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Evolution and application of high-temperature reaction calorimetry at the University of Chicago from 1952 to 2000

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I first came to the University of Chicago in the fall of 1947 with a degree in chemical engineering from the Norwegian Technical University (NTH) in Trondheim. My final graduation there was delayed from 1942 to 1946 by World War II. I started my work in Chicago at the new Institute for the Study of Metals which had been founded there in 1945–46. I recently published a brief history of the first 15 years of this institute in the Journal of Metals [1].

I came to the ISM because I was interested in studying the systematic aspects of the solution chemistry and thermodynamics of the formation of binary alloys. In 1947 the ISM was unique in the USA in having a broad-based interdisciplinary faculty with members drawn roughly equally from the fields of physics, chemistry and metallurgy.

The first director of the new institute was the distinguished metallurgist, Cyril Stanley Smith, who had played a major role in the work of the Los Alamos Laboratory in 1943–45. When I was asked by Cyril what I planned to do, I answered that I wanted to attempt to understand the work of Hume-Rothery, Raynor and their co-workers from the point of view of solution chemistry and thermodynamics.

My first 3 years at the institute from 1947 to 1950 were largely devoted to electrochemical studies of binary liquid alloys where gold was one of the two components. My early experiences with the e.m.f. method using liquid electrolytes led me to recognize two important facts

1. This method, powerful as it is, sometimes does not allow a reliable separation of the measured Gibbs energies into their appropriate enthalpy and entropy contributions.
2. This method, since it requires a significant electrochemical difference between the two components, is not suitable for thermodynamic studies of a wider range of binary alloy systems.

I also considered the possibility of using vapor pressure measurements. This is of course a general thermodynamic method, which in principle can be applied to any solution system. However, I realized that vapor pressure studies of many alloy systems would require experimental work at very high temperatures. For this reason I expected that heat and entropy data derived from vapor pressure measurements might often be associated with significant experimental errors.

I concluded that my experimental approach to the systematic study of the thermodynamics of binary alloys must be based on calorimetry, and more specifically on high-temperature mixing and reaction calorimetry. While I recognized that calorimetric measurements would not give me all the desired thermodynamic information, I inferred that in most cases it would provide the leading terms in the Gibbs energies of alloy formation. My experiences in using this method for nearly 50 years fully support this conclusion.

When I first started my work in the area of high-temperature reaction calorimetry in 1952, I of course first searched the earlier literature. I found that one of the most significant earlier workers in this field had been Masuo Kawakami at Tohoku University in Japan. In the period 1927–30 he had published heat of mixing information for a number of binary liquid alloys. He had worked over a wide range in temperatures, ranging from binary alkali metals near 110°C to binary noble metal alloys at 1200°C [2–4].

However, a more recent and more interesting venture

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into alloy calorimetry had been initiated in 1939 by Kubaschewski and Walter in Stuttgart, Germany [5]. In my first figure, I present a schematic diagram of the calorimeter published by Kubaschewski and Walter (Fig. 1).

Note that the central body and the surrounding jacket of this calorimeter are both made from Thermax, a high-temperature alloy resistant to oxidation, but not a very good heat conductor.

This calorimeter was described by the authors as an adiabatic reaction calorimeter for work at temperatures up to 700°C. The calorimeter was used for direct synthesis of intermetallic compounds formed by relatively low-melting metals. Compressed pellets of a mixture of the powders of the two metals were dropped into the calorimeter, usually from room temperature, and an attempt was made to maintain adiabatic conditions, i.e. a zero temperature difference between the central calorimetric body and the surrounding jacket. Needless to say, this was not easily achieved, since the temperature of the central calorimeter block would first fall, due to the heat content of the dropped in sample, and then rise again due to the heat evolved in the chemical reaction between the two metals.

A general review of what was known about the thermochemistry of binary alloys in the early 1940s was published in Germany in 1943 in a book co-authored by Weibke and Kubaschewski [6]. After the war this book was reprinted in the US in 1948 by J.W. Edwards (Ann Arbor, MI, USA). I acquired a copy in April 1950.

Reviewing this book in 1950–51, I thought that I might be able to improve on the adiabatic calorimeter of Kubaschewski and Walter by constructing both the calorimeter proper and the surrounding jacket from pure aluminum. This would improve the thermal conductivity of both calorimeter and jacket by a large factor, and, I hoped, make it possible to improve significantly on the adiabatic performance of the calorimetric system. However, due to the low melting point of aluminum, I would be limited to operating at temperatures below about 500°C.

I struggled with this problem for some time before I concluded that precise adiabatic reaction calorimetry even at 500°C would be very difficult to achieve. And, since I was looking forward to future work at significantly higher temperatures, I concluded that the increasing importance of heat transfer by radiation would make adiabatic reaction calorimetry at these higher temperatures a real fight against nature. For these reasons I was satisfied to construct, instead, a new mixing and reaction calorimeter of ‘conventional’ or ‘quasi-adiabatic’ design. This apparatus is shown schematically in Fig. 2, and is described in detail in a paper which was published early in 1955 [7]. This paper

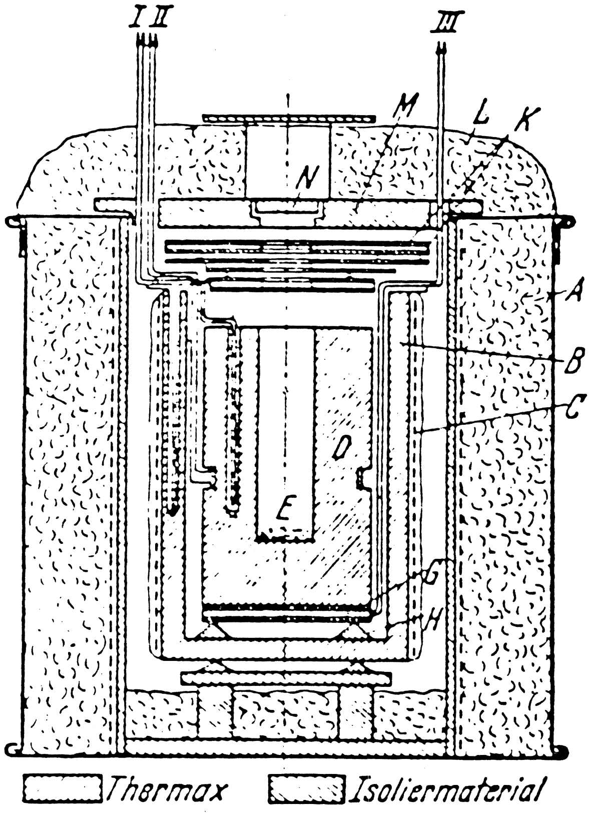


Fig. 1. Schematic diagram of the high-temperature calorimeter of Kubaschewski and Walter [5].

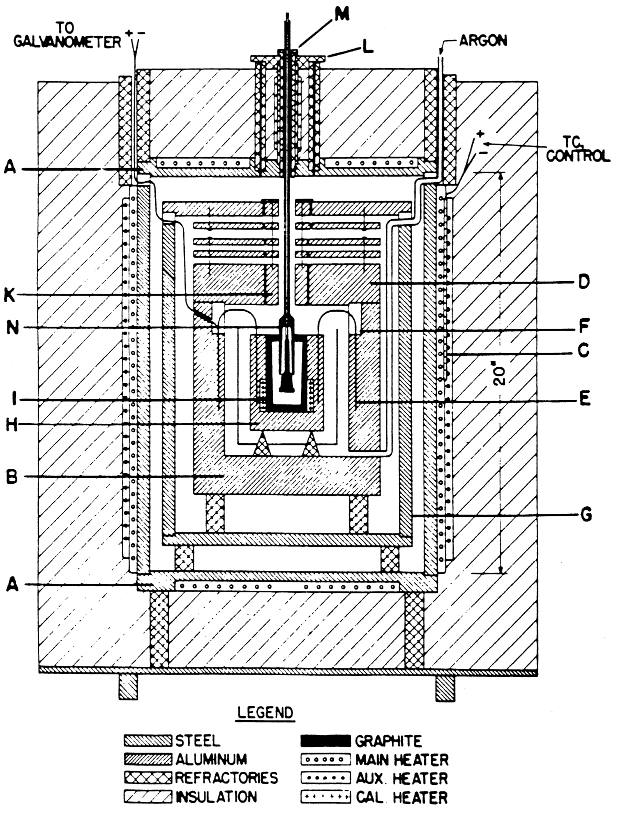


Fig. 2. Schematic diagram of the first high-temperature calorimeter built by the author [7].

also reported our results for the first system we studied, the liquid system lead–tin at 350°C and 450°. You will readily recognize that the design of this calorimeter was influenced very strongly by the earlier calorimeter of Kubaschewski and Walter.

We operated this new calorimeter very successfully at temperatures up to 450°C for about 10 years. The small temperature difference between the central calorimeter block, which contained an easily removable graphite crucible, and the surrounding aluminum jacket was based on a 16-junction chromel–alumel thermopile connected to a sensitive galvanometer. The calorimeter was calibrated using a cylindrical electrical heater which surrounded the graphite crucible.

In typical mixing and solution experiments, which usually lasted 30–40 min the temperature corrections due to heat exchange with the surrounding isoperibol jacket, were of the order of 10–15% of the corrected temperature change. However, the magnitude of these temperature corrections could be determined to about ±1% by numerical integration of the temperature–time curves. The overall precision of the calorimetric measurements were also of the order of ±1%.

Using this calorimeter at 350°C and 450°C we carried out precise measurements of the heats of mixing for a large number of binary liquid alloys formed between low-melting cheap metals such as lead, tin, indium, bismuth, cadmium and zinc. In each experiment we used a total of 0.5–1 g atom of the two metals. Much of our early work is reported in Ref. [8], which covered the binary liquid systems bismuth–lead, cadmium–lead, cadmium–tin and zinc–tin. A more general report on what we had found out about the heats of mixing of low-melting binary alloys was reported to the metallurgical community in the fall of 1957 at the ASM Symposium in Chicago on Liquid Metals and Solidification [9].

While I was struggling with the development of my very first high-temperature calorimeter in 1952 there appeared in the Journal of Metals a paper by Ticknor and Bever [10] entitled Heats of Solution of Group IB Metals in Liquid Tin.

Bever and his many co-workers used this equipment for a variety of different projects. However, from the point of view of alloy thermochemistry, the most significant aspect of their work undoubtedly was that they invented and developed the new experimental technique of liquid tin solution calorimetry. Over the years this technique has been used by many students of alloy thermochemistry, and it has contributed very extensively to what we now know in this field. Even so, since the construction of Michael Bever's calorimeter was based on the Dewar principle, it was restricted to operate at relatively low elevated temperatures. For this reason it has had little influence on developments in reaction calorimetry at much higher temperatures.

Although our own first calorimeter was not specifically designed for tin solution calorimetry, we found that it could readily be applied in this mode. In fact, we used it in this way for a number of years. Note, however, that unlike Bever et al., who always introduced their samples from room temperature, or more frequently from 0°C, our samples were always introduced into the liquid tin solvent from the hollow graphite stirrer, i.e. from the temperature of the calorimeter.

In our applications of our calorimeter for tin solution calorimetry we emphasized systematic work on a series of Hume-Rothery type solid solutions and intermetallic compounds. A summary of our early results is given in my Norwegian doctoral thesis which was submitted to NTH in 1956 [11]. Some of these results, along with some further data on other Hume-Rothery type systems, were also presented to the Symposium on Metallic Solid Solutions organized by Professors Friedel and Guinier at Orsay, France in 1962 [12].

During the academic year 1956–57 I was a Visiting Professor at the Institute of Inorganic Chemistry at the Norwegian Technical University. While I was there, I was fortunate to have as my close office neighbor my former teacher, Professor Hakon Flood, who was the founder of the important Norwegian School of Molten Salt Chemistry. I soon realized that high-temperature reaction calorimetry might prove a very useful new tool leading to a deeper understanding of the thermodynamic properties of mixtures of molten salts. However, the calorimeter which we had used in our work on binary alloys would not be suitable for work on molten salt mixtures.

Fortunately, at this time an important new book on the principles and practice of microcalorimetry co-authored by Calvet and Prat had appeared [13]. I obtained my own copy in 1958, and I immediately started thinking about how to design a twin microcalorimeter suitable for the study of binary molten salts. Since all the simple monovalent nitrates melt below 450°C, I concluded that our first high-temperature microcalorimeter could also be constructed from pure aluminum. And I assumed that a calorimeter operating at temperatures up to about 450°C would be useful for studies of binary alkali nitrates, for mixtures of the alkali nitrates with other low-melting nitrates such as silver nitrate and thallium nitrate, for solutions of some alkaline earth nitrates in the alkali nitrates, for solutions of alkali halides in the alkali nitrates, etc. In due course this all proved to be the case.

With the assistance of Paul Dolmer and of the Central Machine Shop of the Physical Sciences Division of the University of Chicago we built our first successful high-temperature twin microcalorimeter in 1959. This calorimeter is described in [14]. Figs. 3 and 4 give some details of the construction and operation of this calorimeter. Fig. 5 shows our results for the first binary molten salt system which we studied, the enthalpies of mixing and the enthalpy interaction parameters for liquid mixtures of $NaNO_3+KNO_3$ measured at 350°C and 450°C.

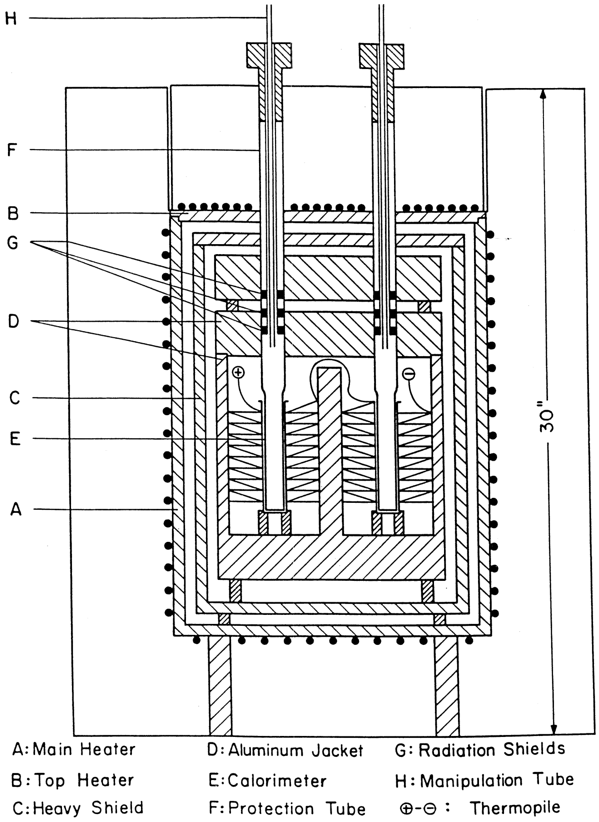


Fig. 3. Schematic diagram of the first Calvet-type twin calorimeter built by the author [14].

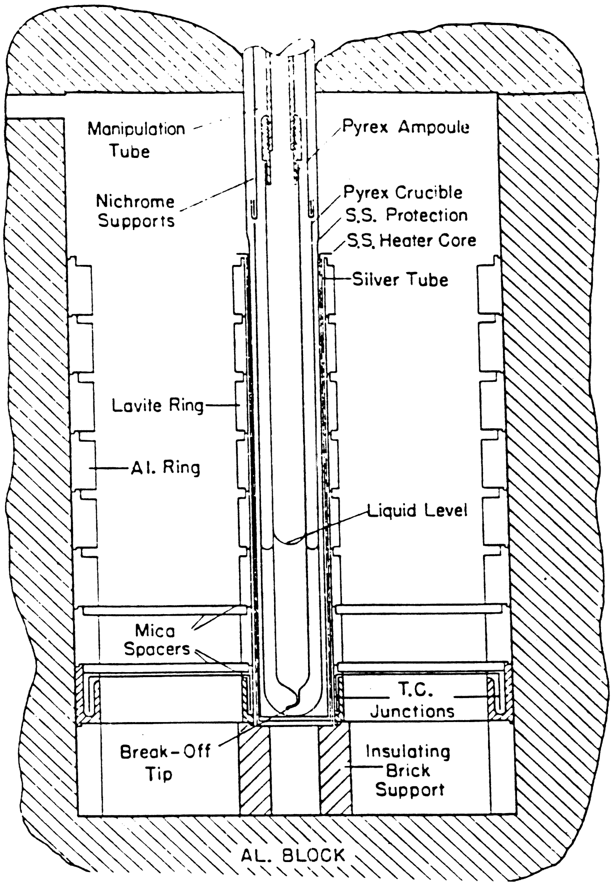


Fig. 4. More detailed sketch relating to the actual operation of the first Calvet-type calorimeter used in the mixing of two molten nitrates at 350°C and 450°C [14].

Our first Calvet-type twin high-temperature microcalorimeter had a thermopile with 96+96 chromel–alumel thermocouples; its twin construction in large measure eliminated most problems associated with precise temperature control. The precision achieved with this new calorimeter was roughly comparable to what we had achieved earlier with our quasi-adiabatic unit. However, the new calorimeter allowed a wide range of different kinds of experiments to be performed, and it could be used for very much smaller samples. It was used in my laboratory for more than 20 years for innumerable calorimetric experiments on very many different kinds of materials.

In the course of these 20 years it was used only to a limited extent for calorimetric work on liquid alloys. It found its most important early application in our studies of the thermochemistry of binary solutions of a wide range of low-melting molten salts. One of my principal collaborators in our work using this calorimeter during the 1960s was Dr. Susan V. Meschel. Susan returned to my laboratory again in 1990 and has been one of the principal organizers of this symposium.

Susan's work on solutions in liquid nitrates ran out with the 1960s. However, during the 1970s this twin calorimeter for work below 500°C got a new lease on life as the basic unit in our calorimetric and equilibrium work on solid solutions of hydrogen and of deuterium in metals.

We will come back to these investigations later. In the meantime let us consider our study of the mixtures of nearly all the binary alkali nitrate systems. These studies were carried out at 345°C and 450°C [15] in collaboration with my graduate student Lee Hersh. (In his thesis he later on studied the corresponding mixtures of the alkali chlorides, alkali bromides and alkali iodides [16]. Systematically, there is a great deal of similarity between all these binary molten salt mixtures.)

In Fig. 6 I show our results for $LiNO_3$–$RbNO_3$ at 345°C taken from [15].

Note that this binary has a much stronger exothermic interaction than our previously presented $NaNO_3$–KNO_3. This stronger interaction explains the parabolic shape of the enthalpy interaction parameter, $\Delta H^M/X(1-X)$. The deviation from the straight line, which we earlier found for $NaNO_3$–KNO_3, can be accounted for quantitatively by assuming a non-random arrangement of the two cations in

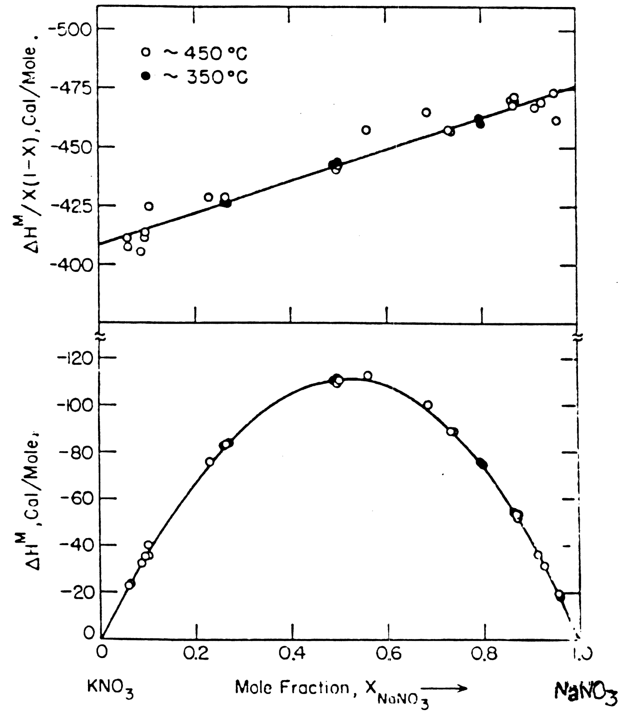


Fig. 5. Enthalpies of mixing ΔH^{M} and the enthalpy interaction parameters ($\Delta H^{M}/x[1-x]$) for the binary system $NaNO_3$–KNO_3 measured at 350°C and 450°C [14]. Note the absence of a significant dependence on temperature.

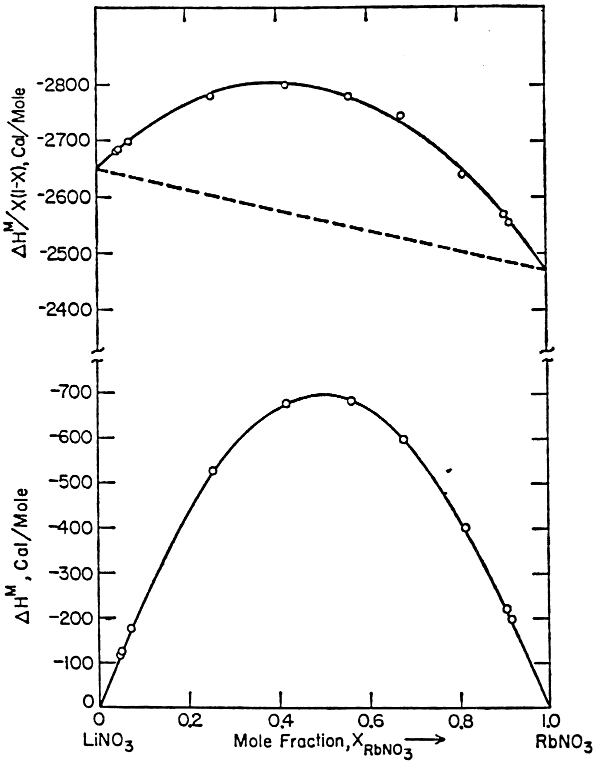


Fig. 6. Enthalpies of mixing and enthalpy interaction parameters for the binary liquid system $LiNO_3$–$RbNO_3$ measured at 345°C [14].

the mixture; i.e. by the short range order in the binary system as estimated from quasi-chemical theory [15].

In 1960–61, when this study was just completed, our institute had an invited colloquium speaker who took a special interest in our results. The speaker was Howard Reiss, then associated with Atomics International. A few years later he moved to UCLA. Also involved in our discussions with Howard Reiss was J.L. Katz, a graduate student who worked with Stuart Rice. But at the time Stuart Rice was in Europe.

As a result of this visit by Howard Reiss a paper was published the following year which had the title Theory of the Heats of Mixing of Certain Molten Salts [17]. I will limit myself to quote the abstract of this paper: “A theory is presented for the heats of mixing of fused salts. This theory is based on an assumption made in earlier work that the short-range potential between ions of like sign can be ignored. The development is essentially a conformal solution treatment modified to apply to the special potentials involved in fused salts. The predicted form for the heat of mixing agrees with that discovered by Kleppa and Hersh in connection with measurements on mixtures of alkali nitrates.”

In Fig. 7 I give a figure from this paper.

In this theory λ_1 represents the sum of the ionic radii for salt 1 and λ_2 is the same quantity for salt 2. By theoretical analysis this paper arrived at the expression

$$\Delta H^{M} = h_{12} = X_1 X_2 \Omega(\mathrm{T,P}) \left[\frac{\lambda_2 - \lambda_1}{\lambda_1 \lambda_2} \right]^2$$

This equation is the basis for the plot in Fig. 7. The term Ω is an unevaluated complicated integral.

I will omit any further discussion here of the extensive work on solutions in liquid nitrates which we did using this new calorimeter. Instead I will outline our development of a series of new microcalorimeters suitable for work above 450°C.

Our first objective was to design and build a new Calvet-type twin calorimeter suitable for operation at temperatures up to 700–800°C, i.e. for work on solutions of liquid alkali chlorides, bromides and iodides. We again wanted a metallic body with good heat conductivity and with good resistance to atmospheric corrosion at 700–800°C. Since we could not afford to build this calorimeter from pure silver (an option which was later pursued by Joe Darby at Argonne National Laboratory [18]) we built our second Calvet-type twin calorimeter in 1961–62 from pure nickel. Nickel is a relatively poor heat conductor compared to copper, silver and aluminum, but a very much better conductor than nichrome, inconel and other refractory alloys.

Fig. 8 shows an early picture of our new nickel block calorimeter taken while it was still under construction. The block is 10″ in diameter and weighs nearly 300 lbs. The

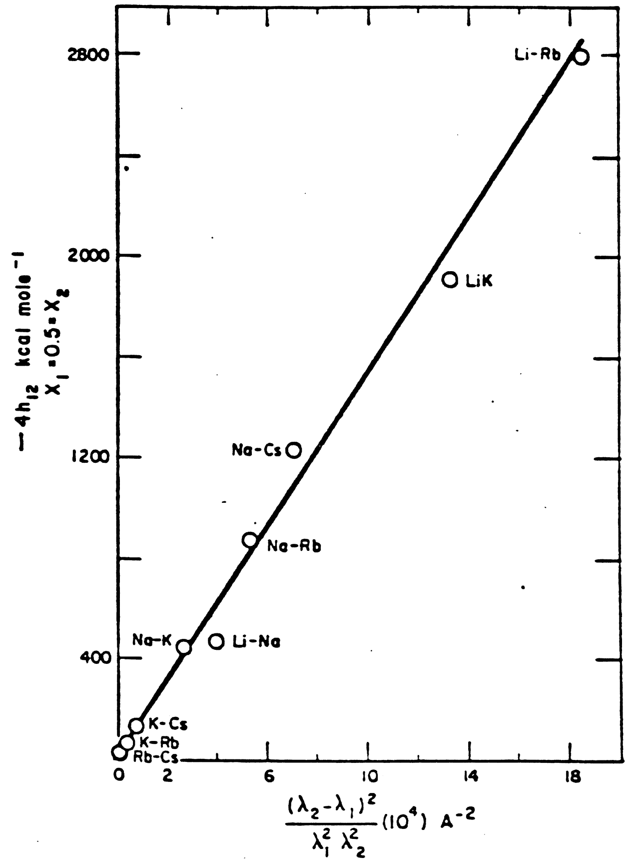


Fig. 7. Plot of 4 $\Delta H^{\frac{M}{0.5}} = 4h_{12}$ against $\left[\frac{\lambda_2 - \lambda_1}{\lambda_1 \lambda_2}\right]^2$ from [17].

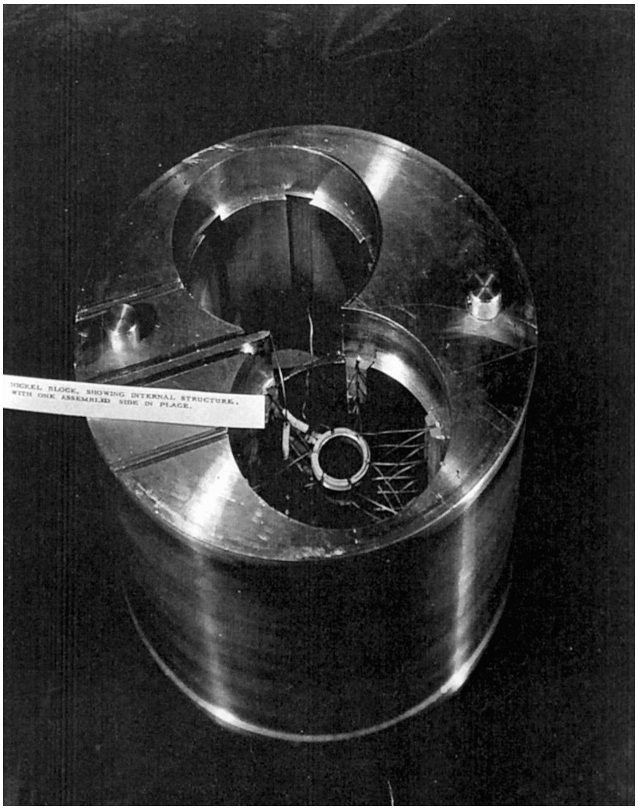


Fig. 8. Photograph of the nickel calorimeter block (with one of the twin calorimeters in place) taken from our second Calvet-type calorimeter during its construction in 1961–62.

nickel block calorimeter was for a number of years our principal twin unit for calorimetric work up to 700–800°C. It was usually maintained near 700°C in order to limit oxidation. During its more than 30-year life, the nichrome wired furnace of this calorimeter had to be rebuilt only once.

Originally the thermopile of this twin calorimeter was made from chromel and alumel wires. However, after about 1 year at 700°C oxidation of the wires made it necessary to rebuild it. It was replaced by a thermopile made from Pt and Pt13Rh wires. At 700–800°C this thermopile essentially lasts forever.

In order to work at temperatures above 800°C we first abandoned any attempt to construct a twin unit. It is so much easier to build a system with cylindrical symmetry. In 1965 we built our first cylindrical calorimeter for work up to 1100°C. It was constructed from a system of pure Al_2O_3 cylinders which surrounded the central calorimetric unit. A picture of this calorimeter assembly taken during the past year is shown in Fig. 9. This picture also shows the pure Pt foil which surrounds the Al_2O_3 cylindrical unit. This foil was grounded in order to protect the output of the thermopile from short term electrical fluctuation in the electrical heating system.

The cylindrical unit of this calorimeter was slightly less than 6″ in outside diameter. It was heated by our first Pt40Rh resistor furnace. The Al_2O_3 core of this furnace was 6″ in inside diameter and 4′ long. With this furnace we were in principle able to attack any calorimetric problem up to about 1200°C. However, since the ‘liner’ of the calorimeter, which contained our experimental samples, was made from fused silica, we were in fact limited to temperatures below about 1100°C.

After our experiences with the single unit Al_2O_3 calorimeter, we finally had the courage to build a twin unit from Al_2O_3. It was constructed from 1″ thick alumina discs which generated a 20″ long alumina unit which is shown in Fig. 10. It was heated in a cylindrical heater which also had top and bottom planar heaters, all wired by Pt40Rh heating elements. A schematic diagram of the calorimeter with the three heaters is shown in Fig. 11.

This unit was built in the early 1970s and was usually maintained at 800–1100°C. However, with the passage of time we noted that the sensitivity and precision of this calorimeter declined very significantly. Finally, after the calorimeter had been maintained at these high temperatures for more than 10 years, we disassembled the furnace and the calorimeter in 1985. We arranged to have an analysis of our thermopile which is shown in Fig. 12. The sensitivity was greatly improved by constructing a new thermopile from Pt and Pt13Rh.

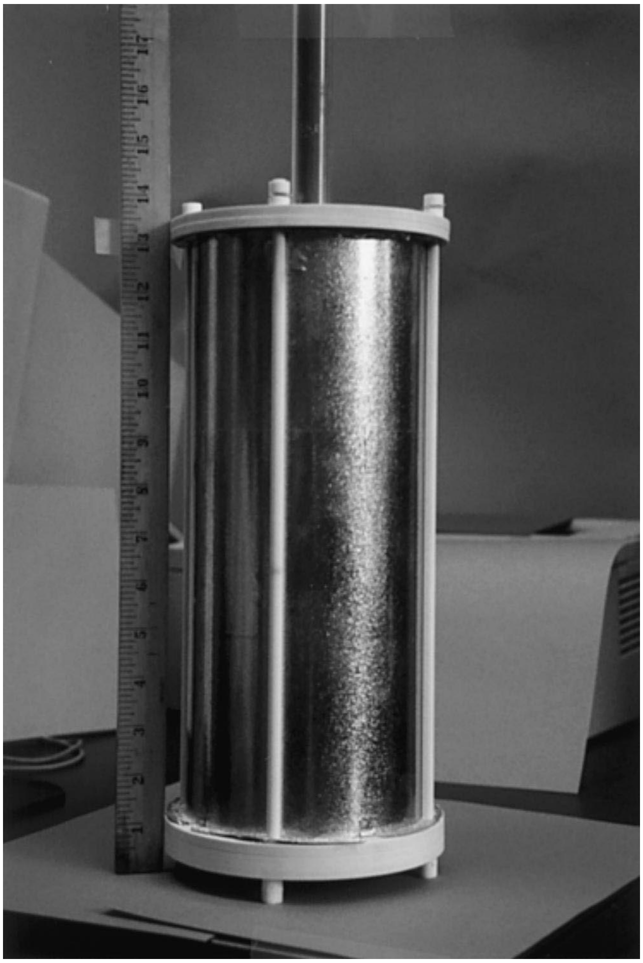


Fig. 9. Photographic picture of our single unit Calvet calorimeter built from an assembly of alumina refractory cylinders in 1965. The photograph was taken after the calorimeter was dismantled in the 1990s.

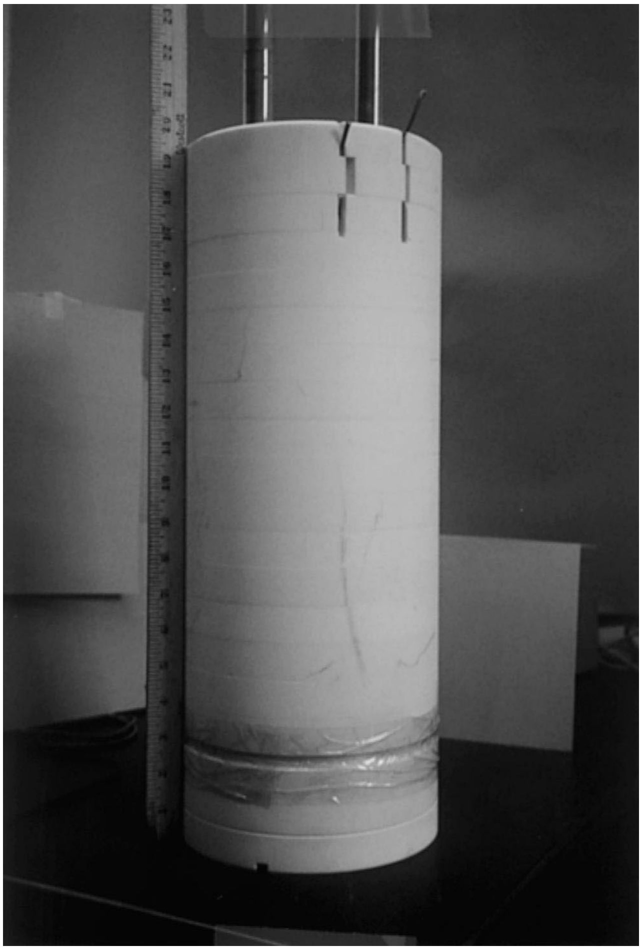


Fig. 10. Photographic picture of our twin Calvet-type calorimeter built from 1″ thick alumina discs in the early 1970s. The photo was taken after the calorimeter was dismantled in the 1990s.

Until 1988 we were satisfied with operating our calorimeter below 1100°C. This temperature was acceptable for work even on the thermochemistry of very refractory compounds such as e.g. LaB_6 which has a melting point near 2700°C. In these experiments we used the new technique of solute–solvent drop calorimetry. The origin and nature of this technique is presented in my Hume-Rothery Award lecture, published in 1994 [19]. However, we soon found that enthalpies of formation for many of the refractory compounds which we had studied by the solute–solvent drop method could be obtained more readily by direct synthesis calorimetry as reported by Gachon who used a modification of the commercial SETARAM calorimeter [20].

However, since we did not want to cycle our high-temperature calorimeter between room temperature and high temperature on a day to day basis, we proceeded to build a new single unit calorimeter for continuous work at temperatures up to 1200–1250°C. This calorimeter is somewhat related to the SETARAM unit. However, its reaction chamber has a much larger diameter than this unit. A schematic diagram of the central section of this calorimeter is shown in Figs. 13 and 14, taken from the paper of Topor and Kleppa [21] published in 1989. This type of calorimeter has been the principal equipment in our work on high-temperature direct synthesis calorimetry which we have pursued intensely during the past 10 years. Reports on these investigation will be given in the papers by Meschel and Kleppa [22] and Guo and Kleppa [23] which will be presented later in this symposium.

We worked fairly intensely in the area of molten salt thermochemistry for 15–20 years. In this period I presented a large number of reviews of our investigations starting with the Faraday Society Discussion in Liverpool in 1962 and the IUPAC Symposium on Thermodynamics and Thermochemistry in Lund, Sweden in 1963 [24,25]. My most recent review of our work on molten salt chemistry was presented to the NATO sponsored conference on molten salts organized by Gleb Mamantov in Italy in 1986 and published in 1987 [26]. This review gives the names of my many students and post–doctoral research associates in this area listed in alphabetical order: B.K.

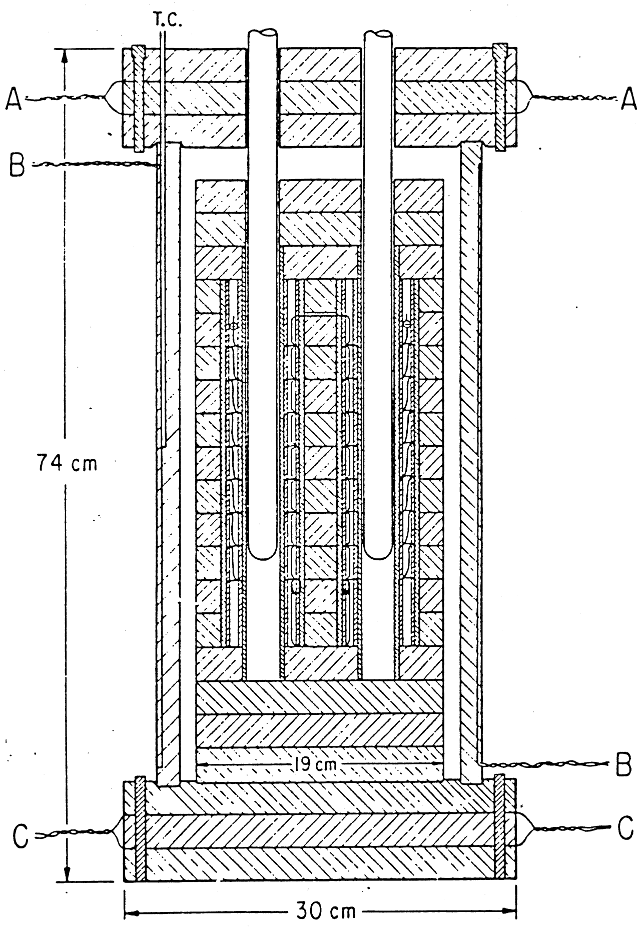


Fig. 11. Schematic diagram of our twin alumina Calvet-type calorimeter enclosed by its cylindrical heater and its twin planar heaters, all wired by Pt40Rh heating elements.

Andersen, P.G. Dantzer, L.S. Hersh, J.L. Holm, K.C. Hong, S. Julsrud, J.L. Katz, R. Clark King, H.C. Ko, F.G. McCarty, M.E. Melnichak, S.V. Meschel, F. Müller, A. Navrotsky, T. Ostvold, G.N. Papatheodorou, S. Sato, J.M. Toguri, M. Wakihara, H. Yokokawa, and T. Yokokawa.

I cannot say very much here about the work of each of these individuals. Some of them are present, and can speak for themselves. However, I should like to mention that Reatha Clark King, who was my first graduate student, was involved in important work both on alloy solid solutions [27], on intermetallic compounds [28], and on molten salts [29].

My first postdoctoral collaborator was Toshio Yokokawa, who is now a retired professor of chemistry at Hokkaido University in Japan. While working in my laboratory he was also involved in several different projects, from mixtures of binary liquid alkali metals [30] to our very first studies of liquid oxide systems [31]. These last investigations led us to develop the important new technique of oxide-melt solution calorimetry. Toshio was my co-author in the very first paper where this technique was applied, a report on the enthalpy of transformation of δ-Al_2O_3 to α-Al_2O_3 [32]. Another early collaborator was Alex Navrotsky whose Ph.D. thesis in 1967 reported on the thermochemistry of the spinel family of double oxides [33,34]. Of course, she has by this time become the world authority on applications of oxide melt solution calorimetry.

Alex was also very important in promoting my own long term collaboration with my now retired colleague, Professor Robert C. Newton in this general area. Newton is an expert on high-pressure studies of minerals and their equilibria. Our collaboration in oxide melt solution calorimetry, which lasted for more than 20 years, was a very productive one. It also brought a number of good scientists to our laboratory.

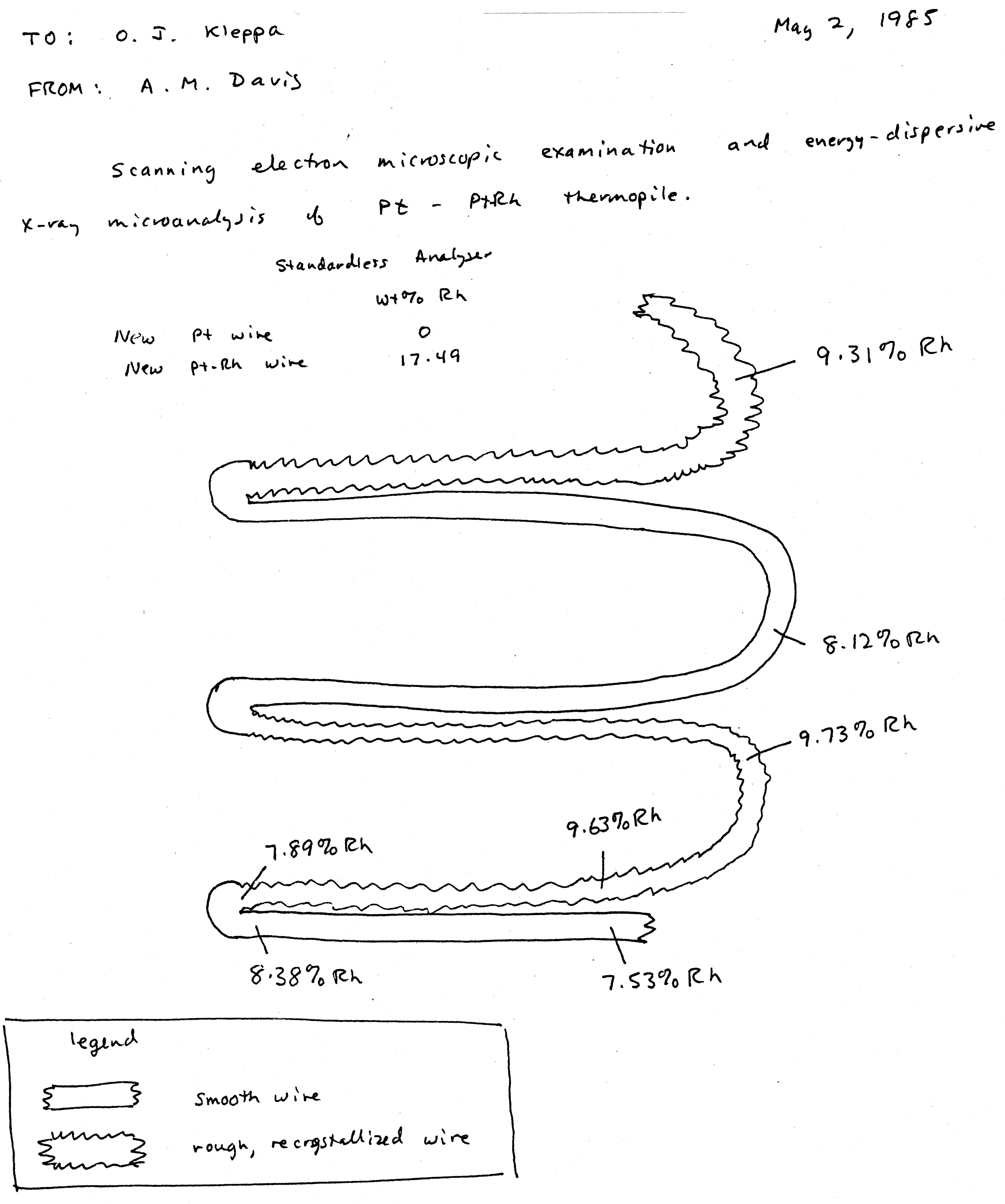
Other collaborators started work in my laboratory on molten salt chemistry, but then in due course moved on to other fields. A good example is Pierre Dantzer, who first came to Chicago to work in molten salt chemistry. However, after about 1 year he got involved in our attempts to apply high temperature calorimetry combined with equilibrium work to metal–hydrogen and metal–deuterium systems. This proved to be a very useful second application of our first Calvet-type calorimeter, since most equilibrium work on metal–hydrogen systems is carried out below 450°C.

We were active in metal–hydrogen studies for about 10 years. In retrospect I appreciate in particular the valuable work carried out by Pierre Dantzer, by Gerard Boureau and by M. Shamsuddin. I presented a review of some of our work on metal–hydrogen chemistry to the Symposium on Alloy Thermochemistry organized by Professor Predel in Stuttgart in 1983 [35].

Our ability to make reliable calorimetric measurements at temperatures up to 1100°C opened up a number of new areas of reaction calorimetry to detailed investigations:

Among these areas I will list only a few

1. Binary liquid mixtures of refractory oxides and fluorides. These investigations. were pursued in collaboration with Jan Holm, T. Østvold, Kuochih Hong, M. Wakihara, S. Julsrud and others.
2. Mixtures of liquid cesium with liquid cesium halides studied in collaboration with Harumi Yokokawa by drop calorimetery (from room temperature to high-temperature) at 925 K [36].
3. Binary liquid alloys among the noble metals and of noble metals alloyed with early and late transition metals (H. Yokokawa, S. Watanabe, L. Topor). A review of some of this work was presented to LAM5, The Fifth International Conference on Liquid and Amorphous Metals in 1983 [37]. A more recent report appeared in Noble Metal Alloys published by The Metallurgical Society in 1986 [38].
4. Solution and reaction calorimetry of selected alloys and compounds involving the volatile elements S, Se, P, As and Sb. These investigations were carried out in col-



TO: O. J. Kleppa
May 2, 1985
FROM: A. M. Davis

Scanning electron microscopic examination and energy-dispersive x-ray microanalysis of Pt - PtRh thermopile.

Standardless Analyser

	wt% Rh
New Pt wire	0
New Pt-Rh wire	17.49

Fig. 12. Chemical analysis of our Pt–Pt13Rh thermopile carried out in 1985. This analysis was carried out after the calorimeter had been maintained at 800–1100°C for more than 10 years.

laboration with L. Cemic, L.T. Bryndzia, Steve Boone and K. Fitzner. Due to the high volatility of these elements, most of the experiments were carried out in sealed fused-silica containers.

5. Solution Calorimetry in high melting transition metals liquid alloys and in liquid copper (Kuochih Hong, S. Sato). For a while we thought that maybe solution calorimetry in high-melting liquid alloys near 1100°C might be a possible key to further calorimetric studies of the thermochemistry of intermetallic and related compounds. However, in due course, these studies carried out in collaboration with Dr. Letitia Topor, led

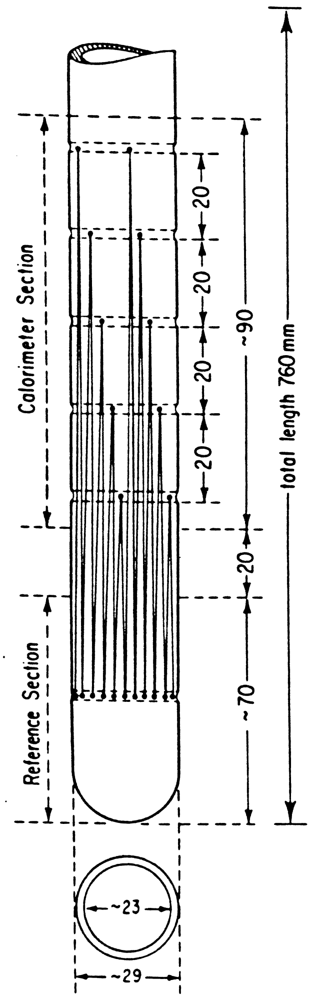


Fig. 13. Schematic view of the calorimetric section and the reference section of the alumina linear cylindrical calorimeter described by Kleppa and Topor in 1989 [21].

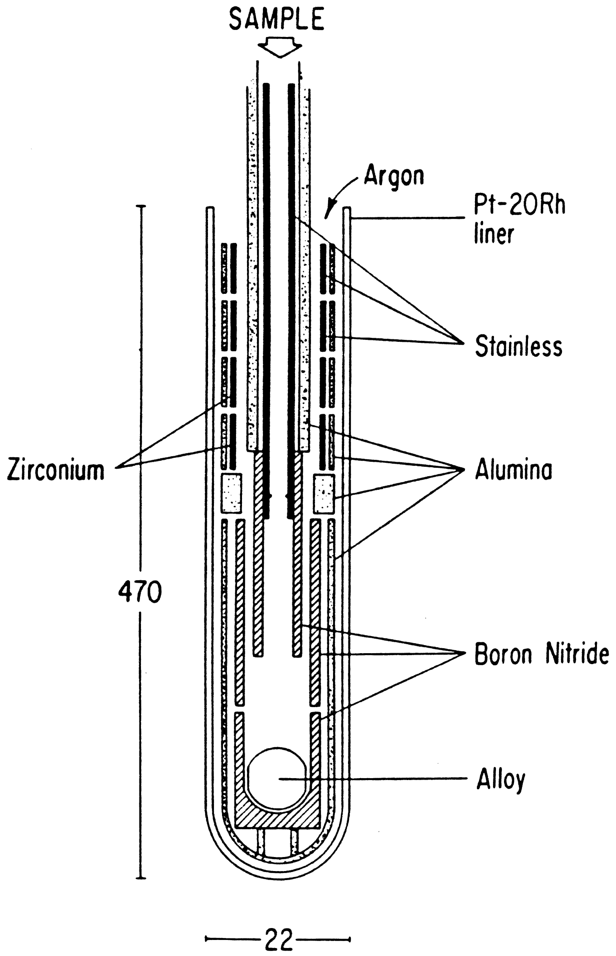


Fig. 14. Schematic diagram of the calorimetric cell assembly showing part of the Pt20Rh liner, the boron nitride crucible, the boron nitride protective cylinder and stirrer (used in solute–solvent drop calorimetry), the alumina protective crucible and protective cylinders, as well as parts of the final gettering system for the argon gas [21]. In direct synthesis experiments there is no stirrer, and usually no liquid is formed in the boron nitride crucible.

us to develop the new technique of solute–solvent drop calorimetry [19]. Later on it made us build our new SETARAM-like calorimeters [21] suitable for work at temperatures up to 1200–1250°C. These calorimeters have been the key to our success in applying high-temperature direct synthesis calorimetry in thermochemical studies of intermetallic and related phases in collaboration with Drs. Meschel, Selhaoui, Guo and Fitzner [22,23].

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In my Hume-Rothery Award lecture [19] I acknowledged the help and listed the names of a number of students and postdoctoral collaborators who had worked in my laboratory over the years on the thermochemistry of alloys. Another list of collaborators, mostly in the area of molten salt chemistry, is published in [26] and is quoted above in this paper. Some names will be found in both lists. I also want to acknowledge a list of collaborators whose work in my laboratory was principally in the area of oxide melt solution calorimetry: (The names are listed in approximately chronological order) T. Hlabse, P.A.M. Anderson, J.M. Neil, T.V. Charlu, J.A. Shearer, B.J. Wood, C. Chatillon-Colinet, D. Perkins III, C. Brousse, C.A. Geiger, J.O. Eckert, Jr., Hui Zhu. Most of these investigators came to my laboratory as a result of my long term collaboration in oxide melt solution calorimetry with my colleague Professor R.C. Newton. Finally, I want to mention the fact that for two periods of time I was engaged as a consultant in the development of new high-temperature calorimeters. The first period was in the 1960s with Joe Darby at the Argonne National Laboratory. It led to the development of the Calvet-type twin calorimeter with a silver body which is described in Ref. [18]. The second period was in the 1980s with Stephen C. Mraw of the Exxon Research and Engineering Co. This collaboration

led to the publication of a detailed description of a Calvet-type [39] calorimeter suitable for temperatures up to 1000°C. Our work in the area of high-temperature thermochemistry was initially supported by O.N.R. However, over the years it has also been extensively supported by NSF (almost continuously since 1961), by A.R.O., by A.R.P.A., by Chicago MRSEC, and by D.O.E. Other supporters have been the Petroleum Research Fund and the Alcoa Foundation.

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