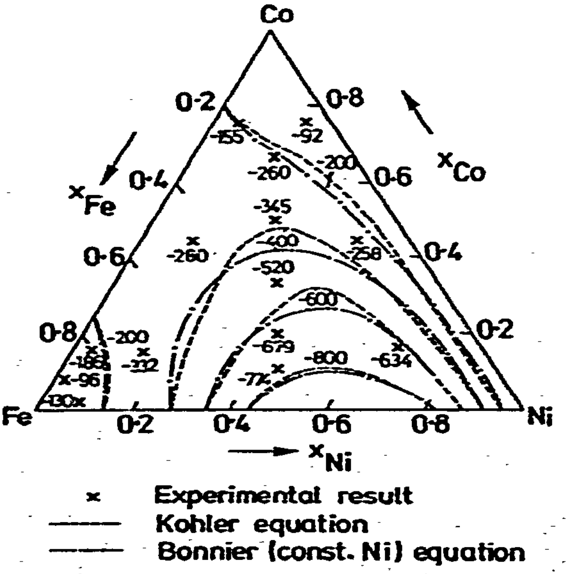


Fig. 3. Heats of mixing, in cal g-at.$^{-1}$, in the system iron–cobalt–nickel as measured calorimetrically and calculated with the Kohler and Bonnier equations, respectively.

The second advantage of the thermochemical over the conventional method of phase diagram investigation already mentioned is as follows. Several semi-empirical methods for the extrapolation of the thermochemical properties of binary into ternary and higher concentration ranges have been suggested, for instance by Kohler[23] and Bonnier[24]. They are semi-empirical in the sense that they are based on the popular regular-solution model which has only restricted validity in alloy or similar systems. Nevertheless, these methods give adequate results as has been demonstrated by comparisons with experimental values[25]. As an example, Fig. 3 shows the heats of mixing in the system iron–cobalt–nickel as measured calorimetrically on the one hand and the calculated iso-enthalpies after Kohler and Bonnier, respectively, on the other[26]. Similarly, good agreement has been found for other systems[25], not only for the enthalpies but also for excess Gibbs energies. Unfortunately, not every method (there are at present about six or seven available—all very similar) produces this type of agreement for all systems so far studied—sometimes the one, sometimes the other. This problem still has to be studied, and an international group called CALPHAD under the chairmanship of L. Kaufmann is engaged in the promotion of the subject. Nevertheless, CALPHAD has demonstrated that reasonably good phase relationships in ternary and even quaternary systems can be produced, not only for alloys but also for ceramic materials and halides. Experimental work must continue to improve the methods of calculation.

The first attempt to calculate phase boundaries in a ternary system in this manner was made by the present author thirteen years ago[27]. The system selected was that of the practically important iron–nickel–chromium alloys. Even then, the results were promising. The graphical mode of evaluation was cumbersome because in the ternary concentration ranges the ΔG–x_i curves become Gibbs energy surfaces and the tangents tangent planes. Further progress would have been slow if it had not

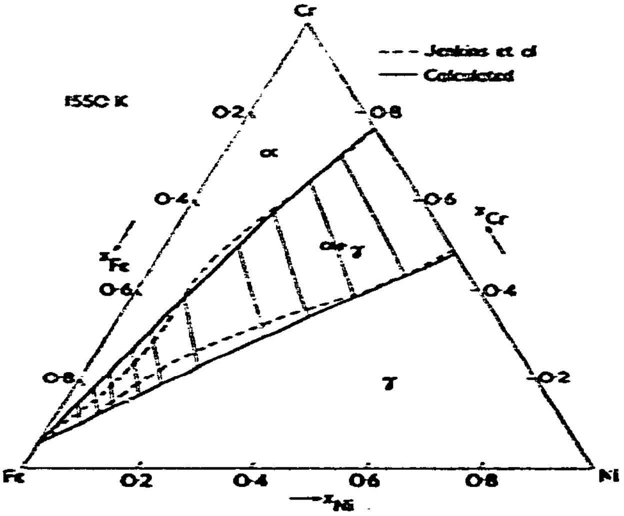


Fig. 4. Calculated and experimental phase boundaries of the austenite–ferrite equilibrium in the system iron–nickel–chromium at 1277°C.

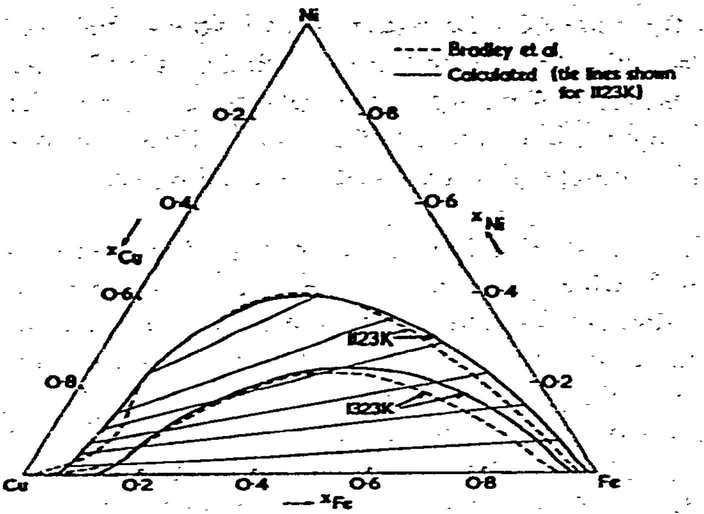


Fig. 5. Calculated and experimental phase boundary of the miscibility gap in the system iron–nickel–copper at two temperatures.

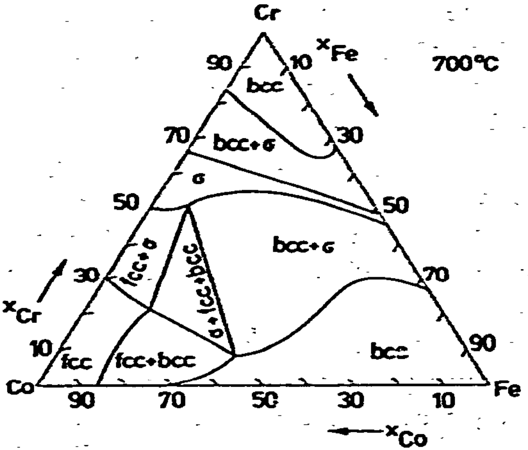


Fig. 6. Calculated phase boundaries in the system iron–cobalt–chromium. Isothermal section at 700°C.

been for the timely arrival of the computer. Its application to the problem requires, however, the conversion of the experimental ΔG values into formulae (so far, mostly polynomials), as indicated above, involving a certain loss of accuracy.

Today, many calculated phase boundaries in ternary metallurgical systems are available. Out of this large number, only two examples are given here. Figure 4 shows an isothermal section of the equilibrium between the face-centred-cubic and the body-centred-cubic phases in the system iron–nickel–chromium, the experimental phase boundaries being also indicated[28]. Further calculations are available, in particular at lower temperatures where the mechanically undesirable σ phase appears.

The second example (Fig. 5) pertains to the miscibility gap in the iron–nickel–copper system at two temperatures [28]. Again, the calculated and experimental phase boundaries are shown. Agreement would be better if the experimental investigators had chosen more reliable data for the binary Cu–Fe system. As a matter of fact, the calorimetric results in the ternary solutions beyond the miscibility gap[28] have eventually been used to calculate the heats of mixing in the metastable Cu–Fe solid solutions—employing the extrapolation methods above "in reverse"[20]. By incorporating other relevant data, the entropies of mixing of these metastable alloys could also be established.

The latest work being done in the author's laboratory along these lines concerns the system iron–cobalt–chromium[15], which is important because of its apparent similarity tc the iron–nickel–chromium system. The results of a provisional calculation of the phase boundaries at 700°C are shown in Fig. 6. However, work on this system is being continued and final results to be awaited.

A further practical application of calorimetry in metallurgy that should be encouraged is the use of the Tian-Calvet or a similar calorimeter at high temperatures to the determination of heats of solution of gases in metals or "compounds". Because of the high sensitivity of the thermopile, it is possible to add very small quantities of gas to the metal in the calorimeter and thus to determine quasi-partial heats of solution. The first example of this type was the measurement of the partial heat of solution of oxygen in the UO_{2+x} phase by Gerdanian and Dodé[30] at 1100°C. The UO_{2+x} phase has rather a wide range of homogeneity. It should be of particular interest to determine the heats of solution of gases in metals where the solubility is relatively small. All such solubility vs. temperature curves have so far been obtained by direct methods relying on second-law evaluation for the extrapolation to lower temperatures, which are normally the practically important ones. An experimental value for the heat of solution at some kinetically convenient temperature would make the extrapolation far more reliable.

Commercial Tian-Calvet calorimeters with temperatures of operation up to 1000°C are available. In many cases, this temperature suffices for the attainment of equilibrium, and the temperature limit has not yet been reached. At the National Physical Laboratory, a thermopile calorimeter has been constructed by W. A. Dench to operate up to 1150°C but not yet employed.

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