J. Indian Inst. Sci., 63 (A), Nov. 1981, Pp. 277–329

Heat capacity measurements: Progress in experimental techniques

S. T. LAKSHMIKUMAR AND E. S. R. GOPAL
Department of Physics, Indian Institute of Science, Bangalore 560 012, India.

Abstract

The heat capacity of a substance is related to the structure and constitution of the material and its measurement is a standard technique of physical investigation. In this review, the classical methods are first analysed briefly and their recent extensions are summarized. The merits and demerits of these methods are pointed out. The newer techniques such as the a.c. method, the relaxation method, the pulse methods, the laser flash calorimetry and other methods developed to extend the heat capacity measurements to newer classes of materials and to extreme conditions of sample geometry, pressure and temperature are comprehensively reviewed. Examples of recent work and details of the experimental systems are provided for each method. The introduction of automation in control systems for the monitoring of the experiments and for data processing is also discussed. Two hundred and eighty references and 18 figures are used to illustrate the various techniques.

Key words: Heat capacity measurement, adiabatic calorimetry, isothermal calorimetry, Tian-Calvet micro-calorimeters, a.c. method of calorimetry, pulse methods of calorimetry, automation in calorimetry.

1. Introduction

The measurement of heat capacity is a major technique of physical investigation for the understanding of materials, because the heat capacity can be calculated *ab initio* from the model of a physical system. Ruhemann[1] suggests that more fundamental significance can be attached to heat capacity measurements than to any other investigation, at least at low temperatures. Even at high temperatures, these measurements are useful in understanding many physico-chemical phenomena. The heat capacity is the temperature coefficient of the average energy of the system and can be readily used as a test for any model or theory, though C_v is an averaged quantity so that its measurement cannot directly shed any light on the finer details of the model[2].

The basic experimental techniques of heat capacity measurements are quite old. The systems based on the isothermal calorimetry (for example, the Bunsen's ice calorimeter, the steam calorimeter, etc.) and the method of mixtures are extensively used even today with little change in the principles of operation. These early systems were discussed in detail by Saha and Srivastava[3]. The basic ideas of adiabatic calorimetry

were developed by Nernst[4] more than 70 years ago. These classical methods are widely used and generally provide very good accuracies ; but newer work has been taken up, where these classical techniques cannot be used. Recently, measurements at high pressures and very low temperatures, and on samples of unusual geometry (for example, thin films and foils) have been undertaken. The active interest in critical phenomena has led to the necessity for very high resolution C_p measurements. Calorimetry has now become a useful tool for biochemists and is even used as a clinical tool[6].

These requirements have led to the development and extensive use of techniques such as the modulation method, the pulse relaxation method, the dynamic pulse methods and others. The commercial development of the DSC (Differential Scanning Calorimeter) has provided another apparatus for very good C_p measurements. These generally have an advantage in that the quantity of sample required for measurements is small, a few mg compared to the 10 g or more generally required by the conventional methods.

The aim of the present review is to provide a coherent picture of the recent progress in heat capacity measurement. Generally, these developments involve, on one hand the use of high precision electronic and scientific equipment to improve the accuracy and resolution of measurements and on the other hand, development of techniques and systems for work under unusual environmental conditions. The easy availability of data processing equipment has led to the development of automated systems. While some automation had been applied to the control functions in the earlier work, the present systems are generally designed for automatic data acquisition and analysis.

The present review starts with a discussion of the relationship of heat capacity to other physico-chemical parameters. While this information is not new, it is intended to provide completeness to the review and also indicate the accuracies and resolutions required in various types of measurement. We also discuss the importance of C_p measurements near phase transitions and under extreme environmental conditions. Section 3 describes the various classical methods and their general limitations. Excellent reviews of this area are available for example in *Experimental Thermodynamics* edited by McCullough and Scott[7], and in Marcus and Friedberg[8], Keesom and Pearlman[9], Kybett *et al*[10], and Sturtevant[14]. The measurements at high temperatures are reviewed by Shelton[11] and by Kingerey[12]. Therefore, we have provided only an outline of the physical principles involved. The types of samples and the experimental conditions required in these measurements are also indicated to show the limitations of these older methods. The newer techniques are discussed in Section 4. Here more details of the principles of operation and of various experimental systems are reported. The DSC has been included, but since excellent reviews of the field are available[13-17], only a brief outline of the important aspects is given. The next section stresses the developments in the field of automatic control of experiments and the computation of C_p data. The last section provides a brief analysis of the recent developments, emphasizing the areas in which each particular technique is most useful.

Calorimetry is a flourishing area of work with a very wide range of application. As a result, some topics had to be excluded or discussed only briefly. For example, the active area of calorimetry of reacting systems, which provides interesting information about chemical reactions and kinetics is discussed very briefly. The fields of DTA and TGA have not been described. Fortunately, these areas have been comprehensively reviewed by Wendlandt[18,19,22] Murphy[20], and others[21,23].

2.1. *Relationship of heat capacity to other physicochemical properties : Basic thermodynamic relationships*

Consider first some basic thermodynamic equations involving the heat capacity.

$$S_T^0 = \int_0^{T_1} \frac{C_p^0}{T}\,dT + \frac{\Delta H_{tr}}{T_1} + \int_{T_1}^{T_2} \frac{C_p^0}{T}\,dT \oplus \cdots \tag{1}$$

Also

$$\frac{H_T^0 - H_O^0}{T} = \frac{1}{2}\left[\int_0^{T_1} C_p^0\,dT + \Delta H_{tr} + \int_{T_1}^{T_2} C_p^0\,dT \oplus \cdots\right] \tag{2}$$

$$\frac{G_T^0}{T} - H_O^0 = -S_T^0 + \frac{H_T^0 - H_O^0}{T}\,. \tag{3}$$

In equations (1) – (3), the system has transitions at temperatures T_1, T_2, etc., H is the enthalpy, S is the entropy and G is the Gibb's free energy. The specific heats at constant volume C_v and at constant pressure C_p, are related by

$$C_p - C_v = Tv\,\beta^2/K_T \tag{4}$$

where $C_p = T(\partial S/\partial T)_p$, $C_v = T(\partial S/\partial T)_V$, $\beta = (1/V)\ (\partial V/\partial T)_p$ and $K_T = -(1/v)\ (\partial v/\partial p)_T$. Equation (7) and the Nernst-Lindemann equation

$$C_p - C_v = A\,C_p^2\,T \tag{5}$$

are used often. In equation (5), A is approximately constant over a reasonably wide range of temperature. Since pressures required for maintaining a constant volume of a solid are very large, only C_p is experimentally measured in a solid.

When a model of a system is developed, the first statistical quantity determined is the partition function Z.

$$Z = \Sigma \exp\ (-E_i/kT). \tag{6}$$

Here E_i are the energy states of the system and k the Boltzmann's constant. Z is related to specific heat as

$$C_v = T[\partial^2 (kT \ln Z)/\partial T^2]. \tag{7}$$

This relates in a fundamental way the specific heat to the model and energy states of the system. In reacting systems or under conditions where changes take place in the number of particles in a given phase, it is customary to introduce the grand partition function in treating the statistical thermodynamics of the system. These considerations are also well-known and will not be pursued here.

The elementary quantum theory of specific heat is based essentially on the Einstein and Debye models which are used to evaluate the contribution to C_p from lattice vibrations (phonons). The basic ideas and the shortcomings of these simple models for the density of phonon states are well-known. These shortcomings are reflected in the θ_D being not constant over a wide temperature range. The Born–Von Karmann model for the lattice vibrations[24] is used to explain the changes in θ_D. However, a detailed knowledge about the energy states in the solid is not available to calculate C_p and hence G directly. So for most systems, S_T and $(H_T - H_0)/T$ are to be obtained from experimental calorimetric measurements only. Spectroscopic data and molecular parameters are available only for some simple gaseous molecules to allow a direct calculation of thermodynamic parameters[25,26].

2.2. *Heat capacity measurements: Resolution and accuracy in main areas of measurement*

We can divide precise calorimetry into three branches : (1) calorimetry for the determination of thermodynamic and other parameters (2) calorimetry in critical regions and (3) calorimetry under extreme environmental conditions. These are now briefly discussed.

The measurement of heat capacity for the evaluation of thermodynamic parameters is undertaken for the determination of C_p and hence S_T and G_T for all equilibrium phases. As newer materials are produced, newer work will be needed. Also some amount of reference data is needed for evaluating primary standards for the calibration of new calorimetric systems. The motivations for this type of work are the determination of θ_D and its variation with temperature, or of magnetic, spin or other contributions to C_p and the determination of physical processes causing them. Alternately, the data may be needed for the evaluation of H, G and S which are needed in defining the chemical kinetics and the energetics of the materials. The data are also used in the study of phase diagrams of materials[27]. From the technological point of view, accurate C_p measurements are needed in the design of systems and in the evaluation of technological materials for practical applications. In this class of work, usually absolute accuracy of measurements is very important since C_p values are directly used in the evaluation of parameters.

The theoretical and experimental aspects of critical point phenomena have been receiving a large amount of attention in recent years[5,38,29]. Following the development of the scaling hypothesis and the use of renormalization techniques, the theoretical

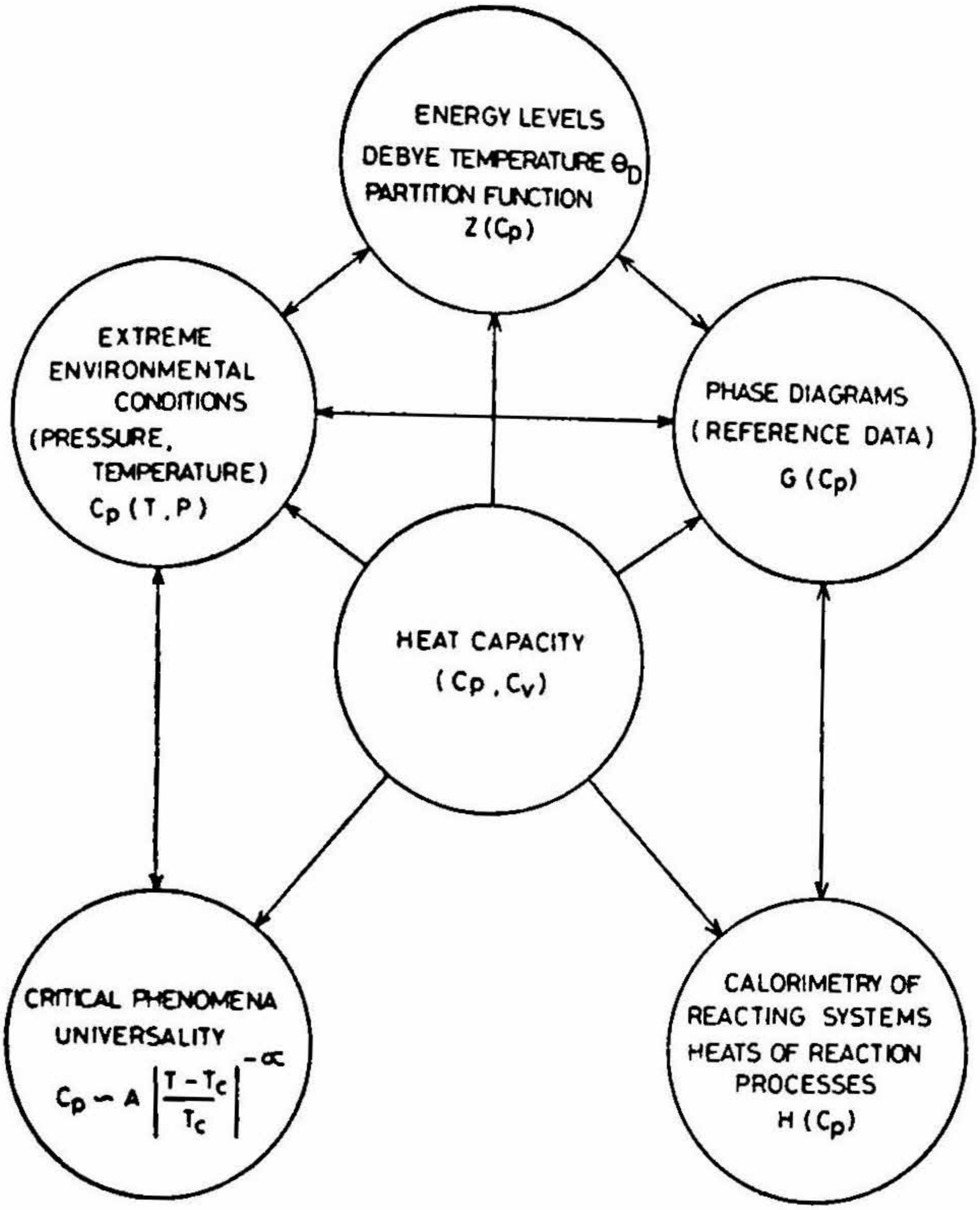


FIG. 1. Relationships of heat capacity to thermophysical properties.

work in this field has become well established. The theory suggests that near a second-order phase transition, C_p varies as

$$C_p \sim A \mid T - T_c \mid^{-\alpha} \tag{8}$$

α is called the critical exponent and is universal, irrespective of the physical system, for a given number of degrees of freedom and the dimensionality. The extensive work on C_p measurements in the critical region have been reviewed by Gronvold[30], Kerimov[31] and others. Near a first-order phase transition, the evaluation of latent heat defines S and G, but near a second order transition, C_p measurements give insight into various aspects of co-operative transitions and critical phenomena. Here accurate measurements of C_p with very high rseolutions are necessary for detailed comparisons with

the theories. Measurements with relative accuracies of 0·1–0·01% are necessary with $t \sim 10^{-4}$ as the required resolution in temperature (here $t = (T - T_c)/T_c$). Since $C_p = (dQ/dT)_p$ the value of dQ will be very small for small dT. Thus the major requirement for the measurements is very high resolution and relative accuracy. Absolute calibration is not of primary importance. In certain areas of critical phonomena, the requirements cannot be met. For example, it is known that the superconducting coherence length is very large[32]. Thus to obtain critical exponents in this case, C_p measurements with $t \sim 10^{-14}$ are needed[30]. This is currently not possible and specific heat measurements in superconductors are used mainly to obtain interesting information about alloying effects, structural transitions, etc.

The measurement of heat capacities under extreme conditions of temperature (very low or very high), pressure (high) or sample geometry and size is another important area of modern calorimetry. The observation of electronic transitions such as the metal-insulator transition[33] has enhanced the interest in high pressure calorimetry. With the use of high pressure as a materials production tool[34] and general interest in high pressure effects on physical properties of materials, high pressure and high temperature calorimetry is fast developing. This importance of measurements of thermodynamic parameters, under pressure, is reflected in the reviews of high pressure calorimetry by Beckett and Cezairliyan[35] and by Loriers-Susse[36]. The current experimental systems can give accuracies of about 2–5% up to 40–60 K bar. In many cases, errors of 5–10% are common.

Heat capacity measurements at ultra-low temperatures serve two purposes. Heat capacity data of all components are essential for the design of efficient cryogenic systems[37,38]. Also, low temperature measurements have an intrinsic interest. If there are any Schottky anomalies, at low temperatures, since very few energy states are involved, C_p measurements can help in completely understanding the phenomena [39,40]. An interesting example of calorimetry at low temperatures is the study of tunneling states in glasses. The two-level tunneling states model, developed by Anderson *et al*[41] and Phillips [42] is widely used for the analysis of the physical properties of glasses at very low temperatures. These were developed, in the first instance, to explain a large linear term found in C_p measurements on amorphous systems [43,44].

Another interesting area for calorimetry concerns samples of unusual geometry such as thin films, where the surface to volume ratio is very large and the thickness is usually 100–1000 Å. These require special methods for C_p determination. It is known for a long time that powders have a $C_p \sim T^2$ term and this term depends upon the surface area per unit volume σ. This is theoretically and experimentally confirmed[45]. However, in the case of thin films, σ is very large and the results are not clear. Since the system is not an infinite medium and there are a large number of free atoms on the surface forming a free boundary, the contribution of the Rayleigh surface states to C_p is to be considered. Optical work has confirmed the presence of these states[46]. Some theoretical work was also undertaken[47] but more experimental results are needed.

Also, a large number of amorphous superconductors are produced as thin films and their C_p measurements at low temperatures are of interest[48].

For the measurement of C_p under extreme conditions, the major requirements pertain to the design of systems for these special conditions. For example, adiabatic isolation of samples is difficult in high pressure calorimetry. Samples have to be small for very low temperature work and then the effect of heat leaks will be large. For thin films, the presence of a substrate is to be considered. Also, the attainment of uniform temperatures will be difficult.

3.1. *Classical methods of measurement : Some new developments*

In this section, we briefly discuss the methods which have been in use for a long time. The basic principles of operation are quite straight forward. A certain quantity of energy is supplied to the sample, usually in the form of electric power, which is accurately determined. The change in temperature of the sample is monitored. Possible heat losses are also evaluated. Then

$$Q = \int_{T_1}^{T_2} C_p dT + \int_t K dt. \tag{9}$$

Here, K represents a parameter of heat leak, which is not used to heat the sample but is lost. There are several distinct classes of calorimeters based on this simple principle and these will be discussed in the next sub-sections. These are very well-known but improvements to the systems for specific cases are still being reported. In each case, we shall discuss the basic principle and a few interesting recent examples in the field.

3.1.1. *Adiabatic calorimetry*

In adiabatic calorimetry, the sample is maintained under adiabatic conditions and the total energy input is used to heat the sample. The comparison between adiabatic and other methods is clearly illustrated in fig. 2. To ensure adiabatic conditions, the sample (with the heater and the thermometer) assembly is provided with a shield of low thermal capacity. A controller is used to maintain the shield at a temperature identical to the sample temperature, even as the sample temperature changes.

A large number of systems based on this principle are reported and the systems due to Southard and Andrews [49] and Furukawa *et al*[50] are examples of the early work, Generally, fairly large size samples (about 5–10 g or more) are used. However, some systems which use smaller samples have been developed by several workers, for example, Morin and Maita[51]. Due to the addition of heater, sensor and other addenda, the errors are likely to increase, particularly if the sample heat capacity is small. It is generally accepted that adiabatic calorimetry is useful up to about 800° C[52]. At higher temperatures, loss of energy by radiation will introduce errors. However, systems capable of working up to 1900 K have been developed by Armstrong[53],

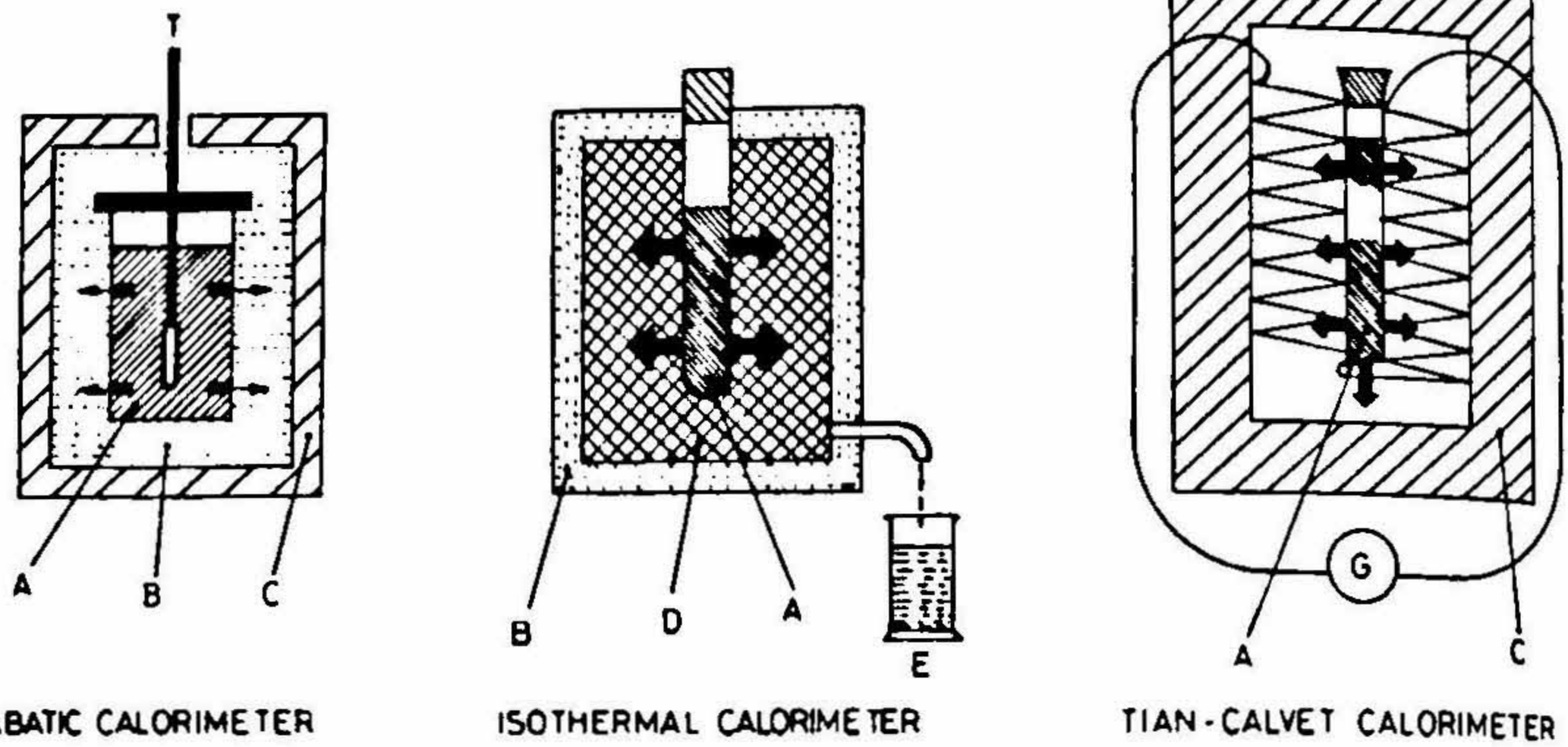


FIG. 2. Different types of calorimeters (Ref. 105).

A = Zone of heat production inside the calorimeter container, *B* = Insulating gap, *C* = External jacket, good conductor of heat. *D* = Ice or other easily melted substance.

Sokolov[54] and others[55,56]. Recently, an adiabatic microcalorimeter which works on very small samples (down to 0·6 g) has been developed[57,58]. This method has also been used for measurements on radioactive samples, where self-heating by radio activity is to be considered[59]. The schematic of an adiabatic calorimeter and control system is shown in fig. 3. The adiabatic method is an absolute method usable over a wide range of temperature. In other methods, either calibration or a knowledge of other thermal constants of the appraratus is needed. Systems capable of very high absolute accuracies (better than 0·1%) are known[60].

The adiabatic method can be used for the study of reactions if the reaction rate is slow. An example of such a system is the one that has been developed by Kubaschewski and Walter[61]. The adiabatic calorimeter can also be used in the differential mode[62,63]. The heater power input in the adiabatic calorimeter can be continuously applied and several of these scanning type adiabatic calorimeters are described in recent literature, for operation over different ranges from liquid Helium temperature ($\sim 2K$) to 1800 K[64–68]. Recently, some improvements to the standard systems involving the reduction of the sample-to-bath thermal link[69] and the sample holder heat capacity, etc.[70,71] have been reported. The adiabatic method is used for measurements at low temperatures, when a magnetic field is present[72] and at very low temperatures (0·02–0·2K) for measuring the specific heats of several amorphous insulators[73]. Here, however, serious consideration to the heat leaks has to be made. The continued interest in adiabatic calorimetry is reflected in the recent development of some systems[74,75] with very high resolutions and accuracies. One such example is a system with high resolu-

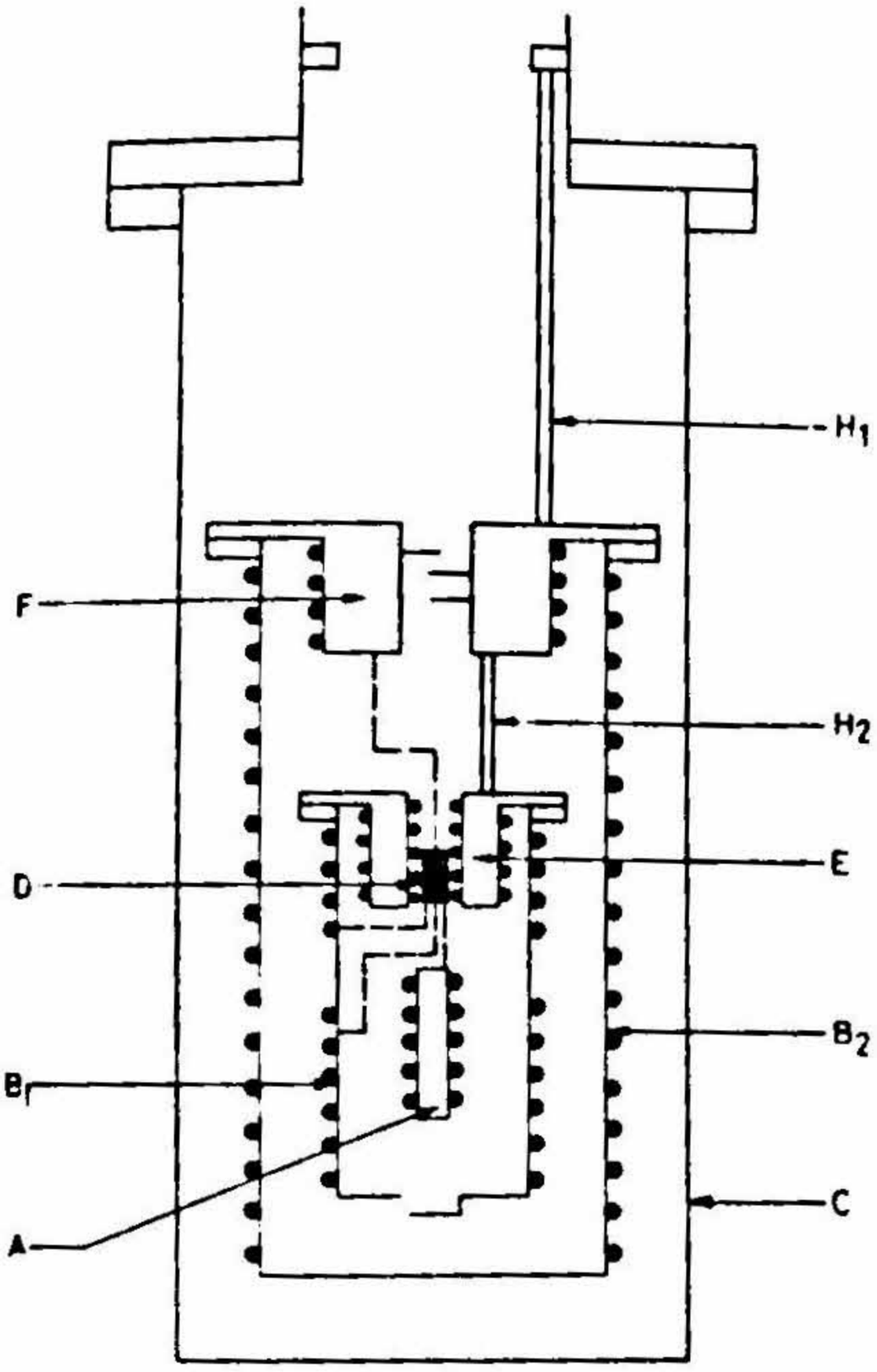


FIG. 3*a*. Schematic diagram of adiabatic calorimeter. H_1 and H_2 are stainless steel supports; F is the outer shield heat sink; E is the adiabatic shield heat sink; A is the specimen; C is the vacuum jacket; B_1 and B_2 are respectively the adiabatic and outer shields, and D is the quartz thermometer. Thermocouples are indicated by broken lines and heaters are indicated by series of points. (Ref. 253).

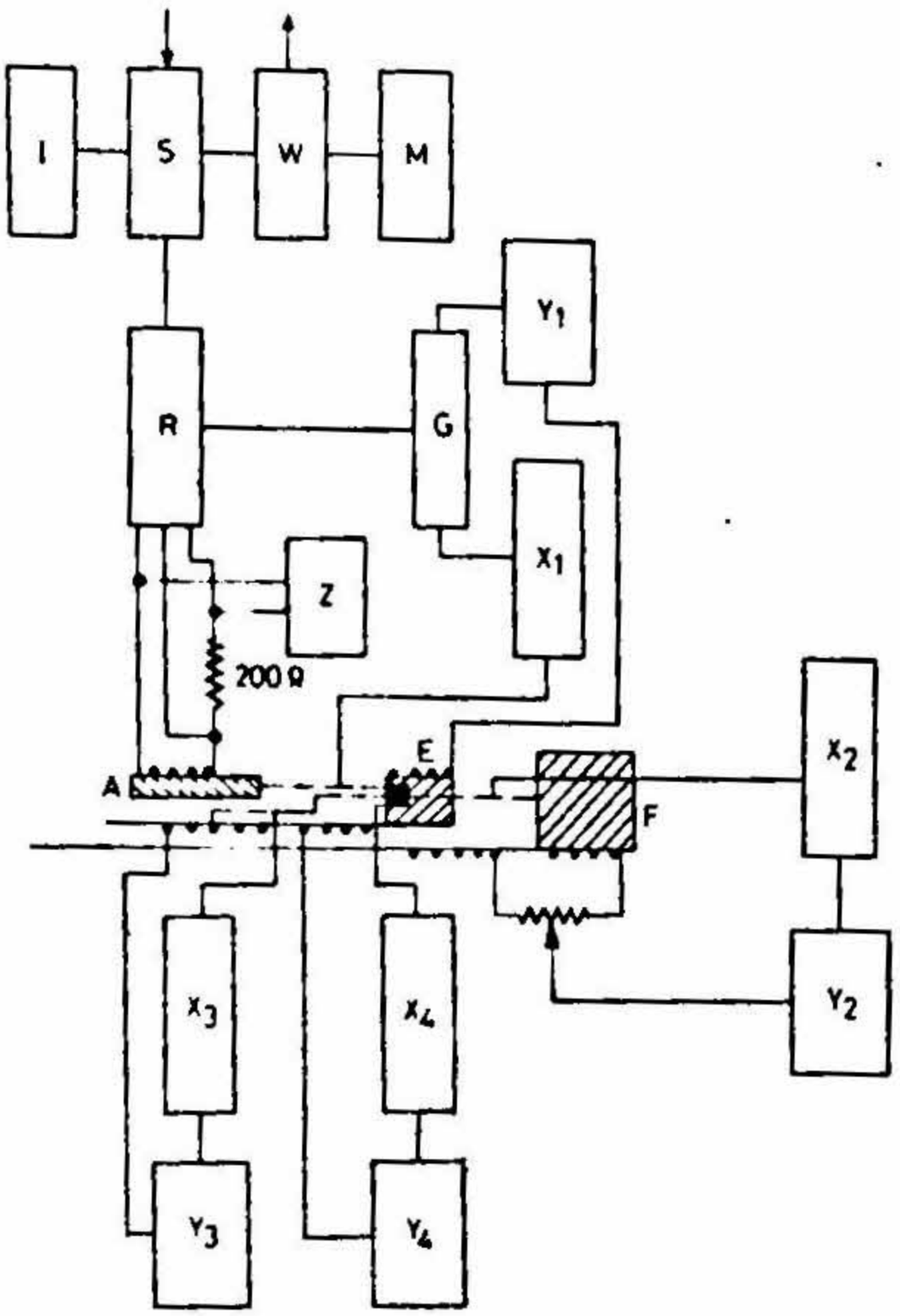


FIG. 3*b*. Block circuit diagram for control and measurement associated with calorimeter. X_1, X_3 and X_4 are Keithley 148 Nanovoltmeters; X_2 is Keithley 149 microvoltmeter; Y_1, Y_2, Y_3 and Y_4 are heater control units; Z is a 0–30 V power supply; G is a 10s integrator; R is a serial interface; S is a data logger; W is a video terminal; M is a magnetic tape recorder, and I is a digital voltmeter. A is the sample, E the Adiabatic heat sink, F the outer heat sink (Ref. 253).

tion with provision for heating the sample in steps of 10 mK[76]. Another recent example of adiabatic calorimetry is the study of C_p and enthalpy changes in He^4 films. The gas is adsorbed on Vycor glass and an adiabatic measurement performed. The resolution is good enough to determine the C_p contributions due to almost monomolecular layers of He^4 films. The temperature range involved is 0·08 K to 1·3 K[77].

3.1.2. *Isothermal shield calorimetry*

This method is used mainly at low temperatures (less than 20 K) where due to cooling power limitations, the sample size is small. Here, maintaining adiabatic conditions is

difficult and so the shield is maintained at a fixed temperature (near the sample temperature). Fortunately, at low temperatures, the radiation loss falls off as T^4 and becomes insignificant. The power input to the sample changes its temperature. The complete time-temperature profile of the system gives the quantity of heat leak which is precisely determined. Hence the quantity of energy used for heating the sample is evaluated and C_p determined. For this kind of set-up, the shield is made very massive so that the temperature of the shield does not change during the experiment[78].

This method has been extensively used by Giauque and co-workers and several practical systems have been described in literature[79-81]. The use of this type of calorimetry for high resolution measurements (temperature resolution of a few μK) for various samples near their magnetic phase transitions has been discussed by Rives[82]. He also discusses the errors in measurement and the use of continuous heating in such systems. A method of successive approximations for evaluation of C_p and heat leak is also reported[83], whereby the accuracy in C_p measurements at low temperatures is enhanced.

3.1.3. *Isothermal calorimetry*

In this type of calorimeter, the sample at a higher temperature is introduced into the calorimeter, where the heat is absorbed under isothermal conditions. Usually, the constancy in temperature is maintained by a phase change. One of the well-known examples is the Bunsen's ice calorimeter. The facts that the heat capacity of the calorimeter is not involved and that the heat leak during the cooling time is negligible have formed important advantages in early work. Various systems have been developed and the units due to Ginning and Corrucini[84] and Hoch and Johnson[85,86] are representative examples. A recent version is reported by Denielou *et al*[87]. Isothermal systems based on diphenyl ether have also been used for a long time[88,89]. Mann[90] has in an early work shown the use of thermoelectric elements for achieving isothermal conditions. The development of semi-conducting thermoelectric elements has made such a scheme easier[91] in modern calorimetry. The Tian–Calvet microcalorimeter uses this type of isothermal calorimetry with a differential sample configuration, as discussed further in Section 3.1.5. The major advantage of the isothermal calorimeter is the good resolution in enthalpy measurements. However, the sample temperature changes by a large amount and the method is useful only if C_p of the sample changes slowly with temperature. The method is mainly used for enthalpy measurements at high temperatures, up to 1600° C.

3.1.4. *The drop calorimeter*

The drop method is similar to the isothermal method in the manner in which the sample is introduced into the calorimeter. However, the temperature of the receiving calorimeter is not constant. The change in temperature of the calorimeter is measured and calibrated with respect to the enthalpy given up by the sample. This is called the receiving calorimeter, the drop method or the method of mixtures. This method is

extensively used up to about 1600° C. A few recent systems have been operated even up to 2500° C. This extensive interest is reflected in a large number of recent practical systems which are reported[92–100].

The basic advantage of this type of system is once again in the accuracy and resolution of enthalpy measurement. High accuracies are facilitated by the fact that the calorimeter is at or near the room temperature. However, the sample temperature changes by a large amount and the method is not useful if C_p changes abruptly (as near a phase transition). The receiving calorimeter may consist of a fluid or a metal block of high thermal conductivity. Usually copper is used. In such cases, the sample and block have to be machined to fit together, so that heat transfer is faster. The sample could be heated in an electric furnace. However, several of the recent systems have used levitation heating of the sample[91–97]. Here the advantages are that complicated radiation baffles need not be used and the contamination of sample is reduced. This method is mainly used for the determination of C_p and enthalpy at very high temperatures. A detailed description of several 'drop' systems has been provided by Kingerey[12]. A schematic representation of such a system is shown in fig. 4.

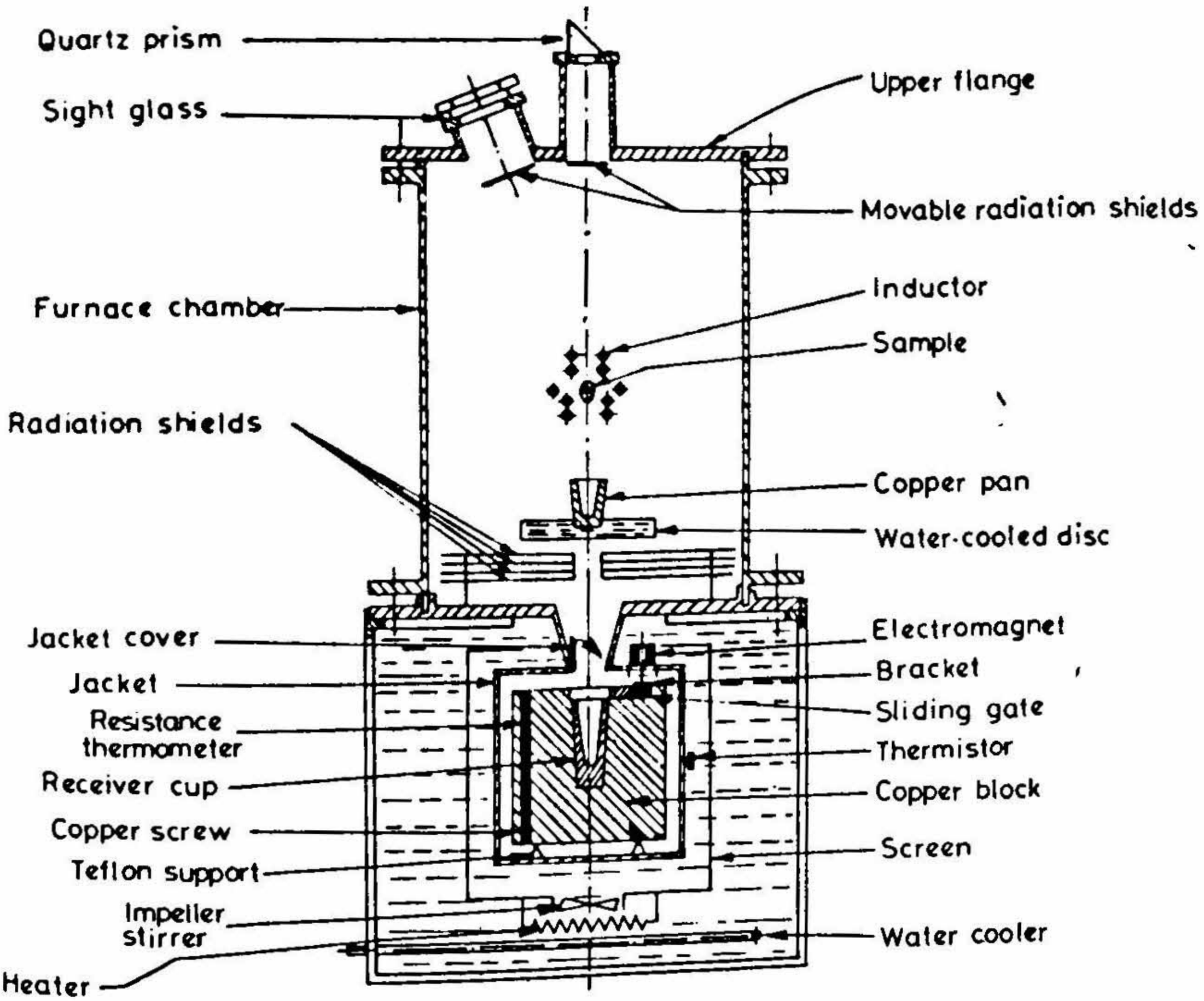


FIG. 4. Schematic diagram of a levitation drop calorimeter (Ref. 11).

3.1.5. *The Tian–Calvet microcalorimeter*

This type of calorimeter was originally developed by Tian[101] and later modified and converted into a differential configuration by Calvet and co-workers [102–104]. Here, changes in sample temperature are held to a minimum and the heat generated or absorbed by the sample is measured by a thermopile. Alternately, Peltier cooling is employed to maintain complete isothermal conditions. The sample chamber is a cylinder

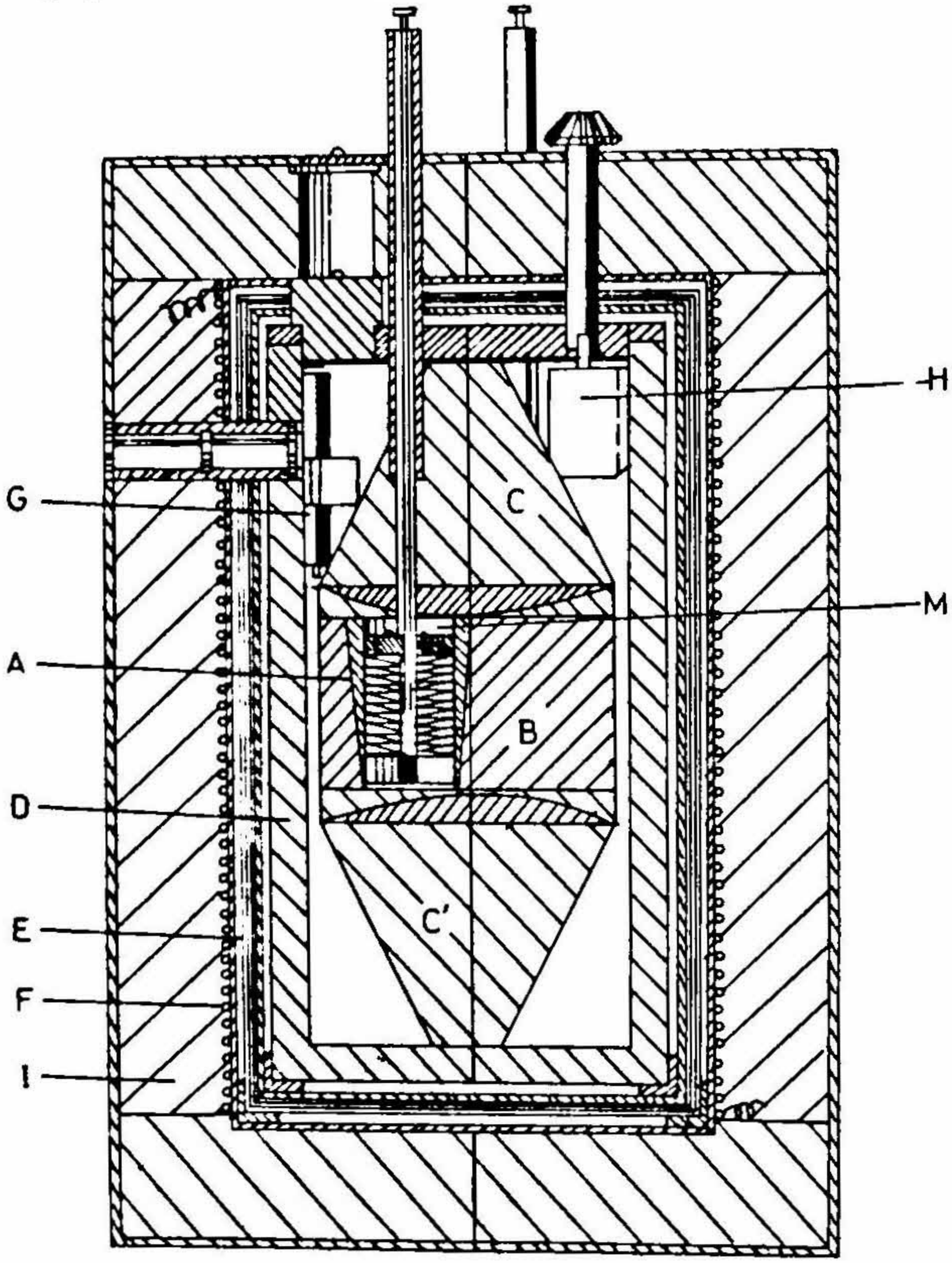


FIG. 5*a*. Vertical cross-section of Calvet's calorimeter cell (Ref. 105).

A= Conical socket, *B*= Metallic block, *C*, *C'*= Cones designed to give equipportion of thermal perturbations, *D*= Metal cylinder, *E*= Thermostat, *F*= Electrical heater, *G* = Galvanomcter, *H*= Switch, *I*= Thermal insulation, *M*= Microcalorimeter assembly placed in *A*.

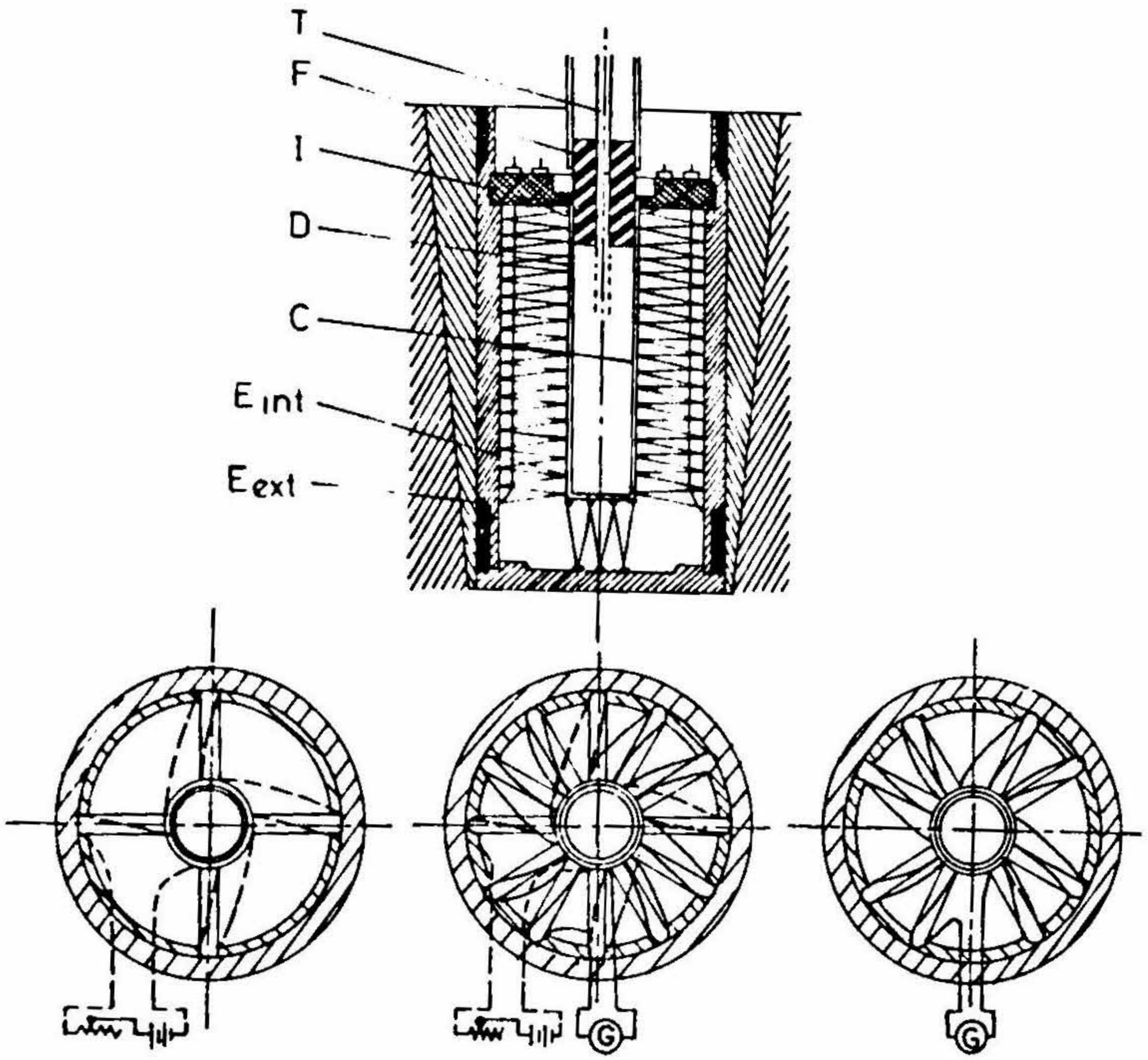


FIG. 5b. Vertical and horizontal sections of microcalorimeter element (Ref. 105).

T = Inlet tube, C = Cylindrical cell, D = Silver cavity for C, F = Insulation, I = Thermopile termination, E_{int}, E_{ext} = Internal and external surfaces of the cell.

of large length-to-diameter ratio and a thermopile is arranged symmetrically and regularly (fig. 5). The differential configuration is very useful in reducing errors [105]. This calorimeter was originally used up to about 1000° C but later improvements. (some of them commercial) have extended the use of this method up to 1600°C[106–108]. The system is extremely useful in the study of reactions and kinetic processes occurring in the sample even if they are very slow. The fidelity of the apparatus is sufficient to allow a study of processes taking place over several hours or even days. This system is useful for physicochemical studies, involving C_p measurements, adsorption processes and chemical kinetics. A large portion of the biological and medical calorimetry is performed using this type of system[105,109–111]. The system is also extensively used in the study of thermochemistry of metals and alloys at high temperatures [112,113]. Recent developments in the instrumentation have made the sample requirements very small and this has added to the utility of the technique[114].

3.1.6. *High speed thermodynamic measurements*

For measurements of thermodynamic parameters above 2500° C, the methods discussed in previous sections have serious limitations. Firstly, the problem of sample reactivity and corrosion are severe. Also the evaporation of the sample and effect of thermionic emission have to be considered. Hence the pulse or high speed methods have been developed and used extensively for measurements at very high temperatures. These have been reviewed by Beckett and Cezairliyan[115]. Here, a sharp pulse of energy is delivered to the sample and the rise in temperature continuously monitored. From knowledge of the incident energy and temperature changes C_p is evaluated. If electrical energy is used, direct measurement of power input is possible. For other types of radiation, calibration is necessary. Since the temperature has to be measured, a large number of times in a short experiment, optical pyrometry is usually used. For conductors, Joule heating is used. The method can be used at high pressures also (see fig. 6). For insulators, external radiative heating is employed. These techniques are generally used at temperatures in excess of 2000° C. However, some workers have used them at lower temperatures also. The systems of Avramescu[116], Kurrelmeyer *et al*[117], Nathan [118], and Wallace *et al*[119] are representatives of early work in the method. Generally, the accuracies in this type of measurement are 2–5%. A modification of this is called the exploding wire calorimetry. Here, a sharp pulse of energy is again applied but the power is so large that the sample which is in wire form completely disintegrates. Thus, the measurements are possible over a wider temperature range. Cezairliyan and co-workers have used this method very effectively [120,121]. This method is obviously useful only for conducting samples. The requirement of fast measurements make the use of automation in this method very attractive. These developments will be discussed in Section 5.

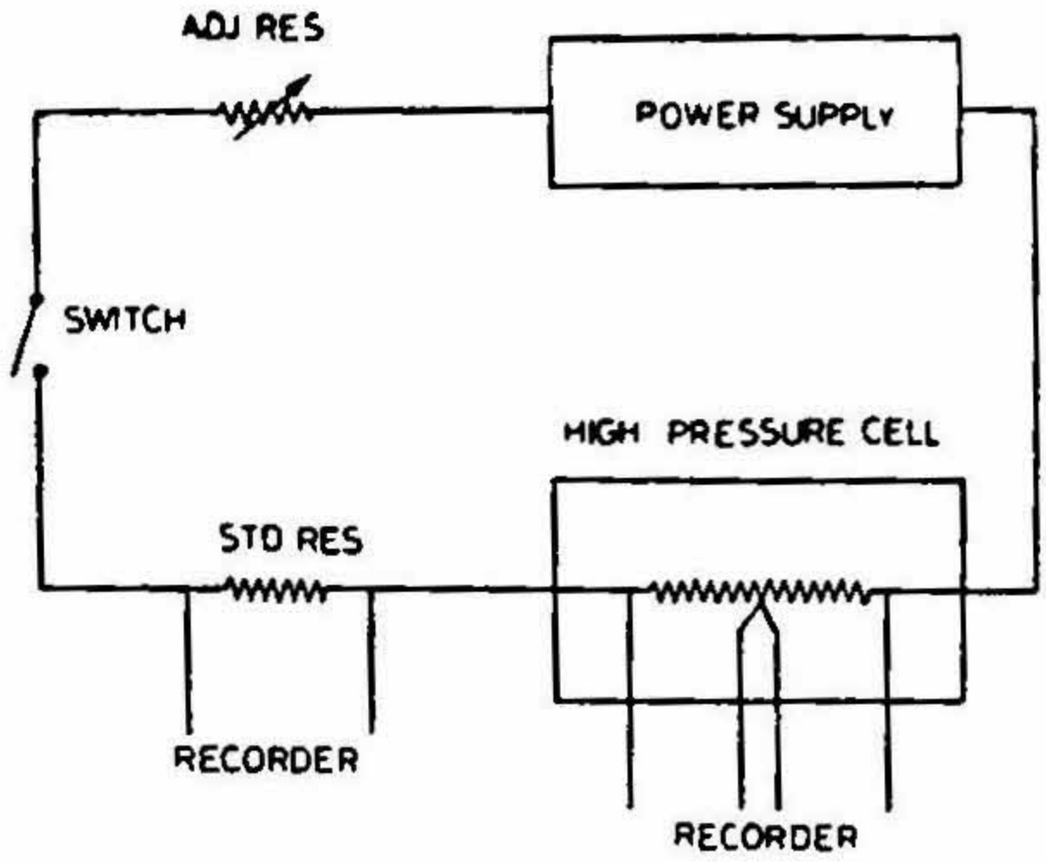


FIG. 6. A simplified block diagram for transient measurements of specific heats at high pressures.

3.1.7. *Calorimetry of reacting systems*

The adiabatic method or the Tian–Calvet system do not work if a fast reaction takes place in the sample. For such applications, other techniques are used. These include the bomb calorimeter, the flow calorimeter and the solution calorimeter. In the bomb calorimeter, the reaction takes place in an atmosphere of either oxygen or any other gas (usually F_2), inside a closed container called the bomb. This is immersed in a regular bath and the enthalpy increments are measured as in the drop method. The system usually has provision for sweeping away the gaseous reaction products for analysis. Sometimes, the bath is flooded and the reaction products dissolved in a solvent for analysis. Benzoic acid is generally used for calibration of the bomb calorimeter. The bomb calorimeter is sometimes made of glass, to assist visual observations during the combustion. The flame calorimeters are used to determine the heats of combustion of gases or substances with high vapour pressures at room temperature. If premixing of constituents is not possible, a continuous flow configuration may also be used.

The solution calorimetry is similar to the bomb calorimetry as far as enthalpy measurements are concerned. Generally, calibration is done by electrical power input. The solution calorimetry is used for the determination of heats of solution, mixing, formation, etc. Solution calorimetry involving molten tin has been widely used. The flow calorimetry is used to determine the heat capacities and energy changes, as a steady flow of fluid passes through a controlled bath. This can be used to determine the heats of reactions of solid-fluid or fluid-fluid systems.

The above methods are well-known and a large number of systems have been built with minor changes as required for individual cases. The reviews by Kybett *et al*[10] and Shelton[11] cover these areas very comprehensively. However, even in recent literature, several systems for individual applications continue to be reported. For example, Lenski and Bohler[122], Olofsson and Sunner[123] and Hagiov *et al*[121] describe some improved models of F_2 and O_2 bomb calorimeters. Isoperibol calorimeters for C_p determinations on fluids and also for aqueous solutions have been reported[125,125a] and flow calorimeters for fluids and fluid-solid mixtures are described by Chourasia *et al*[126]. and Clarke *et al*[127]. Such activity once again shows the continued interest in and importance of such systems. A recent very interesting example is the high temperature, high pressure flow calorimeter developed by Christensen *et al*[128]. Here, measurements of $\pm$ 0·5% accuracy in energy are possible over 273–423 K and up to 4,000 atmospheres.

3.1.8. *Calorimetry of fluids and gases*

Gases and vapours generally have well defined electronic, vibrational and rotational energy levels, which assist in an *ab initio* calculation of the partition function. Also, the molecular parameters are generally well-known and in some cases precision in such calculations is more than the errors in experimental measurements. The basic physical principles of the specific heats of gases and the application of quantum mechanical

methods are well described by Gopal[2]. In the methods discussed above, the adiabatic method can be employed for fluids as already mentioned. The flow calorimetry is another technique used. For gases, there are other specific methods. The Clement and Desormes method is one, where from pressure and volume measurements, the value of $\gamma = C_p/C_v$ is determined. In the case of gases, in addition to C_p, C_v is also experimentally determined. Another method uses the relation,

$$V = \sqrt{\frac{\gamma P}{\rho}}. \tag{10}$$

Here ρ is the density and V is the velocity of sound. From accurate sound or ultrasonic velocity measurements, C_p is easily evaluated. Such classical methods, for measurement of specific heats of gases, are discussed at length by Saha and Srivastava[3]. The thermodynamic data of various gases are of interest and a large amount of compiling work on this line is often performed[129,130]. An interesting recent work has been the use of the transient hot wire method (to be discussed in later sections) for the determination of diffusivities and thermal conductivities of gases[131-133]. The method has been used for studying the thermal conductivity anomaly at the liquid-gas critical point[134].

3.2. *Merits and demerits of the classical methods*

The classical methods have been very widely used and hence are very well documented as regards the important features, design considerations and calibration procedures. They are capable of good accuracies and resolutions. However, these generally require rather large quantities of sample material. So they are not easy to apply if samples are very small in size and weight. Further, their use under extreme environmental conditions is limited. These two factors are the main reasons or motivating forces for the new developments in recent years.

4.1. *The new techniques : General features*

The division of the experimental techniques into the classical and newer methods is somewhat arbitrary and as mentioned earlier is introduced only for the sake of clarity. In the present section, we discuss methods, which unlike the classical methods discussed in the previous section, have come into prominence recently. Here, we discuss the a.c. calorimetry, the pulse relaxation method, the dynamic pulse methods, DSC and a few other techniques such as laser flash calorimetry, ultrasonic, magnetic methods, etc. The first three can be called transient methods and are primarily based on the ideas of heat wave propagation developed by Angstrom[135]. Obviously, the basic idea is quite old but the development as calorimetric systems is quite new. In the following sub-sections, we shall discuss the detailed physical principles involved and then discuss the various experimental arrangements and systems used.

In the transient techniques, the heat capacity is related to the internal relaxation time *i.e.*, the time involved in the sample attaining temperature equilibrium, when a certain amount of heat is supplied to it, and the external relaxation time, *i.e.*, the time

constant characterizing the thermal link between the sample and the calorimeter. This generally means that experimental conditions can be altered to suit requirements for different samples, heat capacity values and sample environments. This is the major advantage of these methods. The DSC, in addition to being a commercially available system, can be programmed to make the measurements at a fixed rate. The laser flash calorimetry and other methods discussed in Section 4.1.5 offer an insight into the many ways in which C_p can be evaluated under various conditions.

4.1.1. *The a.c. calorimetry or the modulation method*

This is the most extensively used of the modern methods and the literature is quite extensive. The basic principle is the use of periodically varying power input for heating the sample. The sample is connected to the bath through a weak thermal link. The amplitude and the phase of the periodic fluctuations in the sample temperature are related to the heat capacity of the sample. The method is ideally suited for work on small samples ($\sim$ 1 mg), thin films, foils, etc. However, the method has also been used for work on bulk samples by Wantenaar *et al*[136]. The method has been used for high pressure calorimetry and has now become one of the most attractive methods for measuring the heat capacities at high pressures. Depending upon the exact sample and calorimeter design, the equations relating T_{ac}, the temperature fluctuations and C_p differ slightly. A clear description of the theory was developed by Sullivan and Seidel[137]. This particular work has played a large role in making this method very popular. It should be mentioned that this method basically depends on the work of Angstrom[125], and is quite old. Early developments in the field have been reviewed by Zavaritsky[138].

Let us consider the system consisting of a sample of heat capacity C_s, heater of heat capacity C_h and thermometer of heat capacity C_θ. These are connected together among themselves and to the bath through thermal links as shown in fig. 7. Let K_b, K_h and K_θ be the thermal links. Here, we initially assume that internal thermal equilibrium in each part is instantaneous. Then, let the heater power delivered be of the form

$$Q = Q_0 (\cos \tfrac{1}{2} \omega t)^2. \qquad (10\,a)$$

The ' modulation calorimetry ' or the ' a.c. method ' is the name acquired due to the use of such a power in the experiment. If T_h, T_θ, T_b, and T_s are the temperatures of the heater, thermometer, bath and the sample, the equations of heat flux are given by

$$\begin{aligned} C_h T_h &= Q_h = Q_\theta (\cos \tfrac{1}{2} \omega t)^2 - K_h (T_h - T_s) \\ C_s T_s &= Q_s = K_h (T_h - T_s) - K_b (T_s - T_b) - K_\theta (T_s - T_\theta) \\ C_\theta T_\theta &= Q_\theta = K_\theta (T_s - T_\theta). \end{aligned} \qquad (11)$$

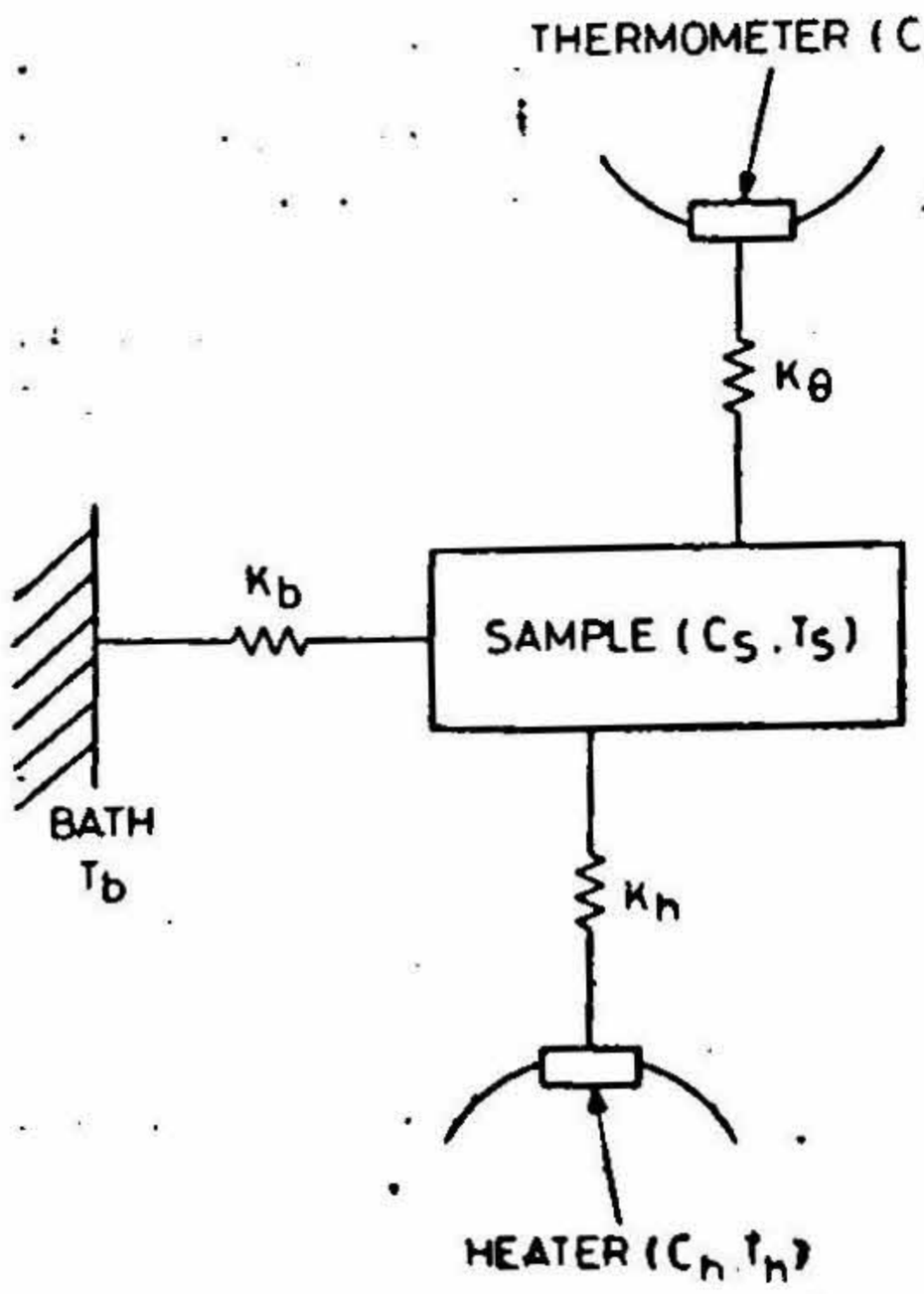


FIG. 7. Diagram of sample coupled to a bath, thermometer, and heater by the thermal conductances K_b, K_θ and K_h, respectively (Ref. 137).

The solution for the temperature T_θ, which is the experimentally determined quantity, is usually quite complex. The solution of Sullivan and Seidel assumes the following:

(i) The heat capacities of the heater and the thermometer are small (we note tha, this constraint on addendum heat capacity is present in the classical methodst but is less serious).

(ii) The sample, thermometer and the heater come to equilibrium in a time much smaller than $1/\omega$

Then

$$T_\theta = T_b + \frac{1}{2} Q_0 \left[\frac{1}{K_b} + \frac{1-\delta}{\omega C} \sin(\omega t - a) \right]. \tag{12}$$

Here $(1-\delta)$ is a complex expression and further simplifications are needed. It has to be noted that the basic idea of the experiment is to feed periodically varying heater power and to detect the periodic variation in the temperature. This is possible if the temperature of the sample, thermometer and heater assembly follows the heater power variation. In a simple electrical analogue, a CR network for low pass filter action, we need $\omega \ll 1/2\pi RC$ where $2\pi RC$ is the time constant τ. If we define relaxation times τ_θ, τ_s and τ_h as

$$\tau_s = \frac{C}{K_b}, \quad \tau_\theta = \frac{C_\theta}{K} \quad \tau_h = \frac{C_h}{K_h}, \tag{13}$$

then the condition needed can be written as

$$\omega^2(\tau^2 + \tau_h^2) \ll 1. \tag{14}$$

In addition we require that

$$\omega\tau_t \gg 1.$$

These assumptions define the value of ω to be used, depending upon the experimenal parameters. We can usually find some value of ω such that these conditions are satisfied whatever be the experimental configuration.

If we introduce

$$\tau_1 = \tau_t$$
$$\tau_2^2 = \tau_\theta^2 + \tau_h^2 + \tau_{int}^2$$
$$\tau_{int} = L^2/(90)^{1/2}\eta \tag{15}$$

where η is the thermal diffusivity, then

$$T_{ac} = \frac{Q_0}{2\omega C}\left[1 + \frac{1}{\omega^2\tau_1^2} + \omega^2\tau_2^2 + \frac{2K}{K_t}\right]^{1/2}. \tag{16}$$

The equation is still quite complex and experimentally there are various ways of determining the heat capacity values. In the method used by Sullivan and Siedel, the sample is electrically heated. The $T_{ac}(\omega)$ is determined for various values of ω to find τ_2. The value of τ_1 is determined by heating the sample with a small d.c. power and following the relaxation of the sample temperature when the d.c. power is stopped. Accuracies of about 1% are reported. The schematic block diagram is shown in fig. 8. The availability of high precision lock-in amplifiers (synchronous detectors) which can detect a coherent a.c. signal of even a few nV in a random noise of IV has made the measurements possible. Several other workers have also used a resistive method for heating[139–142]. Among these, the unit developed by Bruce and Cannell is attractive, since an inexpensive nichrome thin film was used for the work[139]. They have reported the accurate measurement of C_p near the Neel point for Cr_2O_3 using this set-up[142].

In some cases, variation of heat capacity is of more interest rather than absolute values, for example, near a co-operative phase transition. In such cases, this method can be used very efficiently. Since $T_{ac} \sim 1/C$ if we assume very small changes in the other parameters such as τ_1 and τ_2, the determination of T_{ac} is enough for this purpose. In fact, it is known that for several a.c. calorimeter systems, relative accuracy is much superior to the absolute accuracy. Yoshizawa and Fujimura[143] have developed a system which they used to measure C_p of NH_4Cl near the ferroelectric transition. They report an absolute accuracy of only 5% but the relative accuracy is 0·1% and the temperature resolution is 1/300 K. This advantage has been exploited and several workers have used a.c. calorimetry for C_p measurements in the critical region. Interesting examples of such work have been reported by Salamon[144], Handler *et al*[145], Kraftmakher and Romashina[146] and others[147, 148].

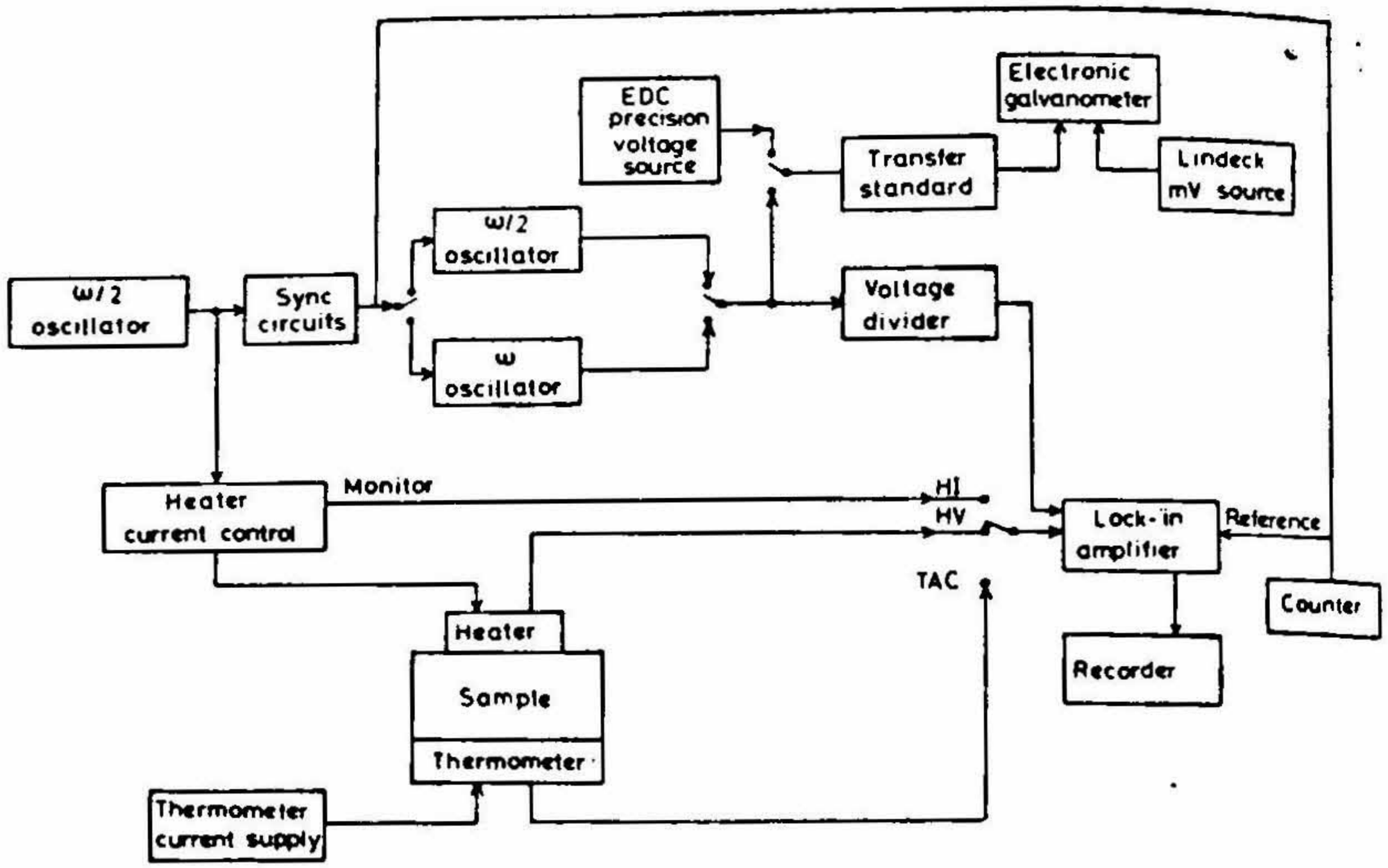


FIG. 8. Block diagram of the arrangement to measure the heat capacity using the a.c. technique (Ref. 137).

A simple comparative system based on this technique has been developed by Viswanathan[149]. This system is very interesting in view of the versatility and simplicity. Here, a laser beam is modulated by a chopper, split into two beams of equal intensity by a Wollaston prism and the two beams heat a sample and a standard independently. τ_1 is kept small in both the specimens by careful design of the thermal link (fig. 9). The T_{ac} for both the sample and the standard are measured.

Then,

$$C_1 = C_2 (\Delta T_2)_{ac}/(\Delta T_1)_{ac}. \tag{17}$$

This comparative technique is very useful since it reduces the number of quantities to be measured. Such a technique is not possible with resistive heating because there is no easy way of ensuring that equal quantities of power are being delivered to the sample and the standard.

The use of optical (laser) or other radiation as the heating source is not limited to systems with differential measurements. Even for single sample geometries, laser heating power was employed by Greene *et al*[150]. Horch[151] and El Shaskowy *et al*[152] have also reported a.c. calorimeters with radiation heating. It can be noticed that if a.c. power is delivered only to some part of the sample, there will exist a phase difference between the a.c. temperature changes at different parts of the sample. The precise value of this phase angle can be measured easily and related to the heat capacity values.

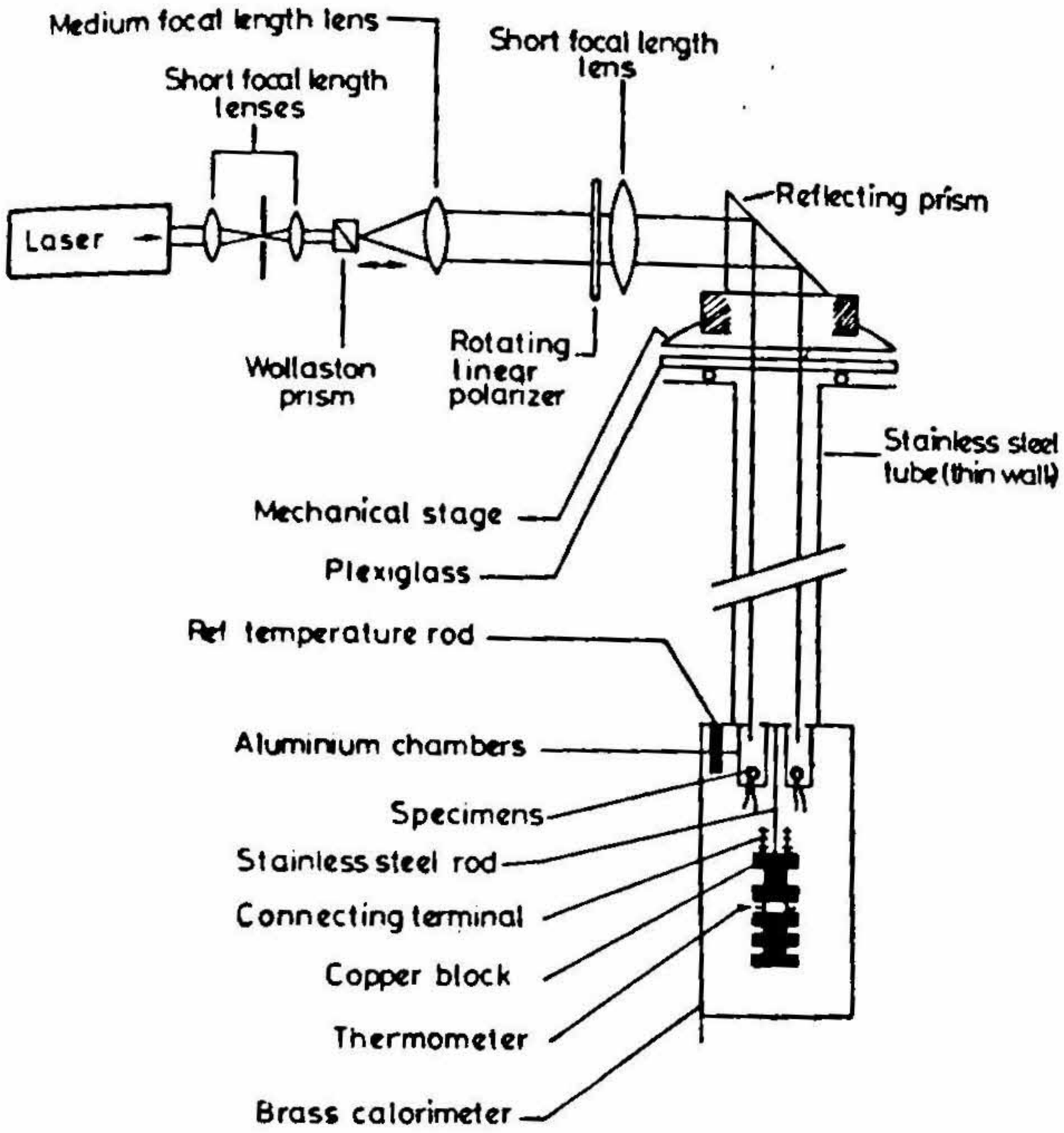


FIG. 9. a.c. calorimetric system with provision for simultaneous optical heating of sample and standard (Ref. 149).

Salamon *et al*[153] have used laser heating of a part of the sample, measured the amplitude and phase of T_{ac} and thus measured the specific heats and thermal diffusivities near phase transitions for a number of samples. A similar system was developed by Yurchak and Khromov[154]. As already mentioned, the a.c. method is very useful if the samples are thin films or foils. In many such cases, *in situ* measurements are necessary. Using either amplitude or phase measurements, a number of workers have measured the specific heats of thin films and foils by this method[150, 155–157].

Another very important regime for a.c. calorimetry is work at high pressures and at high temperatures. For metallic systems, ohmic heating has been employed as a simple way of applying a.c. heating. The details of work at high temperatures has been reviewed by Kraftmakher[158]. For the detection of the a.c. temperature signal, either an electric or an optical detection system using photodetectors can be used. In addition to Kraftmakher and co-workers[160], Holland and Smith[159], Eichler and Gey[162] have used such methods for heat capacity measurements. Similar measurements at high pressures on several samples have been reported by several workers. For a.c.

calorimetry at high pressures also, ohmic heating is employed for metallic samples and indirect electric heater for non-metallic samples. Representative examples of a.c. high pressure calorimetry are reported by Baloga and Garland[163], Itskevich and co-workers[164], Andersson and Backstrom[165] and Sundquist[161].

4.1.2. *The relaxation calorimetry*

This is a method where the basic physical arrangements as well as the experimental set-up are simple and straight forward. The method has been used mainly at low temperatures. The theory of the method is discussed at a number of places but the discussion of Bachman *et al*[166] is easy to follow.

Basically, the adiabatic method uses the equation

$$C = \Delta Q/\Delta T. \tag{18}$$

However, as noted previously, an ideal adiabatic situation is not practical. We can, in general, define a relaxation time τ, for the conductance between the sample and the bath (Obviously $\tau_1 = \infty$ for ideal adiabatic conditions). In the present method, a steady power P is applied for some time. When power P is cut off, the temperature relaxes back to the bath temperature. Here, if we assume that the sample and the addenda reach equilibrium faster than τ_1, (once again as in a.c. calorimetry $\tau_2 \gg \tau_1$) we can write,

$$\text{power in} = \text{power out} + d/dt \text{ (Heat in sample)}$$

or

$$P = Ak\,(\partial T/\partial Z) + C\,(T)\,(\partial T/\partial t). \tag{19}$$

Here Z is the direction of heat flow, A is the area of cross-section of the thermal link and k is the thermal conductivity of the link.

Hence,

$$C(T) = (\partial T/\partial t)^{-1}\left[P - \int_{T_0}^{T_1} K(T)\,dT\right] \tag{20}$$

where

$$K(T) = k(T)\,A/l. \tag{21}$$

If $T_1 - T_0$ is small, then k can be considered to be constant and

$$C(T) = K(T_\infty)/d\,(ln\,\Delta T)/dt. \tag{22}$$

If C is also constant over a small temperature change,

$$d\,(ln\,\Delta T)/dT = -1/\tau_1 = -K/C \tag{23}$$

$$\Delta T(t) = (T_1 - T_0)\exp(-1/\tau_1). \tag{24}$$

Hence C can be evaluated if τ_1 and K are experimentally determined. Howevet, there are some corrections to be applied. Firsıly, we have not considered the contribution to the heat capacity by the thermal link and addendum. If these are included,

$$KT = C_s + C_b + \tfrac{1}{3} C_w, \tag{25}$$

Where C_b is the addendum heat capacity, and C_w is the heat capacity of the wire used as the thermal link. A second source of error is inherent. We note that in the a.c. calorimetry, $\omega\tau_1/10 > 1 > \omega\tau_2 \times 10$ so that $\tau_1 > \tau_2$ is easily satisfied. Here, however, to get the same 1% accuracy in C_s measurements, $\tau_1 > \tau_2$ is to be more rigidly enforced. This is the major problem with the method.

Generally, the experimental set-up for this type of calorimetry is rather simple. A known power P is fed in and K is found as $P/\Delta T_s$ where ΔT_s is the raise in temperature. The P is then cut off and variation of T is plotted as a function of time. The data are fitted to an exponential equation and τ is evaluated. If $\tau_1 > \tau_2$ is not rigidly satisfied, we get a non-exponential plot. The method is mainly used at low temperatures since $\tau_1 > \tau_2$ is more easily satisfied. The method has been used by Bachman *et al* with a silicon infrared bolometer as the temperature sensor and sample holder. The sample holder is shown in fig. 10. Several other workers such as Shutz[167] and Schwall *et al*[168] have also used the method for low temperature work. Lawless[169] has used the method for measurements on a number of ferroelectrics in the 2–34K range. Rade[170] has demonstrated the use of the method by measuring the C_s of a small Sn sample (~ 5 mg). The method has been used for low temperature measurements on some thin films[171] and even at room temperature[172]. A set-up for measuring specific heats in the presence of magnetic fields of 4·4 Tesla in the 1·5–10 K range has been described by Forgan and Nedjat[173]. Djurek and co-workers have modified the method

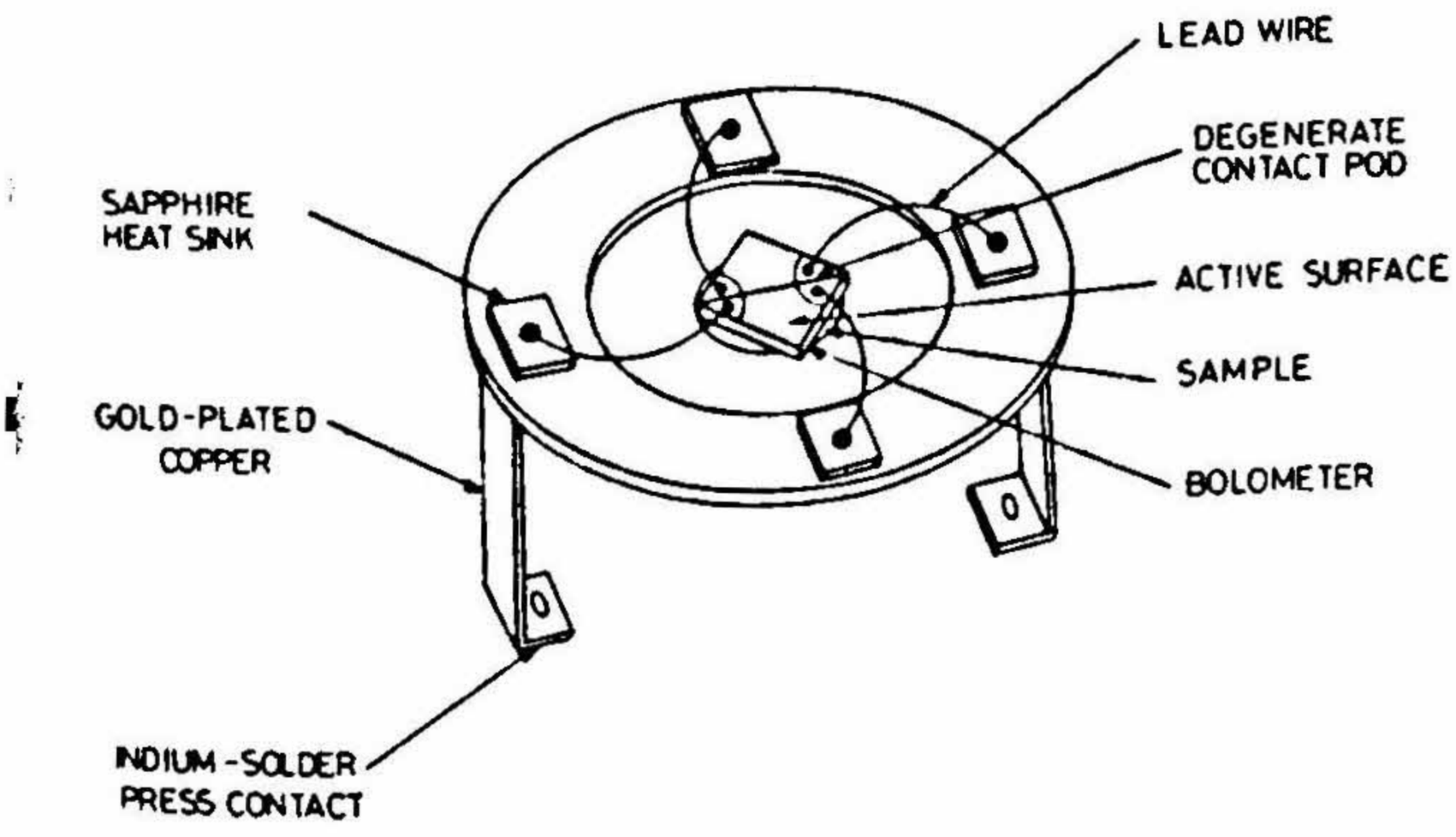


FIG. 10. Sample mounting arrangement for relaxation calorimetry (Ref. 166).

slightly and used their set-up for measurements on some quasione-dimensional systems[174, 175]. In their set-up, the time constant τ is compared with an electrical RC time constant for precise determination. The errors involved in the method have been analyzed by Rubeic and Rubeic[176] and by Bachman *et al*[166].

4.1.3. *Pulse propagation or dynamic pulse methods*

This is a group of methods once again based on Angstrom's work but these differ from the pulse relaxation method. In the relaxation method, the sample and addenda reach internal equilibrium quickly and the temperature of the total system relaxes due to the thermal link to the bath. In the present methods, the heat is applied as a pulse at one part of the sample and the propagation of the pulse of heat through the sample is monitored as a function of position and time. One of the early practical systems of this type has been developed by Parker *et al*[177]. Kruger *et al*[178] have given a good description of the principle of this method which we shall discuss in some detail. Basically the method is used for cylindrical samples. In these techniques, the sample geometries and configurations are very important.

The system of Kruger *et al* is shown in fig. 11. One end of the cylindrical sample is fixed to a bath and is at a fixed temperature. A sharp pulse of heat is applied at the other end. A thermocouple fixed at a point along the axis monitors the temperature

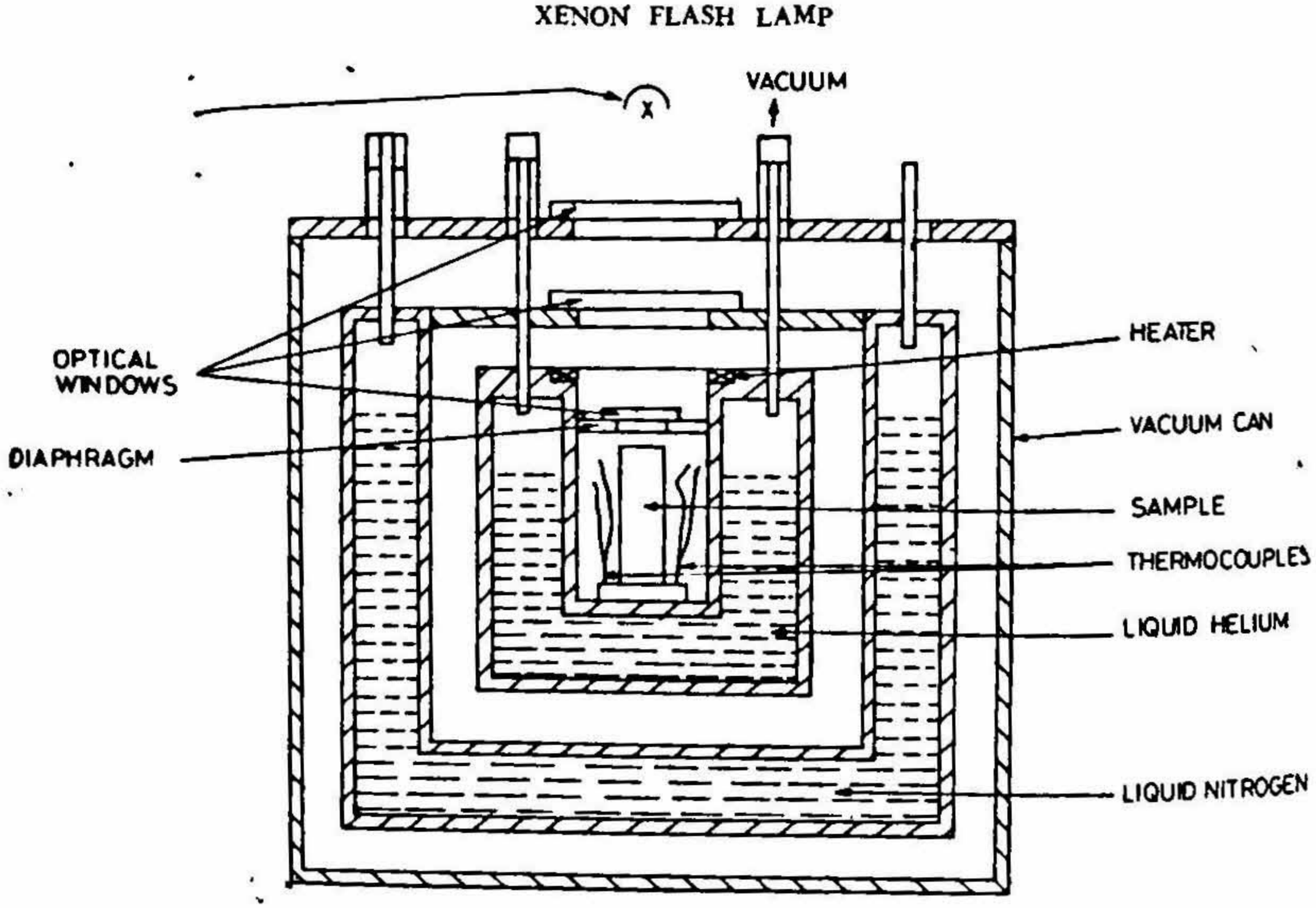


FIG. 11. Schematic of the cryostat for thermal diffusivity measurements down to 1 K (Ref. 178).

at a point $X = X_s$ on the sample, the heat pulse being applied at $X = 0$. The equation for heat flux is

$$(\partial^2 V/\partial x^2) - 1/K(\partial V/\partial t) = 0 \tag{26}$$

where

$$K = \lambda/C\rho \tag{27}$$

K is the diffusivity, ρ is the density, V is the change in temperature. In the present case, with axial symmetry, the solution is a series which converges for $X_s \leqslant 0{\cdot}45\,L$ where L is the total length of the sample. The solution is

$$ln\,(V\sqrt{t}) = -\frac{X_0^2}{4K}\frac{1}{t} + ln\,\frac{V}{\sqrt{\pi K}}. \tag{28}$$

Hence, by plotting ln $(V\sqrt{t})$ vs $1/t$ we get a straight line. The slope is related to the diffusivity K as

$$K = (X_0^2/4) \cdot (\text{slope})$$

Also

$$C = \frac{Q}{\rho F X_0 \sqrt{\pi L/2}} \times \frac{1}{V_{max}}.$$

Here, Q is the total absorbed energy, ρ is the density, F is the area of energy absorption, and V_{max} is the maximum value of V. Then both λ and C can be evaluated. The heat losses through the sensor leads have been shown to be negligible if the time t is less than 5 seconds. This type of experiment has been performed on samples of size $2 \times 3 \times 5$ mm. Several workers have reported such systems for work at low temperatures[179–181]. An analysis of the errors introduced by source sample separation, geometry, etc., have been discussed by Cape and co-workers[182, 183]. Gershenson and Alterowitz[184] have evaluated the errors in using this method with thin films and changing sample size.

The main temperature region for this method, as described above, is at and below room temperatues. A number of measurements on silicon, polymers, etc., have been reported[185, 186]. This method has been used for simultaneous high pressure, low temperature calorimetry on vitreous polymers[187]. A number of workers have used the instantaneous pulse methods at high temperatures. Examples include the measurement on $KNbO_3$ in the 350–700 K regime[188] and the measurement of diffusivity and C_p of a number of refractory materials[189] in the 50–1000 °C range. Systems capable of working at higher temperatures have been reported by Fox and McMaster[190], Vandersande and Pohl[191] and by Taylor[192]. Klimenko *et al*[193] have used a high power laser for heating and used the method up to 3000 °C.

An extension of the method has been used by Filler *et al*[194] for work on thin film samples. An advantage of the method is that the total information is contained in the V vs t curve. This data can be stored and the errors reduced by the use of a multi-

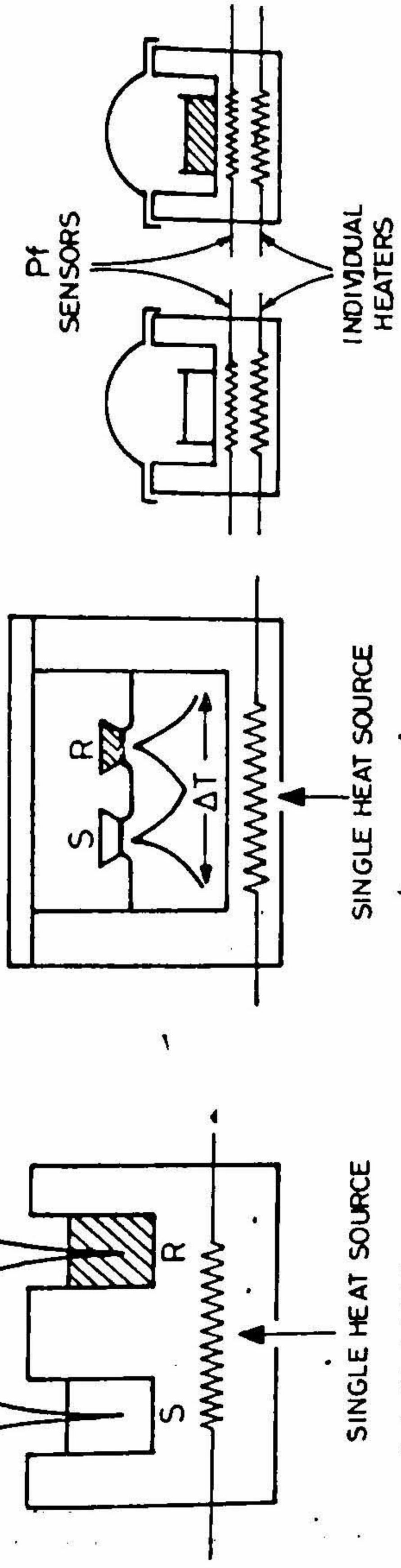
channel analyser and data processing equipment. Usually for cylindrical geometry samples, a xenon flash lamp or other radiative source is used as the source of heat pulse so that the heat pulse is very sharp.

The transient hot wire and the plane wave methods are essentially similar. In the transient hot wire method, a heat pulse is applied along a wire by Joule heating. The sample is such that the wire is embedded in it. The propagation of heat is detected and the heat capacity values are evaluated. Systems of this nature are many and the systems reported by Wernerkieffer[195], Ress *et al*[196] and Schrader and Nolting[197] are examples of the use of this method at high temperatures and high pressures. However, the placing of the wire radially in a cylindrical sample is difficult and the method cannot be applied for work on single crystal samples and solids which are not easily formed into the required shapes. This disadvantage has been avoided in the plane wave method, which has been extensively used by McLaughlin and Pittman[198] Gustafsson and co-workers[199-202] and others[203-206]. Here, the heat is generated in a thin film of heater which is usually deposited on the sample. Two pieces of the sample are used and the heater embedded between them, and since heater thickness is very small, the heat losses are negligible. This method can be used to determine the properties along different directions in a single crystal and the tensorial properties can be determined[207-208]. The method has been extended for use with fluids and fused salts. The transient hot wire method can also be easily used for fluids since casting or preparation of sample is not necessary[209]. Obviously, all these methods depend upon the sample geometries and experimental configurations. Hence, there are generally a number of variables and solutions for the heat equation employed.

4.1.4. *The D.S.C. (differential scanning calorimeter)*

The differential scanning calorimeter is a high accuracy, versatile, commercial instrument for thermal measurements. This method is currently more useful for chemical measurements involving the precise measurement of enthalpy, but its use in heat capacity measurements is also fast increasing. This method has been extensively surveyed by many workers and we shall therefore present only a brief review.

Essentially, this calorimeter consists of a sample chamber and an identical chamber for the standard. The system has independent heaters and sensors. There is provision for heating both the chambers at identical, pre-programmed rate (see fig. 12). The heating power input to the two parts is continuously varied to maintain the heating (or cooling) rate. The difference in power input to the standard and sample is caused by any exothermic or endothermic transformation occurring in the samples and by the difference in heat capacities of the sample and the standard. This difference is continuously plotted. The detailed control configuration is shown in fig. 13. The plot can be analysed to give the heat capacity values, enthalpy changes, etc. The method is generally quite accurate. Values down to 2% are routinely available. The commercial units are capable of operation in the 77–850 K range. (For example, the Perkin Elmer DSC–2 unit). The resolution in heat measurements is less than 1–2 mcal.



(c) DSC

(b) 'BOERSMA' DTA

(a) CLASSICAL DTA

FIG. 12. Schematic representation of the three principal thermal analysis systems (Ref. 13).

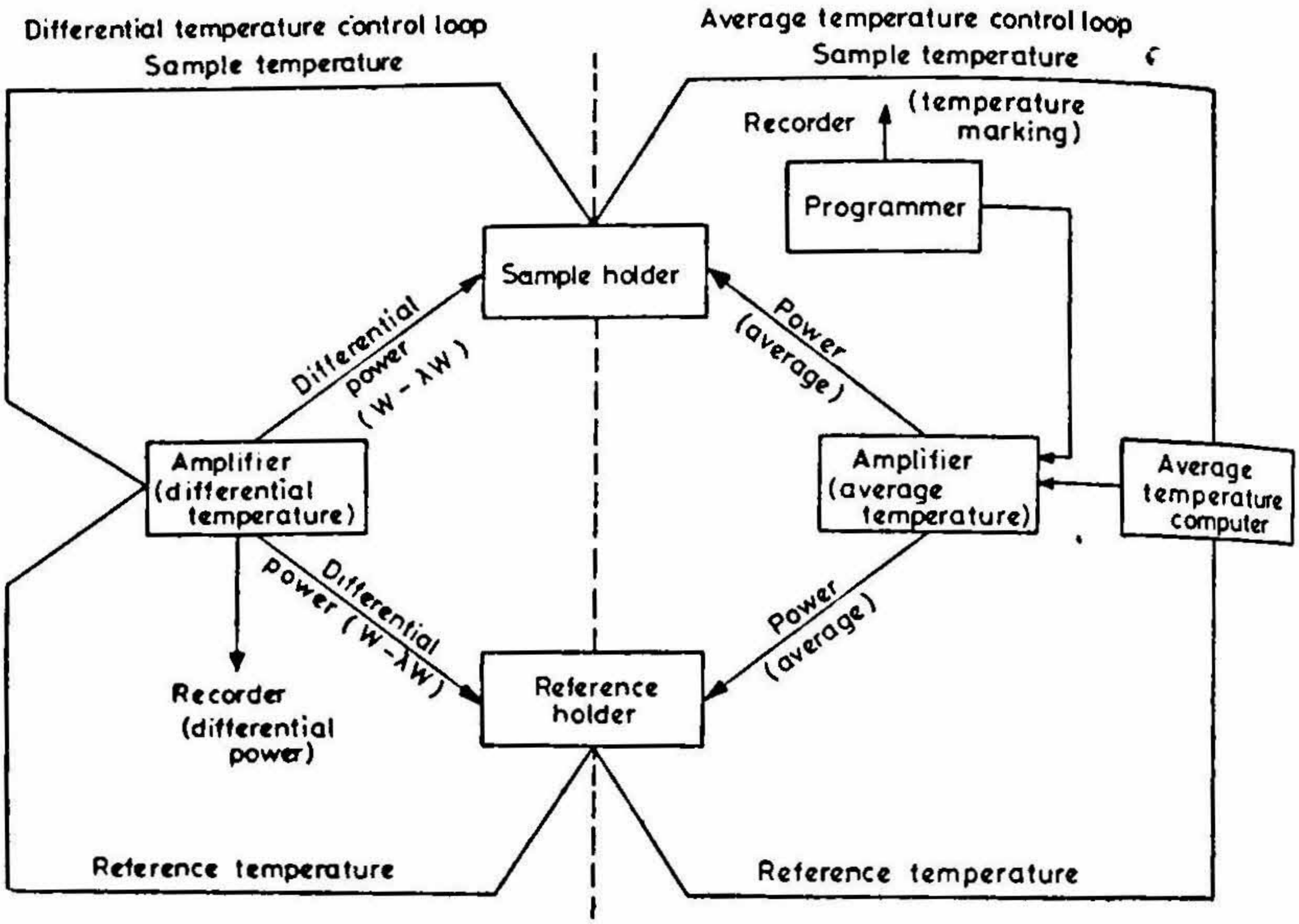


FIG. 13. Schematic diagram of the Perkin-Elmer DSC instrument (Ref. 18).

The quantity of sample required is also small (~ 10–50 mg). The system is used with aluminium or gold sample containers. Special containers for volatile samples are also available[210–212].

As is obvious, the DSC differs from the Calvet–Tian type differential microcalorimeter in the quantity that is monitored. Instead of heat leak being measured by a thermopile, the heater power input is monitored continuously. Also, unlike most other heat capacity measurement systems, the DSC is fast. The normal rates of heating in a DSC experiment vary between 5 and 50 K/min. The normal methods usually employ 5–10 K/hr. This places a serious limitation on the DSC from the physicist's point of view. Since the temperature is continuously changed at such rapid rates, there is a possibility of sample temperatures lagging behind the indicated changes. Also, the lag may depend upon the sample thermal conductivity and the internal relaxation time. The packing of the sample in the container, the thermal conduction barrier between the sample and the container have also to be considered[213]. The variation of the absolute temperature calibration from run to run and the calibration of the enthalpy scale are other factors to be considered in obtaining high accuracy heat capacity data from the DSC[214–215]. For example, the temperature calibration is rarely better than 0·1 K. This limits the application of DSC near phase transitions. Also, work at very low

temperatures is not possible. However, the DSC has been sometimes used for C_p measurements near the second order phase transitions under certain conditions.

The field where DSC is very useful is in the measurement of relative enthalpy changes on a large number of samples for the evaluation of material purity, consistency, etc. The DSC has also been used in the measurement of properties such as electrical resistivity[216], thermal conductivity[13] and emissivity[217]. The use of DSC for high pressure measurements is also wellknown[218,219]. Most often a gas pressure is employed and measurements are reported only in the near atmospheric pressure range (usually up to a few hundred bar). This is useful in the study of a number of chemical reactions and evaluation of chemical parameters. Arntz[218] has developed a DSC system capable of working up to pressures of the order of 4K bar. An interesting feature of DSC and Tian-Calvet systems, indicative of their wide spread use is that several systems with minor modifications are periodically reported. These are all generally differentially configured systems for small samples and the principle of operation is similar to either the DSC or the Tian Calvet system[220–223].

4.1.5. *Other methods of modern calorimetry*

There are a large number of examples of interesting systems developed in recent years, which are not very widely used. However, as they are interesting, we shall discuss a few examples of such work. The physical principles involved in these indicate the different directions from which C_p measurements can be made.

The first method which we shall discuss is the laser-flash-calorimetry. This method has been basically developed by Takahashi and co-workers[224–228]. The method has been used over a wide range of temperature (up to 1000° C) and relatively small samples can be used. The method is a modification of the pulse methods discussed in section 3.1.7. Here, a sharp pulse of laser power is used to heat the sample over a small temperature difference. The change in sample temperature is carefully monitored. The laser power input passes through a partial reflector before falling on the sample. Thus a fixed portion of laser energy is reflected into a photon counting system and the exact power input into the sample is evaluated (fig. 14). From this and the temperature profile of the sample as it is heated, the heat capacity of the sample is evaluated. This method has been used on samples such as Pt, Al_2O_3, US, UP, etc. Another interesting system is described by Kumada[229]. In this method, a disc-shaped sample is used. One surface is heated by a laser, the intensity of which is increased in regular steps. (The intensity thus is represented by a staircase wave form). The temperature on the other surface of the disc is continuously monitored and the change in heat capacity evaluated.

A few other indirect methods are also known. Cherchenko and Ivon[230] have suggested that the C_p can be evaluated by accurately determining the resistivity, I–V characteristics and the temperature coefficient of these and then theoretically correlating the data to C_p. Baranov *et al*[231] have discussed a method where C_p of a disc-shaped

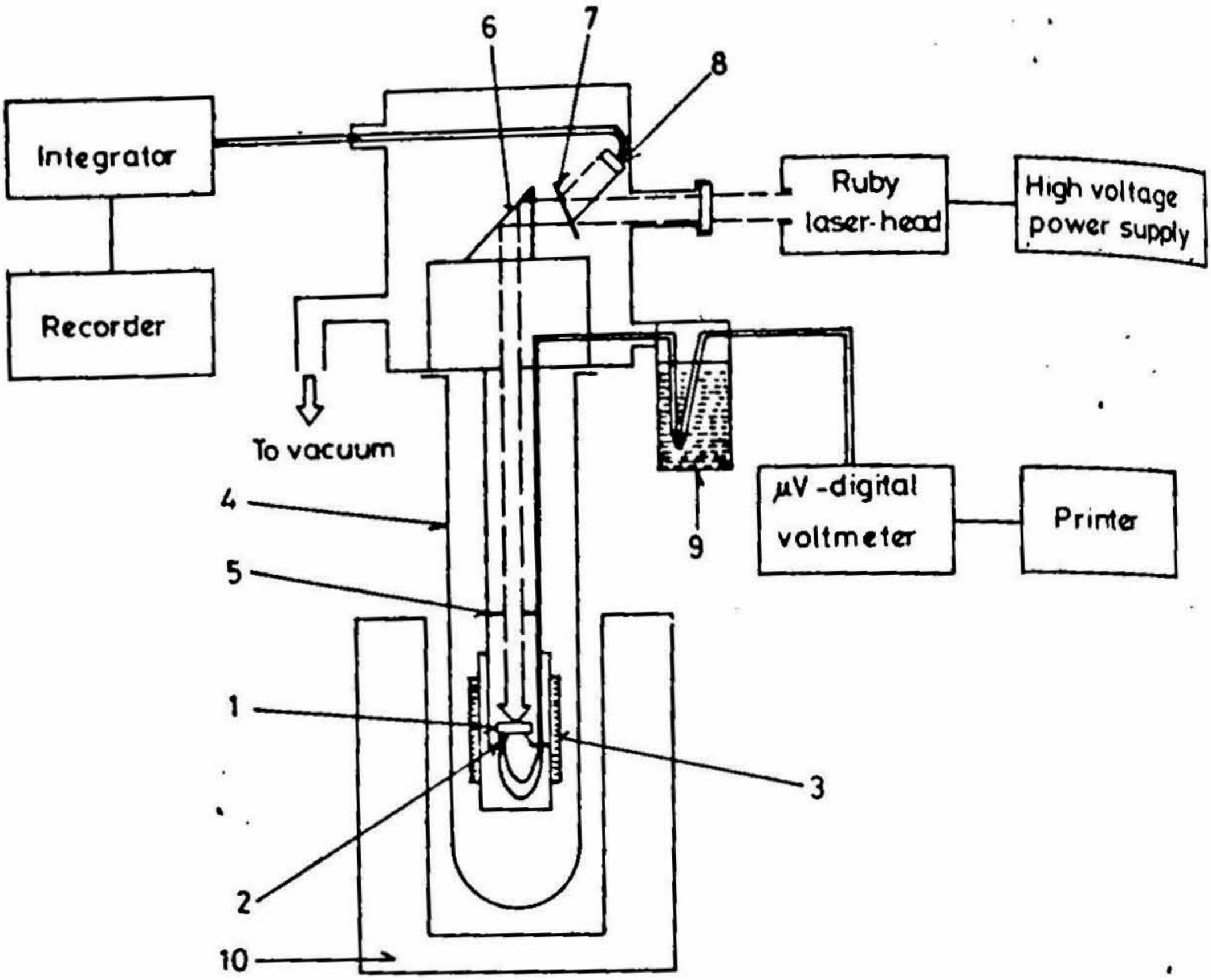


FIG. 14. Schematic diagram of apparatus of laser flash calorimetry : 1. Sample, 2. Thermocouple, 3. Internal heater, 4. Quartz container, 5. Adjusting slit, 6. Prism, 7. Reflecting glass, 8. Si-ph otoelectrie cell, 9. ICE bath, 10. Outer heater or liq. N_2 bath.

sample is measured by monitoring the changes in amplitude of reasonance vibration of such a sample in a heat flux.

Marx[232] has suggested another interesting method. This is called the quotient method. Here, two samples with independent heaters are connected through a thermal link. The same power is fed alternately into the two heaters. The heat flux through the link is measured in both the cases (*i.e.*, when power is fed into one heater and the other). The heat capacities of the samples are related in a simple way to the ratio of the heat fluxes, which are measured.

A method for evaluating the magnetic contribution to heat capacity was originally suggested by Casimir and du Pre[233]. Here, only magnetio properties need be measured. This is an advantage since the lattice contributions will be much larger and the other classical methods are not very useful. The method has been improved by Wolf and

co-workers[234] by using cryogenic tunnel diode oscillators. The method has been used for measurements of C_m of rare earth halides, hydroxides and garnets[235].

The use of SQUIDS for the measurement of physical properties is now very well known. Recently, Park and Vaidya[236] have used SQUIDS for the measurements of heat flux in a calorimetric set-up. They have reported its use in the 1–6 K regime. Though the use is very interesting, the method is obviously limited only to the liquid helium temperature range. In order to prevent the contamination and corrosion problem at high temperatures, several interesting systems are suggested. For example, the use of radiation or solar energy to heat samples and to prevent contamination has been discussed by Lacy and Nisen[242] and by Kirizbaev and Shamuzafurova [241].

Another recent very interesting indirect method for C_p determination is the use of photoacoustic effect for the determination of C_p. This was suggested by Adams and Kirkbright[240] and by Siqueira *et al*[239]. Here, the sample is enclosed in a chamber with low pressure gas. The heater power, in the forms of chopped radiation is fed into the sample. Then heat flows into the gas periodically. This causes compressions and rarifactions in the gas and an acoustic signal is generated. This signal strength is related to the specific heat C_p and thermal conductivity λ which are evaluated.

As mentioned earlier, calorimetry is becoming a powerful tool in biochemical studies, bioprocess investigations and even in clinical work[6,109–111]. Usually, the Tian–Calvet system or the flow calorimeters have been used. An interesting new development is the whole body calorimeter[237, 238]. Here, processes involved in the biological energy conversion of not only specific organs but even the whole body can be investigated.

5. Developments in automation and control systems for precision calorimetry

Automation of data acquisition and control has become a major activity in every field of analytical measurement. While the earlier control systems were invariably of the analogue type, the recent trend has been towards the use of digital systems. This has been made easy by the availability of good microprocessor/computer control systems. Automation helps in the realization of more consistently accurate data and avoids human errors and fatigue. Since high precision is always necessary in heat capacity measurements, various automated high precision calorimeters have been developed.

Historically, temperature control has been the first step in the automation of the adiabatic calorimeter. Early systems are described by Stull[243], Zabetakis *et al*[244] and are reviewed by Hill[245]. These were generally simple systems involving the sensing of temperature and the control of one or two shields or regions. The Tian–Calvet microcalorimeter is also of similar nature where some control is automatic but human involvement is still large. The topic of temperature control has an extensive literature[246–247]. A significant development here has been the application of control theory to situations where the temperatures are varying linearly[248,254].

The next stage in automation has been to integrate the sub-units for data acquisition. In the past two decades several units were developed and those by Martin and co-workers[249–251] and by Shin and Criss[252] are examples, where the primary data like heating rates, temperatures, time intervals, etc., are automatically collected. This has become worthwhile primarily after the advent of digital systems because the same data acquisition systems can easily process the observations to yield secondary results. While this was earlier done by either magnetic tape or disc hook-up with digital computer, the availability of microprocessors has enabled one to get simple dedicated units, which can perform the required tasks without worrying about the spectrum of activities possible in a large computer.

We shall discuss some examples of recently developed automatic calorimeter systems, starting with the adiabatic calorimeters. Gopal and co-workers[253,254] developed a system, where the sample and shield temperature are automatically controlled. Also, there is provision for the system to be hooked up to a large scale computer system for data acquisition and analysis. This system works in the 200–400 K regime and has a very good temperature stability, enabling the system to be used near phase transitions. Similar systems have been described by Avidsson *et al* [255], Bohmhammel *et al*[256], Gereev *et al*[257], and Gmelin and Rodhammer[258]. The general control block diagram for this system is found in fig. 15. The automatic systems are capable of operation up to 800 K as with the regular adiabatic systems.

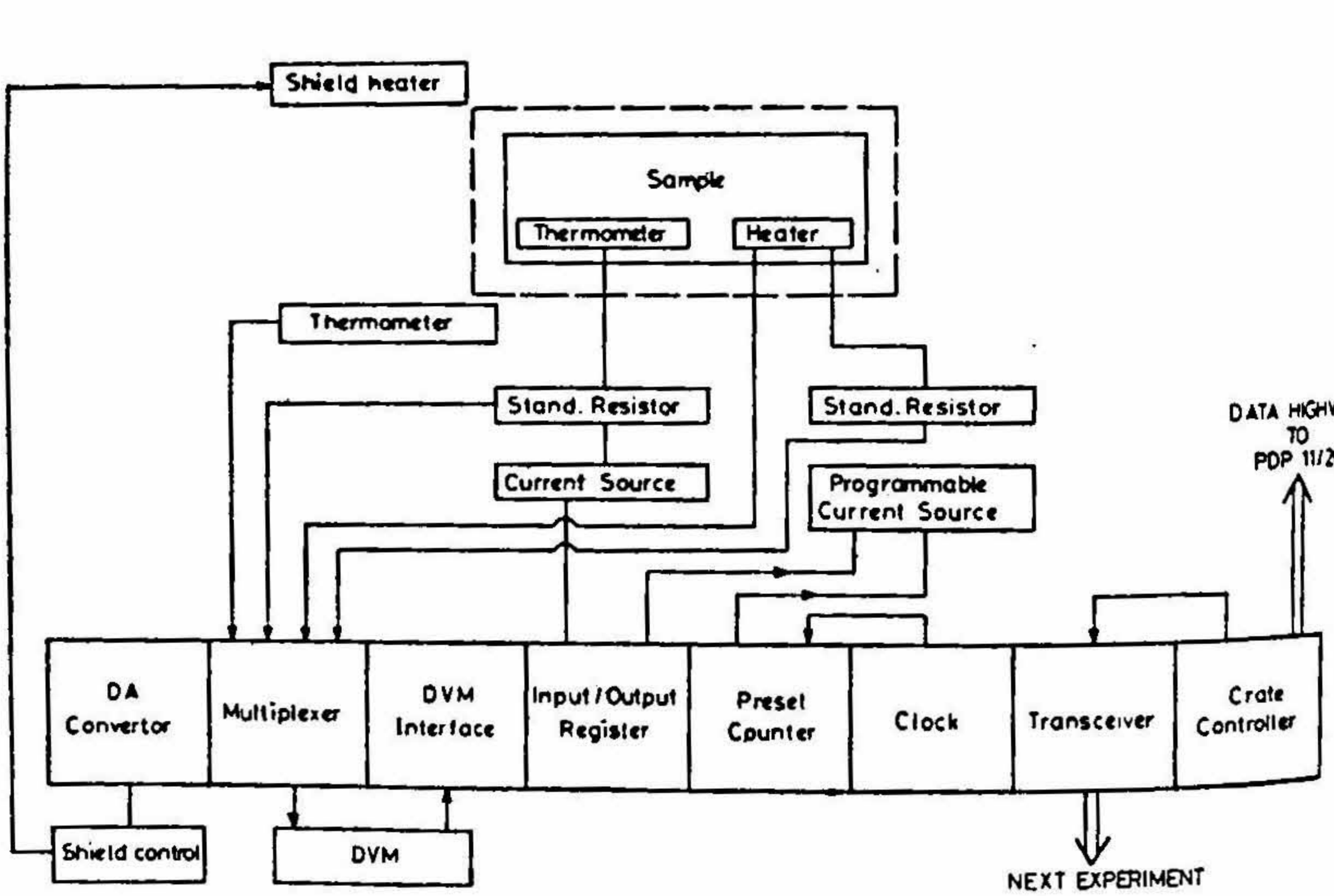


FIG. 15. Block diagram of electronic system for automated adiabatic calorimetry (Ref. 258).

The a.c. calorimeter has also been recently integrated for complete automatic operation. Rade and Ringelmann[259] describe an a.c. calorimeter with provision for continuous recording of C_p data. A computer controlled a.c. calorimeter is described by Ikeda and Ishikawa[260–261]. These systems are capable of 1% accuracies over the temperature range up to 1000 K. As already mentioned, the C_p data in the pulse propagation method is evaluated from the plot of the change of temperature with time. Filler *et al*[194] have developed a system with provision for multichannel analysis of data to assist in the reduction of errors and large scale computer interface for direct data analysis. This system is used for C_p measurements on thin film samples down to liquid helium temperatures. Yoshiwa and Iwata[262] developed an automatic system with a plane heater. The plane source is sandwiched between sample discs and heated with a continuous power input. The temperatures at several points in the sample are monitored automatically and C_p is evaluated. This system is developed for the study of cryogenic construction materials in the 4–300 K temperature range. A system based on the pulse relaxation method has been recently developed by Griffling and Shivashankar[263]. The DSC and the Tian-Calvet systems are, by nature, systems with some amount of automatic control. Even here, a microcomputer control has been recently developed for increasing the accuracies in enthalpy measurement[264].

A detailed analysis of the utilization of computer systems for data reduction and analysis is provided by Koski and McVey[265]. They have discussed in detail, how a large scale computer system used for complex calculations and dedicated microcomputer systems may be effectively used in combination for improving the accuracy of the data. They give an example of a system based on the transient pulse method for measuring both heat capacities and thermal conductivities.

Another very interesting system has been developed by Cezairliyan and co-workers. The basic system developed some time back[266] has undergone a process of improvement recently[267–270]. This system can simultaneously measure the heat capacity, electrical resistivity and thermal emittance of electrically conducting samples in the temperature range of 1200–3000 K. A pulse of 2000 A DC current is passed for less than one second during which time more than 1200 measurements of sample temperature (using a high speed photoelectric pyrometer), sample dimension and expansion (using a He-Ne laser in the configuration of a Michelson interferometer) as well as the power absorbed in the sample are recorded. These are analyzed for producing C_p data. There are attempts to reduce the time of experiment to less than a few micro seconds and to take more than 10^6 data points per second. The block diagram and sample arrangement of a similar system developed by Righini and Rosso[268,270] is shown in fig. 16.

The number of computer-based systems is continuously increasing and newer systems are discussed by several workers. In addition to the adiabatic calorimeters discussed by Lanchester and Baker[271], Joseph *et al*[272] and Cash *et al*[273], a new calorimeter based on the method of mixtures using new types of thermal detectors has been described by Hatem *et al*[274] for evaluating enthalpies in the temperature range 1000–1400° C.

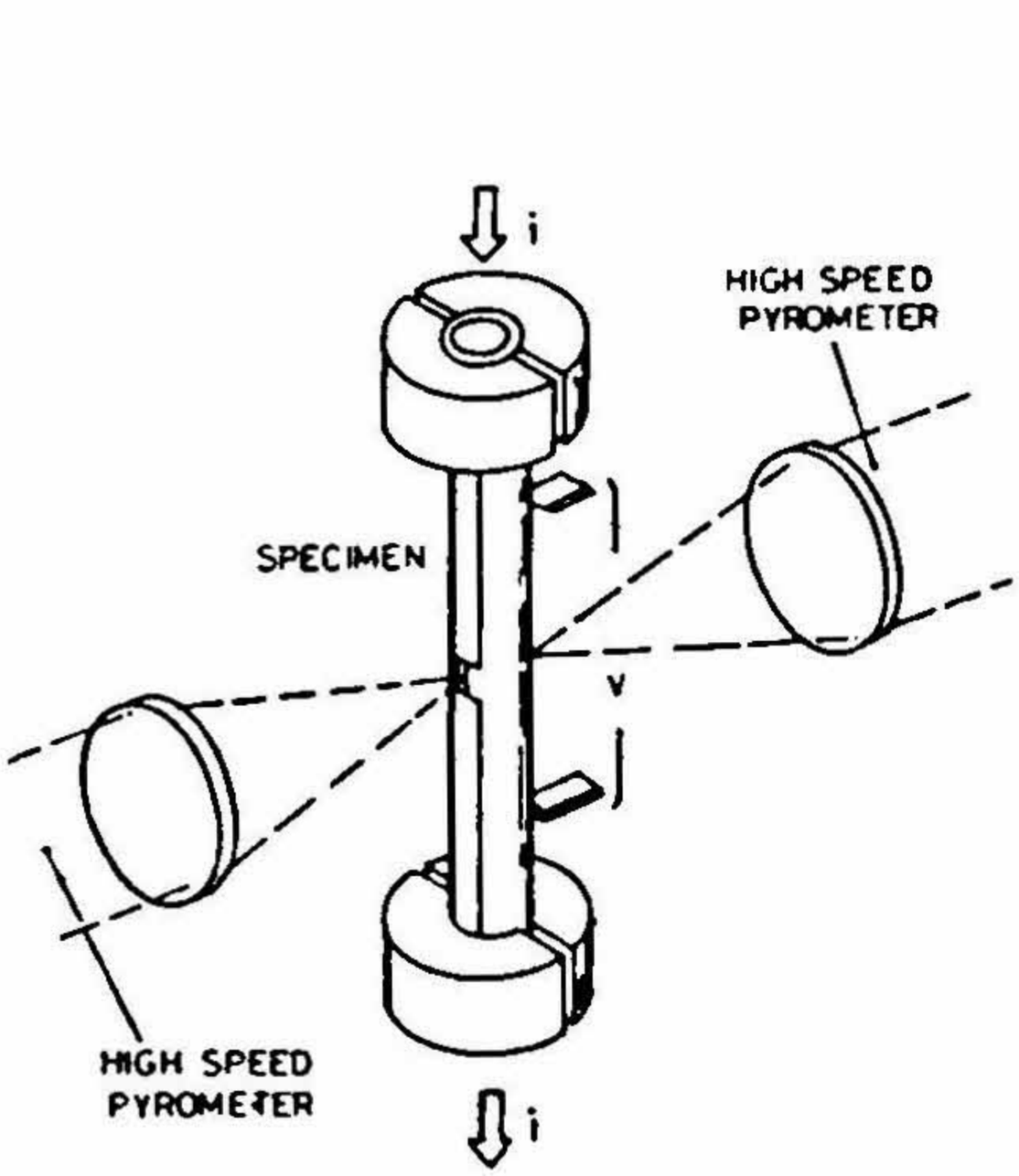


FIG. 16*a*. Schematic representation of the specimen during a pulse experiment (Ref. 268).

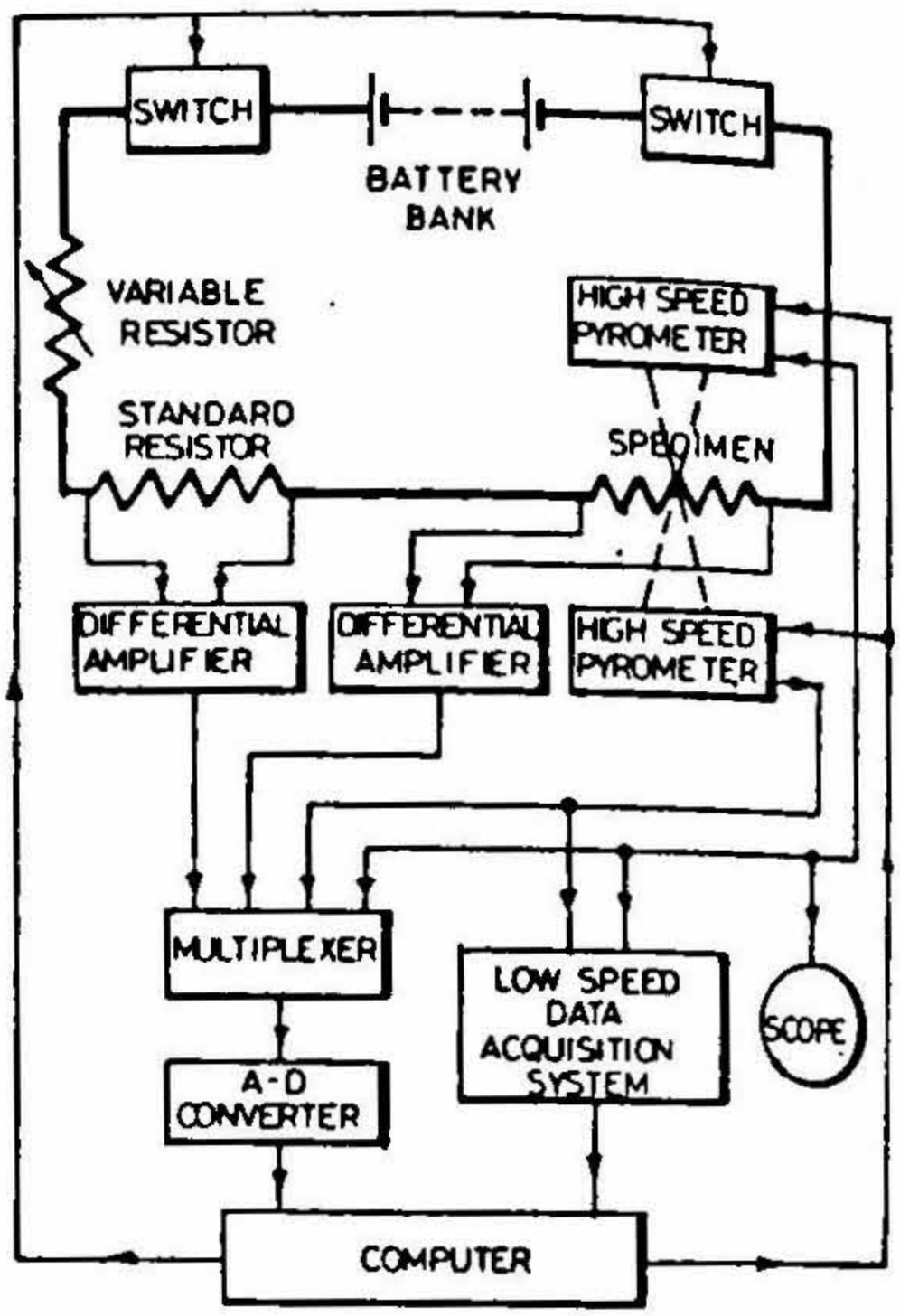


FIG. 16*b*. Block diagram of the experimental apparatus for measurements by the pulse technique (Ref. 268).

One of the major reasons for developing automated systems is to reduce errors and to standardize the systems. Thus the major progress in traditional methods of measurement has been in this direction. The systems developed by Martin and co-workers are examples[248–251] of this. Here, the major emphasis is on the reduction of human errors and the development of samples to be used as calibration standards. Another line of activity is in general physico-chemical property measurements. The results obtained using the computerized adiabatic system of Williams *et al*[275] is an example. They have measured the heat capacity of chromium near the Neel point and have shown the effect of impurities and cold work (see fig. 17)[275]. Another interesting line of work is the measurements of Cezairliyan and co-workers at very high temperatures. Here the computerized system is perhaps the only way reliable data can be obtained. Measurements up to 3500 K both for C_p evaluations and for phase transformation studies of refractory metals and alloys are reported[276–277]. Figure 18 indicates some of the results obtained.

While only a few examples are given in this sub-section, it will be realized that automation has become an integral part of almost every modern measurement process. With the ready availability of minicomputers and microprocessors, which can be dedi-

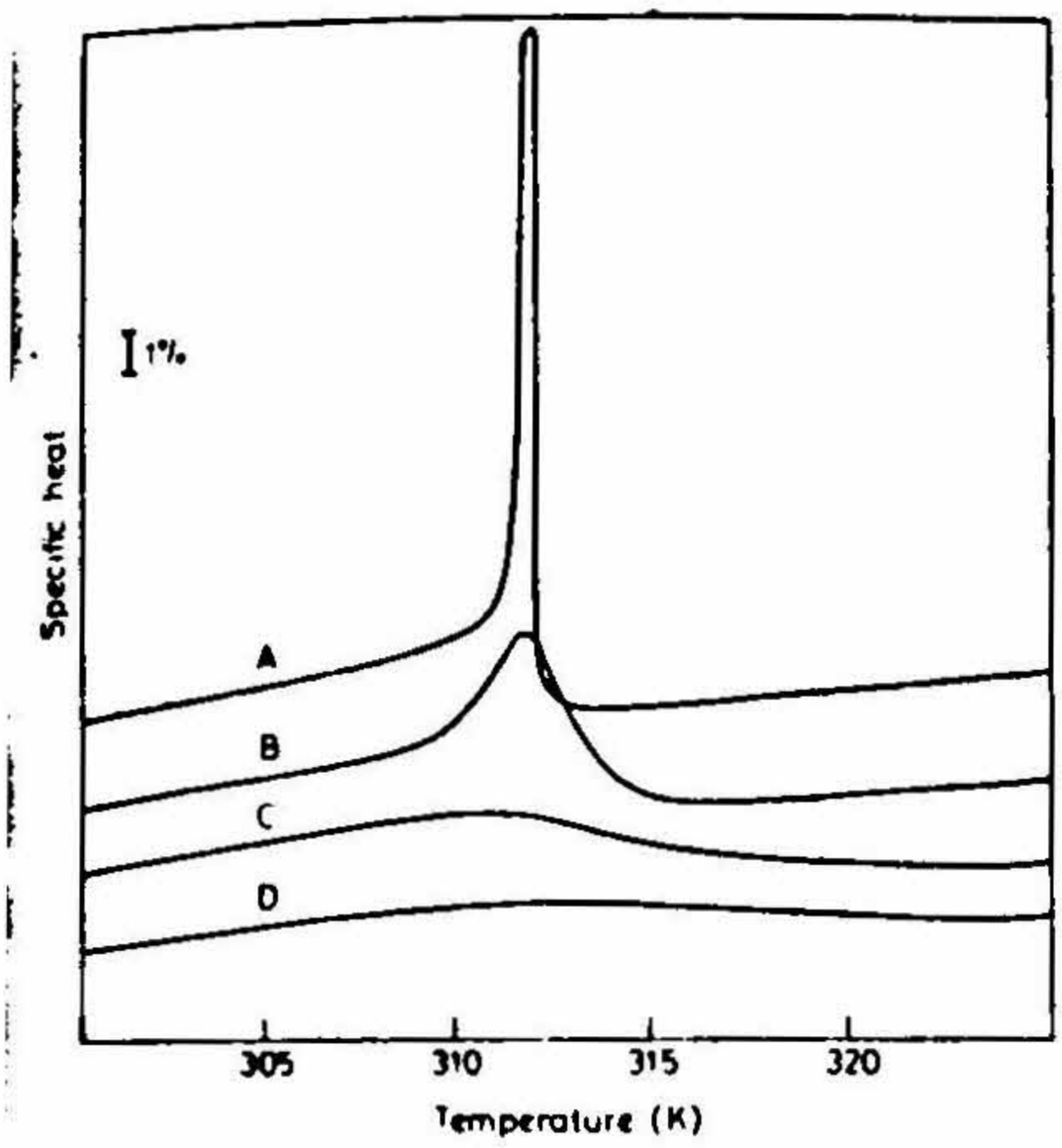


FIG. 17. The temperature variation of the specific heat of chromium in the vicinity of the Néet transition : *A*, annealed at 900° C ; *B*, rolled ; *C*, annealed at 600° C and *D*, swaged (for clarity, curves have been displaced vertically and experimental points are not shown) (Ref. 275).

cated to one use and yet retain general purpose capabilities, it is likely that this trend would continue. The ' heroic ' calorimetric investigations up to the fifties, when point-to-point data had to be patiently and laboriously collected over many days, would become dim memories.

7. Conclusions

The recent developments in calorimetric techniques have been mainly in two directions : (1) reduction of sample size requirements and complexity of experiments and (2) development of newer methods for work under extreme conditions of temperature and pressure. In general, the transient methods, having the advantages of simplicity in systems, small sample utilization and ability to work at extreme conditions, have become very popular. The DSC as well as some versions of the Tian–Calvet microcalorimeter, which are commercially available, have enabled the massive diversification of calorimetry into such fields as materials research and biomedical experiments. The classical methods continue to be of extreme importance in several fields of activity and herein major improvements have been in automation of data acquisition and control. The classical methods are capable of high absolute accuracy and so they reign supreme in areas like the determination of the thermodynamic reference data of the equilibrium phases of various materials[278].

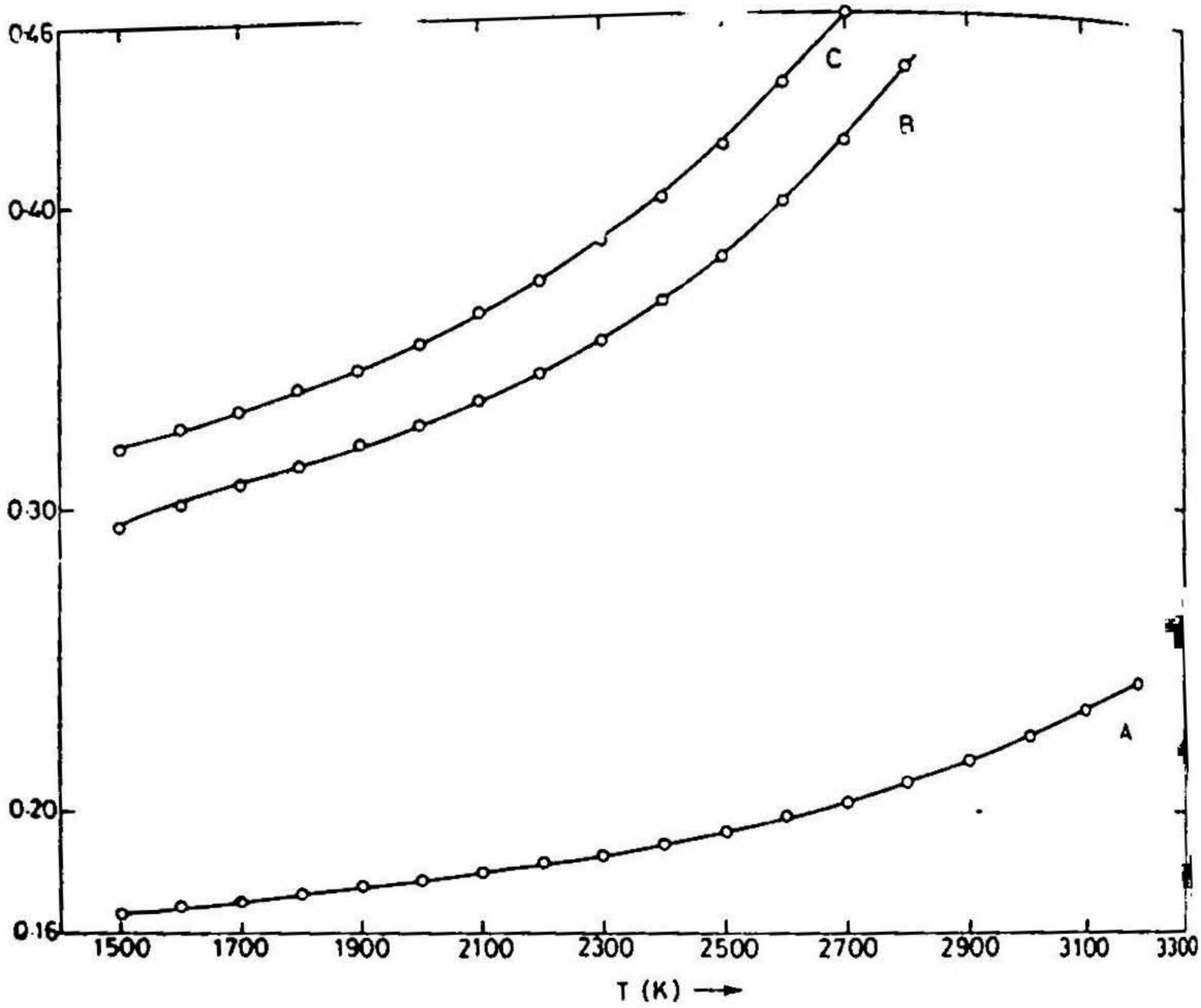


FIG. 18. The variation of specific heats of various refractory metallic alloys at high temperatures. (*A*) $Ta_{.10}\ W_{.90}$. (*B*) $Ta_{.18}\ W_{.10}\ Nb_{.80}$. (*C*) $Nb_{.99}\ Zr_{.01}$. (Ref. 277).

Calorimetry is one of the old traditional experimental techniques in physico-chemical investigations. It appeared by the 1950–60 period, that the techniques are well established and that progress would be largely in applying well established principles. However, history has a way of providing the unexpected. A flood of newer experimental techniques started to appear by the late sixties and one is seeing a resurgence of newer techniques and their application to investigations which were not easily possible using the older techniques. Information about the specific heat exponents near critical phase transitions and about the heat capacity behaviour under unusual environmental conditions are examples of such recent investigations. There is no doubt that the wealth of new information would continue to grow. For example, one may point out some unusual features of the recent techniques which have not been exploited till now. Most of the measurements on biological materials have been *in vitro* observations so far. The a.c. and other methods do not require any isolation of the sample and one may be able to perform *in vivo* measurements. This type of information on the enthalpy and other changes is likely to be of great significance in biological and biochemical investigations.

The major task of the present review has been to discuss the developments in experimental techniques of measurements. The associated question of the new results emerging out of such advances in techniques is obviously of considerable importance. The matter is discussed separately[279, 280].

Acknowledgements

We are very grateful to the large number of friends and colleagues for their valuable assistance and encouragement. In particular, we are thankful to Prof. C. N. R. Rao for his keen interest. We also thank Mr. M. Ranjan, Mss. A. V. Nalini, V. Vani and Hemamalini Naik for valuable assistance in literature survey and proof reading and the secretarial help of the NTPP office staff. The financial assistance from the Department of Science and Technology through the NTPP Project and the Physics Projects is also gratefully acknowledged.

Nomenclature

C_p	—	Specific heat at constant pressure
C_v	—	Specific heat at constant volume
S	—	Entropy
G	—	Gibb's Free Energy
H	—	Enthalpy
β	—	Co efficient of volume expansion
K_T	—	Isothermal compressibility
V	—	Volume
p	—	Pressure
Z	—	Partition function
T_c	—	Critical temperature
α	—	Critical exponent
k	—	Thermal conductivity
ρ	—	Density
τ	—	Relaxation time
K	—	Thermal diffusivity

References

1. Ruhemann, M. B. — *Low temperature physics*, Cambridge University Press, London. 1937.
2. Gopal, E. S. R. — *Specific heats at low temperatures*, Plenum Press, New York, 1966.
3. Saha, M. N. and Srivastava, B. N. — *A treatise on heat*, Indian Press, Allahabad, 1931.
4. Nernst, W. — *Chem. Abstr.*, 1910, 4, 2397.

5. MA, S. K. *Modern theory of critical phenomena*, Benjamin, New York, 1976.

6. LAMPRECHT, I. AND SCHAARSCHMIDT, B. (Eds.) *Application of calorimetry in life sciences*, Walter de Gruyter, Berlin, 1977.

7. MCCULLOUGH, J. P. AND SCOTT, D. W. (Eds.) *Experimental thermodynamics*, Vol. 1. Butterworths, London, 1968,

8. MARCUS, P. M. AND FRIEDBERG, S. A. In *Methods of experimental physics*, Vol. I, (Estermann, I., Ed.), Academic Press, New York, 1959, 235.

9. KEESOM, P. H. AND PEARLMAN, N. In *Methods of experimental physics*, Vol. 6-part A, Lark-Harovitz, K. and Johnson, V. A. (Eds.), Academic Press New York, 1959.

10. KYBETT, B. D., CHARLU, T. V., CHAUDHURI, A., JONES, T. AND MARGRAVE, J. L. In *Treatise on analytical chemistry*, (Kolthoff, I. M., Elving, P. J. and Sandell, E. B. (Eds.)), Wiley Interscience, New York, 1968. Part I, 8, 5109.

11. SHELTON, R. A. J. *I.R.S. Physical chemistry series*, (Skinner, H. A. (Ed.), Butterworths, London 1975, 2(10), 261.

12. KINGEREY, W. D. *Property measurements at high tempetatures*, Wiley, New York,, 1959.

13. MCNAUGHTON, J. L. AND MARTIMER, C. T. *Inter. Rev. Sci. Phys. Chem. Series* 2, (10) (Skinner H. A. (Ed.)), Butterworths, London, 1975,

14. STURTEVANT, J. M. *Physical methods of chemistry, Part* V, (Weissberger, A. and Rossiter, B. W. (Eds.)), Wiley Interscience, New York, 1977 p. 347.

15. BARRELL, E. M. AND JOHNSON, J. F. Tech. Methods, *Polymer Eval.*, 1970, 2, 1.

16. RICHARDSON, J. H. AND PETERSON, R. V. (Eds.). *Systematic materials analysis*, Academic Press, New York, 1978, 4.

17. PRIVALOV, P. L. *Pure Appl. Chem.*, 1980, 52, 439.

18. WENDLANDT, W. W. *Thermal methods of analysis*, Wiley Interscience, New York, 1974,

19. WENDLANDT, W. W. *Technique of inorganie chemistry*, (Jonassen, H. B. and Weissberger, A. (Eds.)), John Wiley, New York, 1963, 1, 209.

20. MURPHY, C. B *Treatise on analytical chemistry* (Kolthoff, I. M., Elving, P. J, and Sandell, E. B. (Eds.)), Wiley Interscience, New York, 1968, Part I, 8, 5243.

21. REDFERN, J. P. *Pure Appl. Chem.*, 1971, 25, 849.

22. WENDLANDT, W. W. *Inter. Rev. Scl. Phys. Chem.*, West, T. S. (Ed.), Butterworths, London, 1973, Series 1, 13, 177.

23. MENIS, O,, ROOK, H. L. AND GARN, P. D. (Eds.) *State of the art of thermal analysis*, NBS, Washington, D.C., 1980.

24. BLACHMAN, M. *Handbuch der Physik*, Springer-Verlag, Berlin, 1955, 7(1), 325.

25. LEWIS, G. N. AND RANDALL, M. — *Thermodynamics*, McGraw-Hill, New York, 1961.

26. GIAUQUE, W. F. — *J. Am. Chem. Soc.*, 1930, 52, 4808.

27. KUBASCHEWSKI, O. AND BARIN, I. — *Pure Appl. Chem.*, 1974, 38, 469.

28. STANLEY, H. E. — *Introduction to phase transitions and critical phenomena*, Oxford University Press, New York, 1971.

29. NAGLE, J. F. — *Treatise on solid state chemistry* (Hannay, N. B. (Ed.)), Plenum Press, New York, 1975, 5, 1.

30. GRONVOLD, F. — *Pure Appl. Chem.*, 1976, 47, 251.

31. KERIMOV, A M. — *Heat transfer—Sov. Res. (U.S.A.)*, 1974, 6, 40 ; Gopal, E. S. R. *Bull. Material Sci.*, 1981, 3, 91.

32. KADANOFF, L. P., GOTZE, W., HAMBLEN, D., HECHT, R., LEWIS, E. A. S., PALCIAUSKAS, V. V., RAYL, M., SWIFT, J., ASPENES, D. AND KANE, J. — *Rev. Mod. Phys.*, 1967, 39, 395.

33. MOTT, N. F. — *Metal—insulator transition*, Taylor and Francis, London, 1974.

34. JEUBERT, J. C. AND CHENAVAS, J. — *Treatise on solid state chemistry* (Hannay, N. B. (Ed.)), Plenum Press, New York, 1975, 5, p. 463.

35. CEZAIRLIYAN, A. AND BECKETT, C. W. — In *Rev. Sci. Phys. Chem. Series* 2, (Skinner, H. A. (Ed.)), Butterworths, London, 1975, 10, p. 247.

36. LORIERS-SUSSE, C. — *High Temp.—High Press.*, 1980, 12, 119.

37. LOUNASMA, O. V. — *Experimental principles and methods below* 1*K*, Academic Press, New York, 1974.

38. ANDERSON, A. C. — *Rev. Sci. Instrum.*, 1980, 51, 1603.

39. WESTRUM, JR. E. F. — *Pure Appl. Chem.*, 1974, 38, 539.

40. WESTRUM, JR. E. F. AND LYON, W. G. — *J. Chem. Thermodyn.*, 1974, 6, 763.

41. ANDERSON, P. W., HALPERIN, B. I. AND VERMA, C. M. — *Phil. Mag.*, 1972, 25, 1.

42. PHILLIPS, W. A. — *J. Low-Temp. Phys.*, 1972, 7, 351.

43. STEPHENS, R. B. — *Phys. Rev. B*, 1973, 8, 2896.

44. GRAEBNER, J. E., GOLDING, B., SHUTZ, R. J., HSU, F. S. L. AND CHEN, H. S. — *Phys. Rev. Lett.*, 1977, 39, 1480.

45. YATES, B. *Thermal expansion*, Plenum Press, New York, 1972.

46. ANDERSON, J. C. *Use of thin films in physical investigations*, Academic Press, New York, 1966.

47. CORVIOVEI, A. AND MOTOC, C. *Acta Phys. Hung.*, 1963, **15**, 299.

48. BERGMANN, G. *Phys. Rep.*, 1976, **27C**, 159.

49. SOUTHARD, J. C. AND ANDREWS, D. H. *J. Franklin Inst.*, 1930, **209**, 349.

50. FURUKAWA, G. T., DOUGLAS, T. B., MCCOSKEY, R. E. AND GINNINGS, D. C. *J. Res. Natn. Bur. Stand.*, 1956, **57**, 67.

51. MORIN, F.J. AND MAITA, J. D. *Phys. Rev.*, 1963, **129**, 1115.

52. WEST, E. D. AND WESTRUM, JR. E. F. *Experimental thermodynamics* Vol. 1 (McCullough, J. P. and Scott, D. W. (Eds.)), Butterworths, London, 1968, p. 333.

53. ARMSTRONG, L. D. *Can. J. Res.*, 1950, **28A**, 44.

54. SOKOLOV, V. A. *Zh. Tekh. Fiz.*, 1948, **18**, 813.

55. CUBICCIOTI, D. AND EDING, H. *J. Chem. Phys.*, 1964, **40**, 978.

56. BACKHURST, I. *J. Iron Steel Inst.*, 1958, **189**, 124.

57. MABYSHEV, V. M., TOPNIKOV, V. N. AND SHCHEGOLEV, I. F. *Instrum. Exp. Tech.* (*U.S.A.*), 1975, **18**, 280.

58. MULLER, R., HASH, G. AND PARELY, H. *J. Chem. Thermodyn.*, 1978, **10**, 591.

59. HALL, R. A. O., LEE, J. A. MORTIMER, M. J. AND SUTCLIFFE, P. W. *Cryogenics*, 1975, **15**, 129.

60. TAKAHASHI, Y. *Pure Appl. Chem.*, 1976, **47**, 237.

61. KUBASCHEWSKI, O. AND WALTER, W. *Z. Electrochem.*, 1939, **45**, 630.

62. AUFFREDIC, J. P. AND LOER, D. *J. Chem. Thermodyn.*, 1978, **10**, 1077.

63. POLOVOV, V. M. AND GAVRILOV, N. M. *Instrum. Exp. Tech.* (U.S.A.), 1973, **16**, 1577.

64. ROGEZ, J. AND LECOZE, J. *Rev. Phys. Appl.*, 1980, **15**, 341.

65. DZHAVADYAN, E. A., GALYUK, O. S. AND ROSENBERG, R. A. — *Ind. Lab.*, 1979, 45, 286.

66. FASENKO, A. I., MENCHEV, YU. P. AND BOVISYUK, V. S. — *Instrum. Exp. Tech.*, 1977, 20, 610.

67. WURZ, U. AND GRUBIC, M. — *J. Phys. E. Sci. Instrum.*, 1980, 13, 525.

68. PIREL, J., LABEAU, C. AND ROBOUTAU, A. — *Rev. Phys. Appl.*, 1980, 15, 75.

69. KLEINKLAUSS, J., TISSIER, G., FOUSSE, H. AND MAIVNARD, R. — *J. Phys. E: Sci. Instrum.*, 1980, 13, 26.

70. GMELIN, E. AND RIPKA, K. — *Cryogenics*, 1981, 21, 117.

71. FESENKO, A. I., BORISYUK, V. S. AND MENCHEV, YU. P. — *Measmt. Tech.*, 1978, 21, 403.

72. BOHMHAMMEL, K., MADGE, H. AND WOLF, G. — *Cryogenics*, 1977, 17, 553.

73. LASJAUNIAS, J. C., PICOT, B., ROVEX, A., THALOUZE, D. AND VANDORPE, M. — *Cryogenics*, 1977, 17, 111.

74. TATSUMI, M., MATSUO, T., SUGA, H. AND SEKI, S. — *J. Phys. Chem. Solids*, 1978, 39, 427.

75. DOWNIE, D. B. AND MARTIN, J. F. — *J. Chem. Thermodyn.*, 1980, 12, 779.

76. MATSUO, T. AND SUGA, H. — *Solid St. Phys. (Japan)*, 1979, 14, 738.

77. TAUT, R. H. AND REPPY, J. D. — *Phys. Rev.*, 1979, B20, 997.

78. SCOTT, J. W. — *Experimental thermodynamics*, (McCullough, J. P. and Scott, D. W. (Eds.)), Butterworths, London, 1968, 1, p. 215.

79. BLUE, R. W. AND GIAUQUE, W. F. — *J. Am. Chem. Soc.*, 1935, 57, 991.

80. BUSEY, R. H. AND GIAUQUE, W. F. — *J. Am. Chem. Soc.*, 1952, 74, 4443.

81. GIAUQUE, W. F. AND ARCHIBALD, R. C. — *J. Am. Chem. Soc.*, 1937, 59, 561.

82. RIVES, J. E. — *Transition metal chemistry* (Carlin, R. L. (Ed.)), Marcel Dekker, New York, 1972, 7.

83. COLLAN, H. K., HEIKKILA, T., KRUSIUS, M. AND PICKETT, G. R. — *Cryogenics*, 1970, 10, 389.

84. GINNINGS, D. C. AND CORRUCINI, R. J. — *J. Res. Natn. Bur. Stand.*, 1947, 38, 583.

85. HOCH, M. AND JOHNSON, H. L. — *J. Phys. Chem.*, 1961, 65, 855.

86. HOCH, M. AND JOHNSON, H. L. — *J. Phys. Chem.*, 1961, 65, 1184.

87. DENIELOU, L., PELITET, J. P. AND TEQUI, C. — *J. Chem. Thermodyn.*, 1975, 7, 901.

88. SACHSE, H. — *Z. Physik. Chem.*, 1929, 143, 94.

89. HOLMBERG, T. — *Soc. Sci. Fennicae. Phys. Math.*, 1938, 17, 9.

90. MANN, W. B. — *J. Res. Natn. Bur. Stand.*, 1954, 52, 177.

91. HAUT, R. M. AND HIRST, M. W. — *IEEE Proc. Third Int. Conf. Thermoelectric Energy*, 1980.

92. CHEKHOVSKOI, V. YA., TARASOV, V. D. AND ZHUKOVA, I. A. — *High Temp.* (U.S.A.), 1974, 12, 1088.

93. LEIBOWITZ, L., CHASANOV, M. G. AND MISHLER, L. W. — *Trans. Met. Soc., A.I.M.E.*, 1969, 245, 981.

94. CHEKHOVSKOI, V. Ya., SHEINDLIN, A. E. AND BEREZIN, B. YA. — *High Temp. High Press*, 1970, 2, 301.

95. BEREZIN, B. YA., CHEKHOVSKOI, V. Ya., AND SHEINDLIN, A. E. — *High Temp. High Press*, 1979, 3, 287.

96. CHAUDHURI, A. K., BONNELL, D. W., FORD, L. A. AND MARGRAVE, J. L. — *High Temp. Sci.*, 1970, 2, 203.

97. TREVERTON, J. A. AND MARGRAVE, J. L. — *J. Chem. Thermodyn.*, 1971, 3, 473.

98. TREVERTON, J. A. AND MARGRAVE, J. L. — *J. Phys. Chem.*, 1971, 75, 3737.

99. FREDRICKSON, D. R., KLEB, R., NUTTALL, E. L. AND HUBBARD, W. N. — *Rev. Sci. Instrum.*, 1969, 40, 1022.

100. KANDYBA, V. V., FOMICHEV, E. N., KVIVOROTENKO, A. D. AND SEMINKO, I. V. — *Measmt. Tech.*, 1977, 20, 9.

101. TIAN, A. — *Bull. Soc. Chim. Fr.*, 1923, 33, 427.

102. CALVET, E. — *C.R. Acad. Sci., Paris*, 1948, 226, 1702.

103. CALVET, E. — *Experimental thermochemistry*, Interscience, New York, 1955, 1.

104. CALVET, E. — *J. Chem. Phys. Acad. Sci.* (*U.S.S.R.*), 1959, 33, 1161.

105. CALVET, E. AND PRAT, H. — *Recent progress in microcalorimetry*, Pergamon Press, New York. 1963.

106. GERDANIAN, P. AND DODE, M. — *Proc. Int. Symp. Thermodynamics of Nuclear Materials*, I.A.E.A. Vienna, 1967, p. 41.

107. BOUREAU, G. AND GERDANIAN, P. — *High Temp. High press*, 1970, 2. 681.

108. KLEPPA, O. J., MELCHINAK, M. E. AND CHARLU, T. V. — *J. Chem. Thermodyn.*, 1973, 5, 595.

109. MARTIN, C. J. AND NARINI, M. A. — *Cri. Rev. Analyt. Chem.*, 1979, 8, 221.

110. SPINK, C. H. — *Cri. Rev. Analyt. Chem.*, 1980, 9, 1.

111. BARISAS, B. G. AND GILL, S. J. — *Ann. Rev. Phys. Chem.*, 1978, 29, 141.

112. BRYANT, A. W. AND PRATT, J. N. — *Thermochemie*, C.N.R.S. No. 201, 1971, 241, CNRS, Paris

113. MILLS, K. C. — *Third Int. Conf. Chem. Thermokynamics*, Butterworths, London, 1973, 6, 158.

114. VANDERZEE, C. E. — *Pure Appl. Chem*,. 1976, 47, 245.

115. BECKETT, C. W. AND CEZAIRLIYAN, A. — *Expl. Thermochemistry*, Vol. 1 (McCullough, J. A. and Scott, D. W, (Eds.), Butterworths, London, 1968, p. 552.

116. AVRAMESCU, A. — *Z. Tech. Physik.*, 1939, 20, 213.

117. KURRELMEYER, B., MAIS, W. H. AND GREEN, E. H. — *Rev. Sci. Instrum.*, 1943, 14, 349.

118. NATHAN, A. M. — *J. Appl. Phys.*, 1951, 22, 234.

119. WALLACE, D. C., SIDLES, P. H. AND DANEILSON, G. C. — *J. Appl. Phys.*, 1960, 31, 168.

120. CEZAIRLIYAN, A. — *J. Res. Natn. Bur. Stand.*, 1971, **75C**, 7.

121. CEZAIRLIYAN, A. AND MILLER, A. P. — *High Temp. High Press.*, 1977, **9**, 319.

122. LENSKI, H. AND BOHLER, D. — *Rev. Sci. Instrum.*, 1980, **51**, 221.

123. OLOFSSON, I. AND SUNNER, S. J. — *J. Chem. Thermodyn.*, 1979, **11**, 605.

124. HAGIOV, S. N., KERIMOV, K. K, HAJIEVA, F. S. AND IGNATYEV, V. L. — *J. Chem. Thermodyn.*, 1980, **12**, 509.

125. RASCHELLA, D. L., FELLOWS, R. L. AND PETERSON, J. R. — *J. Chem. Thermodyn.*, 1981, **13**, 303.

125*a*. KAWAIZUMI, F., NISHIO, N., MOMURA, H. AND MALPAHARA, Y. — *J. Chem. Thermodyn.*, 1981, **13**, 89.

126. CHOURASIA, P. B. L., CHAUDARY, D. R. AND BHANDARI, R. C. — *Pramana*, 1974, **3**, 383.

127. CLARKE, P. H., FRANCIS, P. G., GEORGE, M., PHUTELA, R. C. AND ROBERTS, G. K. ST. C. — *J. Chem. Thermodyn.*, 1979, **11**, 111.

128. CHRISTENSEN, J. J., HANSEN, L. D., EZATT, R. M., EATOUGH, D. J. AND HART, R. M. — *Rev. Sci. Instrum.*, 1981, **52**, 1226.

129. ZHURAVLEV, A. M. (Ed.) — *Thermophysical properties of air and air products*, Israel Program for Scientific Translation, Jerusalem, 1971.

130. DIN, F. — *Thermodynamic functions of gases*, Butterworths, London, 1961.

131. KANNULUIK, W. AND MARTIN, H. — *Proc. R. Soc.* (*London*), 1934, **A144**, p. 496; Kannuluik, W. and Carman, E., *Proc. Roy. Soc. London*, 1952, **B65**, 707.

132. GOVINDARAJAN, K. AND GOPAL, E. S. R. — *J. Indian Inst. Sci.*, 1971, **53**, 21.

133. ASSAEL, M. J., DIX, M, LUCAS, A. AND WAKEHAM, W. A. — *J. Chem. Soc., Faraday Trans.*, 1981, **77**, 439.

134. HARRMAN, J. W. — *AIP Conf. Proc.* (Kestin, J. (Ed.)), AIP, New York, 1973, p. 193. Also Sengers, J. V., p. 233 in the same volume.

135. ANGSTROM, A. J. — *Phil. Mag.*, 1863, **25**, 130.

136. WANTENAAR, G. H. J., CAMPBELL, S. J., CHAPLIN, D. H. AND WILSON, G. V. H. — *J. Phys. E: Sci. Instrum.*, 1977, **10**, 825.

137. SULLIVAN, P. F. AND SIEDEL, G. — *Phys. Rev.*, 1968, **173**, 679.

138. ZAVARITSKY, M. V. — *Prog. Cryogenics* (Mandelssohn, K. (Ed.)), Heywood, London, 1959, **1**, p. 207.

139. BRUCE, R. H. AND CANNELL, D. S. — *Rev. Scl. Instrum.*, 1976, **47**, 1323.

140. SULLIVAN, P. F. AND SEIDEL, G. — *Phys. Lett.*, 1967, **25A**, 229.

141. ZALLY, G. D. AND MOCHEL, J. M. — *Phys. Rev.*, 1972, **B6**, 4142.

142. BRUCE, R. H. AND CANNELL, D. S. — *Phys. Rev.*, 1977, **B15**, 4451.

143. YOSHIZAWA, M. AND FUJIMURA, T. — *Bull. Res. Inst. Tohuku Univ.* (*Japan*), 1977, **26**, 135.

144. SALAMON, M. B. — *Solid St. Comm.*, 1973, **13**, 1741.

145. HANDLER, P., MAPOTHER, D. E. AND RAYL, M. — *Phys. Rev. Lett.*, 1967, **19**, 356.

146. KRAFTMAKHER, YA. A. AND ROMASHINA, T. YU. — *Sov. Phys. Solid St.*, 1966, **7**, 2040.

147. LEDERMAN, F. L., SALAMON, M. B. AND SHACKLETTE, L. W. — *Phys. Rev.*, 1974, **B9**, 2981.

148. EMA, K., HAMANO, K. AND KURIHARA, K. — *J. Phys. Soc.* (*Japan*), 1977, **43**, 1954.

149. VISWANATHAN, R. — *Analytical calorimetry* (Porter, R. S. and Johnson, J. F. (Eds.)), Plenum, New York, 1974, **3**, 81.

150. GREENE, R. L. KING, C. N., ZUBECK, R. B. AND HAUSER, J. J. — *Phys. Rev.*, 1972, **B6**, 3297.

151. HORCH, R. — *Exp. Tech. Phys.* (*Germany*), 1975, **23**, 97.

152. EL SHASKOWY, E. A., ATALLA, S. R., YOUCHACK, R. P. AND FILLIPOV, L. P. — *Rev. Int. Hautes. Temp. Refract.* (*France*), 1976, **12**, 168.

153. SALAMON, M. B., GARNIER, P. R., GOLDING, B. AND BUEHLER, E. — *J. Phys. Chem. Solids*, 1974, 35, 851.

154. YURCHAK, R. P. AND KHROMOV, A. V. — *Ind. Lab.*, 1978, 44, 664.

155. KING, C. N., BINDA, J. A., GREENE, R. L. AND GEBALLE, T. H. — *Low temperature physics*, LT13 (Timmerhaus, K. D., O'Sullivan, W. J. and Hammel, E. F. (Eds.)), Plenum Press, New York, 1972, 3, 411.

156. VIGDOROVICH, V. N., GARANIN, V. G. AND UKHLINOV, G. A. — *Ind. Lab.* (*U.S.A.*), 1979, 45, 545.

157. KING, C. N., ZUBECK, R. B. AND GREENE, R. L. — *Low temperature physics*, LT13 (Timmerhaus, K. D., O'Sullivan, W. J. and Hammel, E. F. (Eds.)), Plenum Press, New York, 1972, 4, 626.

158. KRAFTMAKHER, YA. A. — *High Temp. High Press.*, 1973, 5, 433.

159. HOLLAND, L. R. AND SMITH, R. C. — *J. Appl. Phys.*, 1966, 37, 4528.

160. KRAFTMAKHER, YA. A. AND CHEREPANOV, V. YA. — *High Temp.* (*U.S.A.*), 1978, 16, 557 ; Varchenko, A. A. and Kraftmakher, YA. A., *Phys. Stat. Sol.* (*a*), 1973, 20, 387.

161. SUNDQUIST, B. — *Rev. Sci. Instrum.*, 1981, 52, 1061.

162. EICHLER, A. AND GEY, W. — *Rev. Sci. Instrum.*, 1979, 50, 1445.

163. BALOGA, J. D. AND GARLAND, C. W. — *Rev. Sci. Instrum.*, 1977, 48, 105.

164. ITSKEVICH, E. S., KRAIDENOV, V. F. AND SYZRANOV, V. S. — *Cryogenics*, 1978, 18, 281.

165. ANDERSSON, P. AND BACKSTROM, G. — *High Temp. High Press.*, 1972, 4, 101.

166. BACHMANN, R., DISALVO, F. J., GEBALLE, T. H., GREENE, R. L., HOWARD, R. E., KING, C. N., KIRSCH, H. C., LEE, K. N., SCHWALL, R. E. THOMAS, H. W. AND ZUBECK, R. B. — *Rev. Sci. Instrum.*, 1972, 43, 205.

167. SHUTZ, R. J. — *Rev. Sci. Instrum.*, 1974, 45, 548.

168. SCHWALL, R. E., HOWARD, R. E. AND STEWARD, G. R. — *Rev. Sci. Instrum.*, 1975, 46, 1054.

169. LAWLESS, W. N. — *Phys. Rev.*, 1976, B14, 134.

170. RADE, H. S. — *Feinwk. Tech. Measmt. Tech.* (*Germany*), 1975, 83, 230, *Phys. Abstr.*, 1976, 6, 3743.

171. COMBERG, A., EVERT, S. AND SANDER, W. — *Cryogenics*, 1978, 18, 79.

172. HATTA, I. — *Rev. Sci. Instrum.*, 1979, 50, 292.

173. FORGAN, E. M. AND NEDJAT, S. — *Rev. Sci. Instrum.*, 1980, 51, 411.

174. DJUREK, D. AND PRESTER, M. — *J. Phys. E: Sci. Instrum.*, 1980, 13, 1265.

175. BILJAKOVIK-FRAUNULOVIĆ, K., TOMIC, S. AND DJUREK, D. — *Fizika*, 1978, 10, 254.

176. RUBEIC, J. B. AND RUBEIC, A. — *Electrotechnika Zagreb.*, 1977, 5, 436.

177. PARKER, W. J., RENKINS, R. J., BUTLER, C. P. AND ABOTT, G. L. — *J. Appl. Phys.*, 1961, 32, 1679.

178. KRUGER, R., MEISSNER, M., MIMKES, J. AND TAUSEND, A. — *Phys. Status Solidi* (*a*) 1973, 17, 471.

179. BERTMAN, B., HEBEILEIN, D. C., STANDFORD, D. J., SHEN, L. AND WAGNER, R. R. — *Cryogenics*, 1970, 10, 326.

180. GOBRECHT, H. AND KRUGER, R. — *Proc. Second Int. Cryogenic Engg. Conf.*, Brighton, U.K., Iliffe Science and Technology Publications, Guildford, 1968, p. 301.

181. GOBRECHT, K. H. AND SAINT PAUL, M. — *Proc. Third Int. Cryogenic Engng. Conf.*, Berlin, Iliffe Science and Technology Publications, Guildford, 1970, p. 235.

182. CAPE, J. A. AND LEHMANN, G. W. — *J. Appl. Phys.*, 1963, 34, 1909.

183. TAYLOR, R. E. AND CAPE, J. A. — *Appl. Phys. Lett.*, 1966, 5, 212.

184. GERSHENSON, M. AND ALTEROWITZ, S. — *Appl. Phys.*, (Germany), 1975, 5, 239.

185. GOUBOU, W. M. AND TAIT, R. A. — *Phys. Rev. Lett.*, 1975, 34, 1220.

186. FAGALY, R. L. AND BOHM, R. G. — *Rev. Sci. Instrum.*, 1977, 48, 1502.

187. BELOSTOTSKII, M. V., ARUTYUNOV, B. A., BIL, V. S. AND STEPANOV, R. D. — *Polym. Mech.*, 1977, 13, 159.

188. MEBED, M. M., GAFFAR, M. A. AND SAKNIDY, S. — *Rev. Int. Hautes. Temp. Refrac.* (France), 1979, 16, 340.

189. BUROVAI, S. E. AND KOSHAROVSKII, G. N. — *Phys. Abstr.*, 1975, 5, 44268.

190. FOX, J. N. AND MCMASTER, R. H. — *Am. J. Phys*, 1975, 43, 1083.

191. VANDERSANDE, J. W. AND POHL, R. O. — *Rev. Sci. Instrum.*, 1980, 51, 1694.

192. TAYLOR, K. R. — *J. Phys. E: Sci. Instrum.*, 1980, 13, 1193.

193. KLIMENKO, M. M., KRIZHIZHANOVSKII, R. E. AND SHERMAN, V. E. — *High Temp.* (U.S.A.), 1979, 17, 1006.

194. FILLER, R. L., LINDENFELD, P. AND DEUTSCHER, G. — *Rev. Sci. Instrum.*, 1975, 46, 439.

195. WERNERKIEFFER, S. — *J. Geophys. Res.*, 1976, 81, 3018.

196. RESS, R. G., ANDERSSON, P. AND BACKSTROM, G. — *Mol. Phys.*, 1979, 38, 527.

197. SCHRADER, H. AND NOLTING, O. — *High Temp. High Press.*, 1981, 12, 561.

198. MCLAUGHLIN, E. AND PITTMAN, J. F. T. — *Phil. Trans. R. Soc.*, 1971, A270, 557.

199. GUSTAFSSON, S. E., KARAWACKI, E. AND KHAN, M. N. — *J. Phys. D: Appl. Phys.*, 1979, 12, 1411.

200. GUSTAFSSON, S. E. — *Z. Naturforsch.*, 1967, 22A, 1005.

201. GUSTAFSSON, S. E., HALLING, N. AND KJELLANDER, R. A. E. — *Z. Naturforsch.*, 1968, 23A, 44.

202. GUSTAFSSON, S. E., HAMDANI, A. J. AND KARAWACKI, E. — *J. Phys. E: Sci., Instrum.*, 1979, 12, 387.

203. ANGELL, C. A. — *Rev. Phys. Chem.*, 1971, 22, 420.

204. ODOWARA, O., OKADA, I. AND KAWAMURA, K. — *J. Chem. Engng. Data*, 1977, 22, 222.

205. AMRIKHANOV, D. G., VSMANOV, A. G. AND NORDEN, P. A. — *J. Engng. Phys.*, 1974, 27, 1110.

206. REGEL, A. R., SMIRNOV, I. A. AND SHADRICHEV, E. V.. — *Phys. Status Solidi* (*a*), 1971, 5, 13.

07. BACKSTROM, G. AND CHAUSSY, J. — *J. Phys. E* : *Sci. Isntrum.*, 1977, 10, 767.

208. GUSTAFSSON, S. E., KARAWACKI, E. AND KHAN, M. N. — *J. Appl. Phys.*, 1981, 52, 2596.

209. NAGASAKA, V. AND NAGASHIMA, A. — *Rev. Sci. Instrum.*, 1981, 52, 229 ; Hoshi, M., Omotani, T. and Nagashima, A., 1981, 52, 755.

210. FEEBERGRAND, F. E. AND ALLEMAN, T. G. — *Analyt. Chem.*, 1966, 38, 1806.

211. WENDLANDT, W. W. — *Analyt. Chem. Acta*, 1970, 49, 187.

212. TAYLOR, G. R., DUNN, G. E. AND EASTERBROOK, W. B. — *Analyt. Chem. Acta*, 1971, 53, 452.

213. GRUVER, R. M. — *J. Am. Ceram. Soc.*, 1948, 31, 323.

214. VALLEBOVA, G. — *J. Therm. Anal.*, 1979, 16, 49.

215. MRAW, S. C. AND NASS, D. F. — *J. Chem. Thermodyn.*, 1979, 11, 567.

216. CARROLL, R. W. AND MANGRAVITE, R. V. — *Proc. Second Int. Conf. Thermal Analysis*, 1969, 1, 189. (Schwessker, R. F. and Garn, P. D. (Eds.)), Academic Press London.

217. ROGERS, R. N. AND MORRIS, E. D. — *Analyt. Chem.*, 1966, 38, 410.

218. ARNTZ, H. — *Rev. Sci. Instrum.*, 1980, 51, 965.

219. JOHNSON, J. F. AND MILLER, G. W. — *Thermochim. Acta*, 1970, 1, 373.

220. POPOV, V. N. — *Heat Transfer Soviet Res.*, 1974, 6, 174.

221. LAGNIER, R., PIERRE, J. AND MORTIMER, M. J. — *Cryogenics*, 1977, 17, 349.

222. BELYAEV, A. A. — *Ind. Lab.*, 1977, 43, 549.

223. GAVRILOV, N. M., POLOVOV, V. M. AND PONOMAREVA, R. R. — *Instrum. Expl. Tech.*, 1979, 22, 1422.

224. TAKAHASHI, Y. — *Thermal analysis* : *Comparative studies on materials* (Kambe, H. and Garn, P. D. (Eds.)), Halsted Press, Tokyo, 1974, 8.

225. TAKAHASHI, Y., YOKOKAWA, H., SEKINE, Y., KODOKURA, H. AND MUKAIBO, T. — *Ann. Rep. Engng. Inc.*, Fac. Engng., Univ., Tokyo, 1976, 35, 209.

226. TERAI, R. — *Yogyo-Kyokai-Shi* (*Japanese*), 1977, 85, 979. *Phys. Abstr.*, 1977, 7, 69124.

227. TAKAHASHI, Y., YOKOKAWA, H., KADOKURA, H., SEKINE, Y. AND MUKAIBO, T. — *J. Chem. Thermodyn.*, 1979, 11, 379.

228. YOKOKAWA, H. AND TAKAHASHI, Y. — *J. Chem. Thermodyn.*, 1979, 11, 411.

229. KUMADA, T. — *J. Nucl. Sci. Tech.* (*Japan*), 1975, 12, 154.

230. CHERCHENKO, K. M. AND IVON, A. I. — *Ind. Lab.*, 1976, 42, 1091.

231. BARANOV, V. M., KUDRJAVTSEV, E. M. AND SOMOKHVALOV, A. N. — *J. Engng. Phys.*, 1976, 30, 625.

232. MARX, R. — *Rev. de Phys. Appl.*, 1978, 13, 298.

233. CASIMIR, H. B. G. AND DU PRE, F. K. — *Physica*, 1938, 5, 507.

234. SKJELTROP, A. T. AND WOLF, W. P. — *Phys. Rev.*, 1972, B8, 215.

235. ALBERTSSON, J., CHEN, P. Y. AND WOLF, W. P. — *Phys. Rev.*, 1975, B11, 1943; Clover, R. B. and Wolf, W. P. *Solid St. Commun.*, 1968, 6, 331.

236. PARK, J. G. AND VAIDYA, A. W. — *J. Physique Colloq.* (*France*), 1978, 39, C6, 1228; Park, J. G. and Vaidya, A. W., *J. Low Temp. Phys.*, 1980, 40, 247.

237. JEQUIER, E. — *Applications of calorimetry in life sciences*, (Lamprecht, I. and Schaarmidt, B. (Eds.)), Walter de Gruyter, Berlin, 1977, p. 261.

238. TSCHEGG, E., SIGMUND, A., VEITL, V. AND IRSHGLER, K. — *J. Phys. E: Sci. Instrum.*, 1981, 14, 550.

239. SIQUEIRA, M. A. A., GHIZONI, C. G., VARGAS, J. L., MENEZES, E. A., VARGAS, H. AND MIRANDA, L.C. M. — *J. Appl. Phys.*, 1980, 51, 1403.

240. ADAMS, M. J. AND KIRKBRIGHT, G. F. — *Analyst*, 1977, 102, 281.

241. KIRIZBAEV, R. A. AND SHAMUZAFUROVA, G. SH. — *Appl. Sol. Energy*, 1978, 14, 29. *Phys. Abstr.*, 1979, 9—95222.

242. LACY, L. L., NISEN, D. B. AND ROBINSON, M. B. — *NASA Tech. Briefs*, USA, 1979, 4, 89.

243. STULL, D. R. — *Analyt. Chim. Acta*, 1957, 17, 133.

244. ZABETAKIS, M. G., CRAIG, R. S. AND STERRETT, K. F. — *Rev. Sci. Instrum.*, 1957, 28, 497.

245. HILL, R. W. — *Progress In cryogenics* (Mendelssohn, K. D. (Ed.)), Heywood, London, 1959, 1, 179.

246. COXON, W. F. — *Temperature measurement and control*, Heywood, London, 1960.

247. KUTZ, M. — *Temperature control*, Academic Press, New York, 1968.

248. HECK, H. — Reports on the adiabatic calorimeter temperature controller, Res. School Phys. Sci., Aust. Natn. Univ. (Unpublished reports), 1976 and 1979.

249. MARTIN, D. L. AND SNOWDEN, R. L. — *Rev. Sci. Instrum.*, 1970, 41, 1869.

250. MARTIN, D. L. — *Rev. Sci. Instrum.*, 1972, 43, 1762.

251. MARTIN, D. L., BRADLEY, L. L. T., CAZEMIA, W. J. AND SNOWDEN, R. L. — *Rev. Sci. Instrum.*, 1973, 44, 675.

252. SHIN, C. AND CRISS, C. M. — *Rev. Sci. Instrum.*, 1975, 46, 1043.

253. WILLIAMS, I. S., STREET, R. AND GOPAL, E. S. R. — *Pramana*, 1978, 11, 519.

254. HECK, H., WILLIAMS, I. S., GOPAL, E. S. R. AND JYOTHI, S. — *Pramana*, 1980, 14, 349.

255. AVIDSSON, K., FALK, B. AND SUNNER, S. — *Chem. Scr.*, 1976, 10, 193.

256. BOHMHAMMEL, K., SCHMIDT, H. G. AND WOLF, G. — *Expl. Tech. Phys.* (Germany), 1980, 28, 275.

257. GEREEV, O. A., FRENKEL, I. M. AND KULOGIN, V. I. — *Measmt. Tech.* (U.S.A.), 1974, 17, 706.

258. GMELIN, E. AND RODHAMMER, P. — *J. Phys. E : Sci. Instrum.*, 1981, **14**, 223.

259. RADE, H. S. AND RINGELMANN, F. R. — *Feinwerk. Tech. Measmt. Tech.* (Germany), 1977, **85**, 223. *Phys. Abstr.*, 1977, 7–82518.

260. IKEDA, S. AND ISHIKAWA, Y. — *Japan. J. Appl. Phys.*, 1979, **18**, 1367.

261. IKEDA, S. AND ISHIKAWA, Y. — *Solid St. Phys.* (Japan), 1979, **14**, 469.

262. YOSHIWA, M. AND IWATA, A. — *Cryogenics*, 1977, **17**, 273.

263. GRIFFLING, B. F. AND SHIVASHANKAR, S. V. — *Rev. Sci. Instrum.*, 1980, **51**, 1030.

264. DICKENS, K. J. KLEPPA, O. J. AND YOKOKAWA, H. — *Rev. Sci. Instrum.*, 1980, **51**, 672.

265. KOSKI, J. A. AND MCVEY, D. F. — *Proc. Eighth Conf. Thermophysical Properties*, American Society of Mechanical Engineers, New York, 1981.

266. CEZAIRLIYAN, A. — *J. Res.*, Natn. Bur. Stand. Report, 1970, **75**, 793.

267. PORTER, G. — *Dimensions, NBS* (USA), 1980, **64**, 3.

268. RIGHINI, F. AND ROSSO, A. — *Proc. Symp. Temp. Measmts.*, Karlovy Vary Checkoslovakia (Preprint), 1981.

269. CEZAIRLIYAN, A. AND MILLER, A. P. — *Int. J. Thermophys.*, 1980, **1**, and Cezairliyan, A., Miller, A. P., Righini, F. and Rosso, A., *High Temp. Sci.*, 1979, **11**, 223.

270. RIGHINI, F. AND ROSSO, A. — *High Temp. High Press.*, 1980, **12**, 355.

271. LANCHESTER, P. C. AND BAKER, D. P. — *J. Phys. E : Sci. Instrum.*, 1981, **14**, 805.

272. JOSEPH, O., MOODY, D. E. AND WHITEHEAD, J. P. — *J. Phys. E : Sci. Instrum.*, 1976, **9**, 595.

273. CASH, W. M., STANBURY, E. E., MOORE, C. F. AND BROOKS, C. R. — *Rev. Sci. Instrum.*, 1981, **52**, 895.

274. HATEM, G., GANNE, P., BROS, J. P., GEHRINGER, F. AND HAYER, E. — *Rev. Sci. Instrum.*, 1981, **52**, 585.

275. WILLIAMS, I. S., STREET, R. AND GOPAL, E. S. R. — *J. Phys. F : Metal Phys.* 1979, **9**, 431.

276. CEZAIRLIYAN, A. AND MILLER, A. P. — *High Temp. High Press.*, 1977, 9, 319,; *J. Res.*, Natn. Bur. Std., 1978, 83, 127.

277. CEZAIRLIYAN, A. — *High Temp. High Press.*, 1972, 4, 541; *J. Res.*, Natn. Bur. Std., 1973, 77A, 45 ; *J. Chem. Thermodyn.*, 1975, 6, 735; *J. Res. Natn. Bur. Std.*, 1975, 79A, 431.

278. SENGERS, J. V. AND KLEIN, M. K. (Eds.) — The technological importance of thermophysical information, NBS, Washington D.C., 1980.

279. LAKSHMIKUMAR, S. T. AND GOPAL, E. S. R. — *Recent developments in the techniques of heat capacity measurement*, NTPP—report, Department of Physics, IISc., (unpublished) 1981.

280. LAKSHMIKUMAR, S. T. AND GOPAL, E. S. R. — Recent applications of heat capacity measurements in physico-chemical investigations, *Int. Rev. Phys. Chem.* (To be published).