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Neither calorimeters nor calorimetrists are what they used to be

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Abstract

Until quite recently, calorimeters were often 'home built', but new hi-tech commercial instruments dominate the field. However, these developments have also produced problems. Some thoughts are expressed which relate to the developments in calorimetry since the mid-part of the century. © 1997 Elsevier Science B.V.

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1. Introduction

A few decades ago, scientific calorimetric measurements were normally made with 'home made' instruments in laboratories specialising in thermochemistry. By present standards, calorimetric measurements were tedious and large amounts of material were used in the experiments.

Times have changed. Almost all calorimeters used today are commercial instruments and the developments in calorimetric instrumentation have led to convenient experimental procedures which often are fully automatic. Samples are often orders of magnitude smaller than those needed a few decades ago. The time spent on theoretical and practical training of scientists and technicians has, in most cases, been reduced to a small fraction of what was earlier considered necessary. While calorimetric research in areas like biochemistry and cell biology in the mid-part of the century was thought of as an exotic exercise and the use of calorimetry in industrial laboratories was rare, precise calorimetric work is nowadays routinely conducted in such areas.

My scientific work has, over a long period, been connected with the development of instruments and working procedures in calorimetry. Many of the problems discussed in this essay relate to successful commercial implementations of such academic work.

2. Thermochemistry was a world of instrument builders

One of the chapters in the second volume of IUPAC's monograph, Experimental Thermochemistry [1] is titled, The Design and Operation of Reaction Calorimeters, and was written by three of the leading names in thermochemistry and calorimetry in the early 1960s: H.A. Skinner at the University of Manchester, J.M. Sturtevant at Yale University, and S. Sunner at the University of Lund. It opens with the following paragraph:

> The design and construction of a suitable calorimeter is one of the first problems facing the experimental thermochemist planning to measure directly the heat of a chemical reaction.

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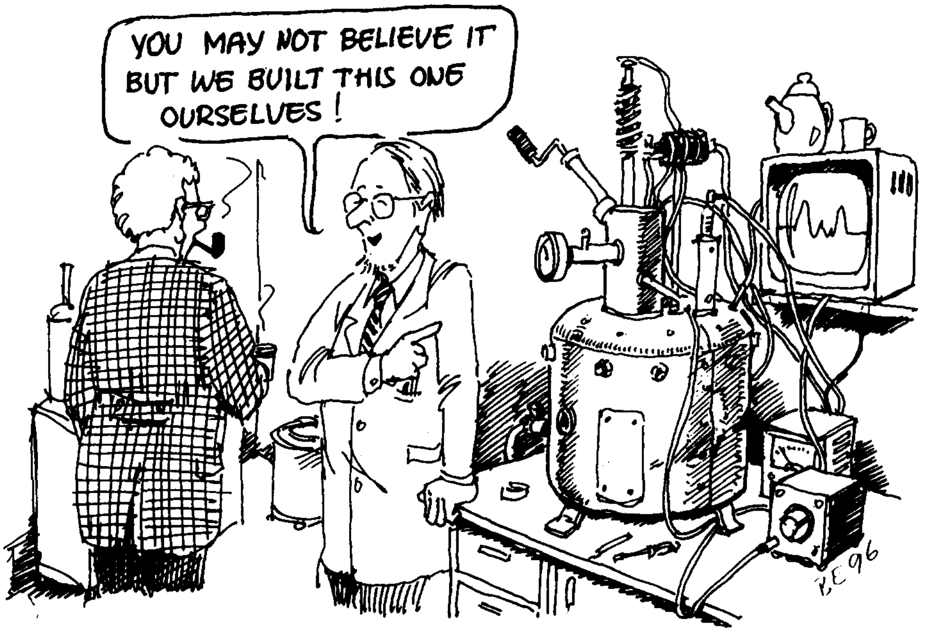

Fig. 1.

> During the past 30 years [i.e. about 1930–1960] over 300 papers on reaction calorimetry have been published, and more than 200 different reaction calorimeters have been described. This evident need for variety in calorimeter design reflects the very variegated nature of the chemical reactions that have been thermochemically studied. Fig. 1

There are probably several explanations for the excessive construction work in reaction calorimetry 35 years ago and earlier. Commercial instruments were not yet available and, surprisingly, modular design principles, which would enable one instrument system to be employed in a wide range of different applications were not applied. In some laboratories, it was probably of some importance that students were regarded as inexpensive labour. Possibly, in some cases, it was also recognised that it would be beneficial for the quality of the calorimetric work if the students would study the properties of the instrument before they began their own thermochemical investigations. Not many current students in thermochemistry get the opportunity to learn the calorimetric technique at a corresponding depth. That is not always necessary, but calorimetric measurements are not as simple as they may appear, and the risk of making systematic errors and recording artefacts still exists, in particular, for modern commercial instruments which now approach the level of being 'black box' instruments.

Calorimetry continued to be a stronghold for 'home builders' long after these were almost extinct in most other instrument disciplines. Around 1965, I happened to read a report from a calorimeter salesman, after he had made a market survey at some universities in the USA. A university professor and prominent thermochemist was quoted as telling the salesman, in an ice-cold voice, that calorimeters could not be built by commercial companies. However, a new era was under way when I met that professor a few years later. He was then very enthusiastic about the performance of his commercially produced instrument.

3. Accuracy or precision?

Following the developments in microcalorimetry in the late sixties, commercial instruments started to reach new groups of users with new and interesting applications in chemistry and biology. To some extent, these new groups of calorimeter users introduced a scientific culture which was different from that honoured by the classical thermochemist. Many of the new calorimetrists, particularly those within the applied sector, used their calorimeters mainly as 'process monitors' and as other kinds of analytical tools, rather than as thermodynamic instruments. Thermodynamic studies in biochemistry, for example, were conducted on samples which were poorly defined by traditional standards in thermochemistry. Properties like 'precision', 'baseline stability' and 'detection limit' often took preference over 'accuracy'.

These developments, although not entirely profitable for the quality of calorimetric work, added a breeze of fresh air to thermochemistry. For example, I think the (North American) Calorimetry Conference showed signs of inbreeding in the late sixties, before influences from bio-oriented calorimetrists and other new groups of thermochemists brought this important conference back to life. With some exaggeration, one could say that many classical thermochemical groups used to work with only two goals in mind: that their data should be of a quality which would make them last forever, and that the data should find their way into thermochemical tables. However, even though the thermochemical work was of top quality, many of us started to feel that the science was a bit sterile.

The situation some 30 years ago, as described here could also be expressed in another way. The productivity, in terms of the amount of published data, was quite low even in some of the best thermochemical laboratories in the world. I remember a meeting I had with W.H. Evans, a well-known analyser and compiler of thermochemical data at the National Bureau of Standards, Washington, D.C. (now the National Institute of Standards and Technology, NIST). He told me, with a sigh of resignation, that he would prefer to have a fair amount of new experimental data of moderate accuracy, rather than those very few of superb quality he keeps receiving. Many important thermochemical problems do not require the most accurate thermochemical data, now or in the foreseeable future. Quite naturally, in some thermochemical circles such views were not appreciated, but the problem was recognised by a large number of users of thermochemical data and - not the least - by the various bodies financing such work.

Some thermochemical data of the highest possible accuracy are needed, however, and there are very few of them produced today. Even more alarming is the fact that, in some areas we are heading in a direction, where we will lose the ability to produce high quality data. In particular, I am thinking about high accuracy combustion calorimetry for the determination of enthalpies of formation and low temperature heat capacity measurements for the determination of entropies. Those calorimetric techniques dominated the thermochemical scene until a few decades ago, but are now practised in very few laboratories. The measurements are difficult to master at a level of accuracy where they become useful, and commercial instruments are neither available nor likely to become available. However, those techniques will also be needed in the distant future. If they are lost, it will require much time and money to restore that knowledge.

How accurate are the results of calorimetric measurements in fields where commercial instruments dominate and more scientists, than ever before in the history of calorimetry, are active? Actually, I doubt that many of the present calorimetrists really know how accurate their results are. Both users and manufacturers are usually content with reporting values for 'precision' rather than combining such values with estimates of possible systematic errors, in order to obtain values for 'accuracy'. I think this, at least partly, reflects a low level of awareness of the inherent problems in calorimetric measurements by users today.

Practically all processes in nature produce heat, which means that calorimeters have a very broad application range both in thermodynamics and as general analytical tools. This will also make calorimeters uniquely sensitive to many systematic errors: evaporation, condensation, adsorption, corrosion and chemical side reactions, etc. In general, commercial calorimeters marketed today are high quality instruments, but results of measurements can still be impaired by significant systematic errors due to unidentified problems in the instruments or in the working procedure.

Further, calorimeters must be calibrated, which is not a simple task if the objective is to produce results of high accuracy. It should be recognised that certain calorimeters, 'home-built' and commercial, are difficult to calibrate accurately by the release of heat from an electrical calibration heater. In the old days, calorimetrists were well trained in calibration procedures -

and much time was spent on such activities. Today, calibration experiments are normally reduced to a push button operation, leaving the user with little insight into the calibration process and with little worry about the result. For some calorimetric vessels, not the least in microcalorimeters, the heat-flow pattern from the electrical heater can be very different from that of an investigated process. It can then be advantageous to use a chemical calibration technique [2,3]. Regardless of the calibration method being used, one should control the overall performance of a calorimeter, and of its operator, by running chemical test experiments [2,3]. Unfortunately, many calorimeter users do not do that. Further, more test processes should be developed, in order to allow the users to better mimic different types of processes.

In my view, we should also be more concerned about using an accurate terminology when calorimeters are described. In particular, the marketing people of some commercial companies can be blamed for their invention of terms which often are far below a decent scientific level. What, for instance, is an 'ultrasensitive microcalorimeter'? Instead of inventing useless terminology of that sort, we should demand that manufacturers characterise their instruments by means of experimental values for key properties determined under standardised conditions. Unfortunately, there do not yet exist any authoritative international guidelines on these matters, but the need has been recognised in discussions at recent international conferences.

4. Some areas are neglected

The focus of interest in thermochemistry has completely changed during the past few decades. The situation for combustion calorimetry and low-temperature heat capacity calorimetry was commented upon in the foregoing. But there are also other important disciplines which are neglected at present. I will give three examples from areas where I have had some experience. Accurate values for vaporization (sublimation) enthalpies at ambient temperatures are of key importance in many areas of thermochemistry. However, for compounds with low vapour pressure, in particular for solids, the available data are very unsatisfactory, and practically no new calorimetric results are currently reported. To some extent this might be due to lack of suitable microcalorimetric techniques.

Heat capacity data are of general importance in fundamental research and in industrial research and development. It is surprising to find how few reasonably accurate values exist for heat capacities of simple organic compounds, even at 25°C. In addition, most of the existing values were determined at a time when we were not aware that different polymorphic forms (in a broad sense) of solid organic compounds are common [4].

In biothermodynamics, it is often important to have available good data for enthalpies and heat capacities of protonation of different buffer substances and other compounds in solution. More first class calorimetric determinations of such data are desirable.

Academic researchers in the thermochemical field will often recognise the need for new or improved determinations of such basic data. However, they will usually feel that careful determination of such data 'for the tables' is far from the research front-line, and is not very rewarding. In addition, it is not likely that their granting agencies would support such 'non-glamorous' projects. Scientists in the industry often feel the need for extension of existing data compilations, but normally they cannot spend much time producing data for the general scientific community. In my view, we have reached a point where the production of basic thermochemical data should be encouraged. The question is how?

5. Conclusions

In this report I have expressed some reflections on modern calorimetry, perhaps with a touch of nostalgia. Techniques and directions of research have changed dramatically during the last few decades. One can clearly note an increase of vitality of the field. Thermochemistry has entered exciting areas in biochemistry and cell biology, and many new uses for calorimetry have been found in the industry. Some important 'classical' areas accompanying those developments are neglected, which gives reason for some concern.

Old calorimeter designs have been phased out by computer-controlled instruments, which have performances we hardly could imagine a few decades ago. As in other instrument disciplines, calorimeter users are now normally customers of commercial instruments and not 'home builders'. However, as we rapidly approach a state where calorimeters become 'black boxes', users should realise it will remain a challenge to produce good results in thermochemistry.

Acknowledgements

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