Thermochimica Acta, 100 (1986) 271–282
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

SOME REFLECTIONS ON CHANGES IN THE FIELD OF SOLUTION CALORIMETRY OVER THE PAST TWENTY-FIVE YEARS

J.L. OSCARSON, R.M. IZATT and J.J. CHRISTENSEN

Departments of Chemical Engineering and Chemistry, Brigham Young University, Provo, UT 84602 (U.S.A.)

(Received 3 February 1986)

ABSTRACT

The field of calorimetry has changed in many dramatic ways during the past 25 years. The authors' observations of the changes in equipment, measurements made, and automation are recorded. The number of uses of calorimeters has increased as have the ranges of temperature and pressure over which they have been operated. Automation and the use of computers have made the operation of calorimeters and the reduction of calorimetric data less tedious and less time consuming. The authors see the future of calorimetry to be bright and expanding.

INTRODUCTION

This paper was written to record some observations by the authors of the science of calorimetry over the past 25 years. The observations made are necessarily biased by the authors' own experiences. It is not meant to be an exhaustive survey of all that has happened in the wide field of calorimetry over these years, but is meant to give the authors' perceptions of what has happened during the time they have been involved in this field. The reader is referred to the references for specific examples. Much of the material comes from a review article on the uses of calorimetry by Izatt et al. [1].

Many changes have occurred in calorimetry over this time period. New types of calorimeters have been designed. Their operation has been made much easier by the incorporation of solid-state electronics in the instrumentation and by automation of the instruments [2]. Interfacing computers with calorimeters has made possible extremely rapid data reduction. Computer codes have been developed which have made possible the rapid calculation of related thermodynamic quantities from measured heats [3]. The determination of an ever widening array of chemical and thermal properties and the analyses of an ever increasing variety of chemicals and their reactions have been accomplished using calorimeters. Calorimeters have been designed to measure ever smaller heats [4] and to explore high temperature and pressure regions [2,5]. Novel designs have been made to allow more precise and accurate measurements. Today the field of calorimetry appears to be changing more rapidly than at any time in the past and the variety of these changes confirms that future developments will be limited only by the imagination and creativity of calorimetrists.

USES OF CALORIMETERS

Indicative of the changes which have occurred are the type and number of presentations given at the Annual Calorimetry Conferences. A summary of the number of presentations in different areas at these conferences since 1960 is given in Table 1. Examination of the program of the 15th Annual Calorimetry Conference held in 1960 shows that calorimeters at that time were used mostly for measuring heats of formation, heats of combustion, heat capacities, heats of phase transitions, and heats of dilution for elementary inorganic and organic compounds [6]. These quantities are useful in calculating energy balances in industrial chemical processes and probably reflect the close association of calorimetry with industry at that time. Low temperature heat capacity data are used in theoretical third law investigations. A few papers dealt with measurements of heats of reaction in solution using either aqueous or nonaqueous solvent systems. An examination of Table 1 shows that in the early 1960s few calorimetric measurements were being made on biological and model biological systems. Few researchers realized the potential uses of calorimeters in the field of biochemistry. Twenty-five years ago, calorimetry stood at a threshold. Researchers were just beginning to realize the vast potential of calorimetry, that it could be applied to study a wide variety of chemical and physical processes. Furthermore, it was becoming apparent that measured heats could give considerable insight into the chemistry of the process undergoing measurement.

Titration calorimetry was relatively new 25 years ago. A few workers appreciated the potential of this technique. The early 1960s saw development of titration calorimetry into an important field of research. One significant development was the determination from calorimetric titration data of the equilibrium constant (K) value as well as the ΔH value for a chemical reaction provided the K value was of the appropriate magnitude [7]. Although determination of K values using this procedure was not widely accepted at first, it has now been shown to be an excellent method. This method of determining K values has been extended to many reactions by choosing an appropriate overall reaction with a K value in the correct range which consists of the reaction of interest and a competing reaction with a known K value [8]. The K value of interest may then be calculated by taking the difference between the calorimetrically determined K value of the overall reaction and the K value of the known reaction. Today, by using complex computer codes to reduce the raw calorimetric data, the K, ΔH,

TABLE 1

Summary of the number of presentations at annual calorimetry conferences from 1960 to 1985 broken down by general subject as listed in the abstracts of papers [a]

Year	C_p, H, ΔH_{trans}	ΔH_{comb}, ΔH_{form}	Biol	$\Delta H_{\text{react non-soln}}$	ΔH_{dil}, ΔH_{soln}, $\Delta H_{\text{react in soln}}$	Instru Devel	ΔH_{mix}	ΔH_{adsorb}	Miscel
1960	10	3	0	2	5	5	0	0	5
1961 [b]	19	7	3	1	6	9	3	1	7
1962	14	4	1	0	5	3	3	1	5
1963	21	10	0	0	2	7	0	0	9
1964	14	11	5	2	5	8	1	2	9
1965	12	8	1	3	2	10	3	0	5
1966	21	7	1	2	14	5	2	0	3
1967	19	9	2	2	4	3	4	0	7
1968	19	5	0	0	9	11	1	0	7
1969	11	14	1	1	9	5	0	0	8
1970 [b]	12	7	26	0	5	9	1	0	6
1971 [b]	21	9	13	2	15	11	4	1	23
1972	11	9	19	1	9	5	1	2	12
1973 [b]	18	6	15	8	8	11	0	0	16
1974	11	7	27	1	5	8	2	0	8
1975	15	4	20	2	10	6	1	0	10
1976	15	3	19	1	9	9	4	0	11
1977	13	9	17	2	14	5	5	0	7
1978	13	6	9	3	12	6	3	1	28
1979	17	5	18	0	8	10	6	1	6
1980	15	8	12	4	7	10	3	0	10
1981	27	6	20	3	10	4	5	3	26
1982	26	8	5	2	12	1	7	5	17
1983 [b]	16	7	32	5	20	6	8	7	37
1984	46	9	18	6	12	11	12	5	31
1985	30	8	13	3	13	17	9	7	22

[a] C_p, H, ΔH_{trans} are heat capacity, enthalpy changes due to heating from a reference temperature, and the enthalpy changes due to phase changes or transformation changes, respectively. ΔH_{comb} and ΔH_{form} are heats of combustion and heats of formation, respectively. Biol = biological systems. $\Delta H_{\text{react non-soln}}$ is the heat of reactions that do not occur in solution. ΔH_{dil}, ΔH_{soln}, and $\Delta H_{\text{react in soln}}$ are enthalpy changes which occur for dilution, solution, and reactions in solution, respectively. Instru Devel = instrument development. ΔH_{mix} = heat of mixing. ΔH_{adsorb} = heat of adsorption. Miscel = miscellaneous.

[b] Held in conjunction with another conference.

and ΔS values can be measured for reactions of this type at conditions of temperature and pressure far removed from ambient. At high temperatures and pressures it has proven very difficult to measure these values by any other method [3].

Few workers, 25 years ago, had used calorimeters in the identification of the chemical species or the measurement of the amount of a species in a mixture, but the use of calorimetry to perform these tasks has evolved to be a widely accepted and reliable method of analytical chemistry [1]. The use of calorimetry as an analytical tool was reviewed in 1974 [9]. Of the various types of calorimeters used for such purposes, those involving thermometric titrations have proven to give good quantitative analyses, and can give more definitive data in many cases than conventional methods. In addition, they usually produce data more rapidly than conventional calorimeters. Calorimetry has proven to be a useful method for identifying species in a mixture. Clever selection of the reactants and careful evaluation of the heats evolved have allowed researchers to identify many species in complex mixtures that have been difficult if not impossible to analyze by conventional methods.

Twenty-five years ago, few workers were measuring heats of mixing. The heat of mixing data available were not extensive and most were measured at or near 25°C [10]. Measurement of heats of mixing was time consuming by the batch procedures used and it took many measurements on one system to get the complete heat of mixing curve. Such heats, for the most part, were felt to be uninteresting as the heats were small in magnitude. This situation changed markedly with the development of precise flow calorimeters about 15 years ago. Development of these instruments has made possible the rapid and precise measurement of heats of mixing not only at ambient conditions, but at elevated pressures and temperatures as well. As the temperature and pressure capabilities of these flow calorimeters have expanded, interesting phenomena have been observed in certain temperature–pressure regions, especially near the critical points of the mixtures [11]. The use of heats of mixing to predict other thermodynamic properties of mixtures was considered a possibility 25 years ago but very little actual work had been done in this area. About twelve years ago, workers began to predict vapor–liquid equilibria from heats of mixing [12]. The parameters in semi-empirical excess Gibbs free energy equations were adjusted so that these equations would fit the heat of mixing values. These equations with the fitted parameters were then used to predict the vapor–liquid behavior of the mixtures. This type of work is still being done. More recently workers have fitted the heat data with equations of state [13]. The resulting equations can then be used to predict vapor–liquid equilibria. Recently, heat of mixing curves have been used to measure phase behavior directly. The "breaks" in the heat of mixing versus composition curves give a direct measurement of the composition of the phases in equilibrium. This method has proven useful in measuring liquid–liquid [14] as well as vapor–liquid equilibria [15]. The method holds promise for future development since these measurements can be made without the removal of samples. This eliminates the inherent problems associated with sample removal from sample cells which are at temperatures far removed from 25°C.

A recent development has been the use of calorimetry to measure the activity coefficients of solutes in aqueous solutions [16]. The activity coefficients determined calorimetrically are model dependent, as are the vapor–liquid equilibria predicted from heats of mixing. However, calorimetry allows the measurement of these values under conditions far removed from ambient where conventional isopiestic measurements become difficult.

About ten years ago, it was discovered that very sensitive Calvet type calorimeters could be used to non-destructively estimate the life of batteries [1]. This testing is extremely important in cases such as pacemaker batteries or batteries used in military equipment. Today, virtually all battery manufacturers use this type of testing [17]. Since this method involves the measurement of heat changes produced by very slow reactions, it should prove valuable in many areas where such reactions occur. Such areas include aging processes of all types (paper, fiber, etc.), corrosion processes, and chemical transformations at elevated temperatures and pressures (engine oil deterioration, etc.).

Until 1970, only a few workers were using calorimetry to study reactions of biological significance. In 1970, a special session of the Calorimetry Conference was devoted to biological applications of calorimetry [18]. Since then, calorimetry has become an important tool in the investigation of problems in the areas of biology, biochemistry and pharmacology. This trend is seen in Table 1. Such diverse quantities as the heats of germination of seeds, the growth rate of bacteria, the heats of conformational changes in drugs, and the heats of protonation of certain sites on proteins have been measured [1]. Calorimetry has also been used in the identification of certain biochemicals. This is an area that has grown rapidly in the past 15 years and which should continue to grow as its usefulness in these and other areas becomes more widely recognized.

Twenty-five years ago few studies had been reported involving the calorimetric measurement of enthalpy changes and equilibrium constants for metal–ligand interactions in aqueous or other solutions [19]. The amount of work in this area has increased dramatically since that time [1]. A related area that is receiving much attention today is the interaction of organometallic compounds with other chemicals such as protons, other metal ions, and polar organic compounds in many different solvent systems [1]. Study of these reactions requires special types of calorimeters since most of the systems are sensitive to air, have volatile solvents, and involve expensive and/or rare chemicals. These properties have caused workers to design small, sensitive, air-tight, pressurized reaction vessels.

The calorimetric measurement of the heats and equilibrium constants for solid–liquid interactions has become an important area of investigation [1]. Included in these interactions are the measurement of adsorption of a fluid or a solute in the fluid on the surface of a solid, the heat of dissolution of a soluble solid, and sometimes the catalytic effect of the solid on a reaction. Presently, there is much interest in the development of a calorimeter capable of measuring the heats of these types of interactions over a wide temperature–pressure range [17].

There has been a rapid growth in the past decade in the use of differential scanning calorimetry. Such instruments are ideally suited for the measurement of the heats of transition (ΔH_{trans}) which occur as temperature increases. These transitions include the heats of fusion, vaporization, isomerization, conformational changes, and crystal structure changes. Data from such studies can be used to determine the enthalpy (H) relative to some base temperature and the heat capacity (C_p) of a material as a function of temperature. This accounts in part for the increase during the last few years in the measurement of C_p, H, and ΔH_{trans} shown in Table 1. Twenty-five years ago, measurements of thermodynamic quantities involved in phase transitions which occur in materials were done almost exclusively with drop calorimeters. The development of scanning calorimeters has given new impetus to this field.

The previous paragraphs have mentioned a few of the developments in the use of calorimetry during the past 25 years. The use of calorimeters to measure radioactive emissions and the further development of heat of combustion calorimeters are only two of the areas not mentioned. However, the above partial list gives an idea of how the field of calorimetry has changed during this period and suggests that many interesting developments will be forthcoming in the future.

EQUIPMENT DEVELOPMENT

As shown in Table 1, instrument development has continued at a steady pace during the past 25 years. The development of calorimeters for the variety of uses described in the preceding section has been made possible by the imagination and creativity of workers in the area of calorimetry and by the development of sophisticated scientific equipment. Some of the changes in calorimeter operation during the past 25 years are shown in Table 2. The past decade has seen an exponential growth in the area of solid-state electronics. This growth, together with the development of new temperature sensing devices and equipment hardware, has revolutionized the field of calorimetry. Since the availability of this new equipment and of these new devices has played such a large role in the development of modern calorimetry, a brief discussion of this development is presented here.

The changes which have occurred in the authors' own equipment are typical of those which have taken place in calorimetry generally during the past 25 years. The first titration calorimeters used by us were kept in a constant temperature water bath which was inside a large metal water bath. Beckman thermometers were used to check the temperature of each water bath. The titrant was delivered by the use of a mercury displacement pump with the mercury in a glass container inside the inner bath. The electronic equipment used consisted of K3 potentiometers, galvanometers, knife

TABLE 2

Some changes which have occurred in the hardware used in calorimeters since 1960

Year	Temperature measurement	Temperature control	Raw data collection	Data reduction	Equipment control
1960	Beckman thermometers, thermocouples, first generation thermistors	Manual, first generation temperature controllers (good to ±0.01°C)	Stripchart recorders, visual reading of instruments	Visual reading of recorder traces, slide rule and mechanical calculator computations, some computer calculations using punched cards	Manually thrown switches at appropriate time as indicated by visual inspection of instruments, manually actuated stopwatches
1986	Very sensitive thermistors or resistance thermometers connected to Wheatstone bridges and sophisticated electronics	Very precise solid-state temperature controllers (good to ±0.0002°C)	Digital readout, data read directly to computer file	Built-in micro-processors which reduce data rapidly, external computers which make calculations on data stored on a disk	Micro-processors, external mini-computers, external main-frame computers, combination of above

switches, timing clocks, and a stripchart recorder. These control devices were all on a panel which covered half a wall. It was very impressive looking, but required constant supervision by an operator. Each function was initiated by the operator who threw a switch at the appropriate time. The output was the trace on a stripchart recorder. This trace was analyzed by manually counting squares. The resulting numbers were then typed onto keypunch cards and these cards placed in the back of a large stack of keypunch cards which contained the computer program used to reduce the data. We considered ourselves fortunate to have access to an IBM 650 computer despite the fact that it was large and cumbersome and overheated frequently. Despite these drawbacks, this new tool was far superior to the alternative, a mechanical calculator. The large stack of data cards was carried to the IBM 650 computer where, if all was working well, they would be fed to the instrument by an operator sometime within the following 24 h. The output could then be checked for errors in reading the stripchart trace or in keypunching. The program used to find both the K and the ΔH values was so long that the computer operators always complained that it took too much computer time. As we look back from our present vantage point, it is evident that equipment and data reduction changes during the past 25 years have made a tremendous difference in how we, as well as other calorimetrists, gather data.

The introduction of better temperature controllers has made it possible to eliminate the large water baths of former years and replace them with single, well insulated, small water baths. Improved temperature control devices have been made possible by the advancement of the science of electronics and by the introduction of more sensitive thermistors. It is of interest that one important development 30 years ago was the substitution of a thermistor for a bulky thermometer [20]. This important substitution allowed the accurate measurement of small heats and accelerated the development of titration calorimetry and of calorimetry involving small quantities of expensive or scarce reactants.

From the beginning to the end of a determination, all steps are now programmed and the control of the entire process is automated. Either small built-in microprocessors are used to control the equipment or the equipment is run by an external computer. This automation has made the operation of the calorimetric system much less tedious and has improved the reproducibility of the results. However, as the use of these "black boxes" increases, the individual experimenter becomes more dependent on other people for equipment maintenance and modifications become more difficult and expensive. Individual researchers thus lose much of the control over their equipment that they once had.

The collection of the data has been automated as well. At the 20th Annual Calorimetry Conference in 1965 [21], a paper was given on the use of a digital voltmeter as an output device for a calorimeter. In 1986, the output from the typical calorimeter goes directly to a computer where it either is reduced directly or is stored in a file until an operator sitting at a terminal can have the raw data reduced by calling the appropriate computer program. This has greatly increased the speed of data output and has eliminated much of the tedious work associated with data collection. Again, this is a mixed blessing as blind acceptance of numbers given out by computer codes can lead to serious errors. Since such data reduction does not force the investigator to seriously evaluate the data, particular care must be taken to verify the correctness of the results.

The use of improved Peltier devices, more sensitive resistive type thermometers, and sophisticated electronics has resulted in the development either of new types of calorimeters or of improvements on existing types of calorimeters. The development of new flow calorimeters has greatly extended the temperature and pressure range of calorimetric measurements. The use of Peltier devices has allowed the development of extremely sensitive calorimeters of the Calvet type [22]. Electronic developments have allowed the construction of alternating type scanning calorimeters which give more precise data than the direct heating type [23]. Thus, improvements in the accuracy and precision of the measurements as well as the extension of the workable temperature and pressure ranges of the calorimeters have resulted from equipment development.

Advancements in computer science have allowed more sophisticated data reduction. The programs that were too long for the computer operators 20 years ago are considered to be small today. The use of computer codes allows the heat data obtained from calorimeters to be used to calculate other related quantities. The use of these codes makes it possible to calculate several K values simultaneously as well as corresponding ΔH values from data collected for the interaction between species when more than one reaction is occurring. This is especially important when studying reactions in aqueous solutions at high temperatures where almost all cations and anions begin to associate [24]. The prediction of vapor–liquid equilibria from heat of mixing data would be impossible without the use of computers. It is to be expected that the use of computers will continue to increase the amount of information which can be extracted from calorimetric data.

EQUIPMENT MANUFACTURERS

As most calorimetrists are interested in measuring thermodynamic quantities, not in developing equipment, the commercial manufacture of calorimeters is extremely important to the advancement of the science of calorimetry. Twenty-five years ago, it was necessary for the authors to develop their own titration calorimeter. Since that time, several companies have become involved in the manufacture of calorimeters. Since the calorimeter is a specialty type instrument, the number sold has not been large and as a result those available today generally are manufactured by small companies. Today, solution calorimeters are manufactured by the following companies (listed in alphabetical order): American Instrument Co.; Hart Scientific; LKB Instruments AB; Parr Instrument Co.; Sanda, Inc.; Setaram; SKC, Inc.; Techneurop, Inc.; and Tronac, Inc. Flow calorimeters are made by Hart Scientific, LKB Instruments, Microscal Ltd., Steinberg Associates, and Tronac, Inc. Bomb calorimeters are made by Gentry Instruments, Inc., Parr Instrument Co., and VWR Scientific. Differential scanning calorimeters are manufactured by Buck Scientific, DuPont Instruments, Hart Scientific, Micro Cal, Inc., Netzsch, Inc., and Perkin-Elmer. Calorimeters made to test batteries are manufactured by Hart Scientific and Tronac, Inc. Calorimeters for determining thermal information and for evaluating thermal and pressure hazard potentials of materials under operating conditions simulating industrial and laboratory environments are manufactured by Columbia Scientific Industries Corporation and System Technik AG (SYSTAG). Tronac has reported an increased demand, during the 1980s, for calorimeters by both academic institutions and commercial companies [17].

CALORIMETRY IN THE FUTURE

The changes in the past 25 years indicate that future developments in calorimetry may be expected. It is always dangerous to predict future trends, so the predictions here will tend to be conservative.

Calorimetry in the future will rely even more on automation. The use of solid-state electronics will continue to grow as new and improved procedures become available. The equipment will continue to become more sophisticated and expensive.

The temperature and pressure ranges of calorimetry will be expanded to collect the data needed for many industrial processes. Particularly important will be the development of flow calorimeters capable of studying solute–solute interactions in aqueous solutions near the critical temperature (374°C) of water.

The further development of calorimeters capable of determining energy, time, temperature, and pressure relationships of reactions under conditions which simulate those found in industry is needed. These types of calorimeters can be used for the evaluation of thermal and pressure hazard potentials, the quality control of products and raw materials, energy and environmental considerations, and process optimization and development in chemical industries.

The development of innovative calorimeters to handle solids at high temperatures and pressures will be made. The need for calorimeters of this type has been noted [17].

The development of more precise calorimeters capable of delivering very small volumes will continue. Calorimeters with this capability are needed to measure heats of reaction using expensive or rare chemicals, especially biochemicals.

The resurgence of the measurement of heats of combustion and formation will occur as the need to characterize the host of new organic molecules is recognized. A key point made in the recently published Pimentel report [25] is that the number of new compounds produced by chemists is increasing at a rate that is faster than exponential. For example, in 1950 the number of known compounds was 2000000. In 1985, this number is nearly 9000000. As seen in Table 1, the number of presentations given at the Annual Calorimetry Conferences, which involve compound characterization, has not reflected this growth in the number of compounds. This rapid rise in the number of new compounds has not been accompanied by an increase in the number of individuals and laboratories characterizing these compounds with respect to bond energies; K, ΔH and ΔS values (where appropriate) for their interactions with protons and metal ions; and other thermodynamic properties. Such data are as important for the understanding and prediction of chemical phenomena today as they were a half century ago. It is hoped that the need for this characterization will be recognized and that an important area of research in the future will involve trained calorimetrists in the study of such systems.

REFERENCES

1 R.M. Izatt, E.H. Redd and J.J. Christensen, Thermochim. Acta, 64 (1983) 355.
2 J.J. Christensen and R.M. Izatt, Thermochim. Acta, 73 (1984) 117.
3 P.R. Brown, Ph.D. Dissertation, Brigham Young University, 1986.
4 L.D. Hansen and R.M. Hart, J. Electrochem. Soc., 125 (1978) 842.
5 J.J. Christensen, L.D. Hansen, R.M. Izatt, D.J. Eatough and R.M. Hart, Rev. Sci. Instrum., 52 (1981) 1226.
6 15th Annual Calorimetry Conference Abstracts, Gatlinburg, TN, 1960.
7 J.J. Christensen, R.M. Izatt, L.D. Hansen and J.A. Partridge, J. Phys. Chem., 70 (1966) 175.
8 J.J. Christensen, D.P. Wrathall and R.M. Izatt, Anal. Chem., 40 (1968) 175.
9 L.D. Hansen, R.M. Izatt and J.J. Christensen, in J. Jordan (Ed.), New Developments in Titrimetry, Dekker, New York, 1974, p. 1.
10 J.J. Christensen, R.W. Hanks and R.M Izatt, Heats of Mixing, A Compilation, Wiley-Interscience, New York, 1982.
11 J.J. Christensen, D.M. Zebolsky, R.S. Schofield, D.R. Cordray and R.M. Izatt, J. Chem. Thermodyn., 16 (1984) 905.
12 R.W. Hanks, A.C. Gupta and J.J. Christensen, Ind. Eng. Chem. Fundam., 10 (1974) 504.
13 J.J. Christensen, D.M. Zebolsky and R.M. Izatt, J. Chem. Thermodyn., 17 (1985) 1.
14 T.A. McFall, M.E. Post, J.J. Christensen and R.M. Izatt, J. Chem. Thermodyn., 14 (1982) 509.
15 C. Pando, J.A.R. Renuncio, R.M. Izatt and J.J. Christensen, J. Chem. Thermodyn., 15 (1983) 231.

16 J.M. Simonsen, R.H. Busey, D.G. Archer and R.E. Mesmer, Paper No. 77, Abstracts of Papers, 40th Annual Calorimetry Conference, Asilomar, CA, 1985.
17 P.S. Bullock, President of Tronac, Inc., personal communication.
18 Abstracts of Papers on Calorimetry in Biology, 25th Annual Calorimetry Conference, Gaithersburg, MD, 1970.
19 J.J. Christensen and R.M. Izatt, Handbook of Metal Ligand Heats and Related Thermodynamic Quantities, 3rd edn., Dekker, New York, 1983.
20 H.W. Linde, L.B. Rogers and D.N. Hume, Anal. Chem., 25 (1953) 404.
21 G.T. Furukawa, Paper, No. 13, Abstracts of Papers, 20th Annual Calorimetry Conference, Ames, IA, 1965.
22 E. Calvet and H. Prat, Recent Progress in Microcalorimetry, translation by H.A. Skinner, Pergamon, London, 1963.
23 J.E. Smeardyk and J.M. Mechol, Rev. Sci. Instrum., 49 (1978) 988.
24 J.W. Cobble, Science, 26 (1966) 1479.
25 Opportunities in Chemistry, National Academy Press, Washington, DC, 1985.