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NEW DIFFERENTIAL SCANNING CALORIMETER. NEW THERMOCHEMICAL APPLICATIONS

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The described calorimeter is of fluxmetric, differential type. Thanks to the surrounding arrangement of the heat-flux-sensor, the sensitivity is independent of the sample characteristics: size, container type, kind of gas etc. Application to high-pressure experiments, is outlined.

The general arrangement gives direct access to the sensitive zone from the outside: direct introduction of the sample; setting of electrical, mechanical, or pneumatic connections; application to the study of "open" chemical systems (gas-solid reactions). Examples of application are given.

For the past few years, several quantitative thermal analysis instruments have been marketed: they are either differential scanning calorimeters with power compensation, or improved differential thermal analysis apparatuses.

They have allowed much work, particularly in the field of the control and study of polymers; the study of polymerization itself; the study of solid structure and state changes; phase diagram establishment; purity control; etc. The value of these instruments is well known but they admit two main defects which limit their application possibilities (Fig. 1 A). The thermosensitive elements (temperature sensors or power compensation devices) are too concise and do not surround the studied sample. The thermal connections between the sample and its environment are too weak; they are badly determined and they depend on secondary factors such as the sample setting or size, the sample container type, and the nature or pressure of the gas. In some cases this difficulty is increased, because the active parts of the device – sample and thermosensitive elements – follow a temperature law quite independent of the temperature of the chamber which surrounds them.

Consequently, important and parasitic thermal exchanges occur which cannot be controlled or symmetrized. The small detector and the bad control of the thermal connections, as well as the very small dimensions of the samples usually used, do not allow the fitting of "experimental connections" between the sample and the outside. Indeed, the measurement accuracy is satisfactory only for the study of an isolated sample, usually confined in a tight capsule set on the thermal detectors. The surrounding atmosphere must be constant and well defined. The sample cannot be extracted or introduced during the apparatus operation.

To extenuate these drawbacks, we have designed a small sized calorimeter whose temperature can be scanned quickly in a decreasing or increasing direction. This calorimeter operates according to the heat flow principle created by Calvet.

Many years' experience of such a mode of operation have shown us that it is possible to measure simultaneously the quasi-totality of the thermal exchange between the sample and its environment independently of the experimental conditions, while maintaining easy access to the experimental zone from the outside.

The basic equipment includes (Fig. 1 B):

– a thermostatic block surrounding the experimental zone and the sensor completely; this chamber imposes its own temperature on the studied system.

– a heat flow sensor set inside the thermostatic block, but itself widely surrounding the experimental zone where the sample is located. The thermal connection ensured by the heat flow sensor between the sample and the block is very strong, so that some auxiliary connections can be fitted between the sample system and the

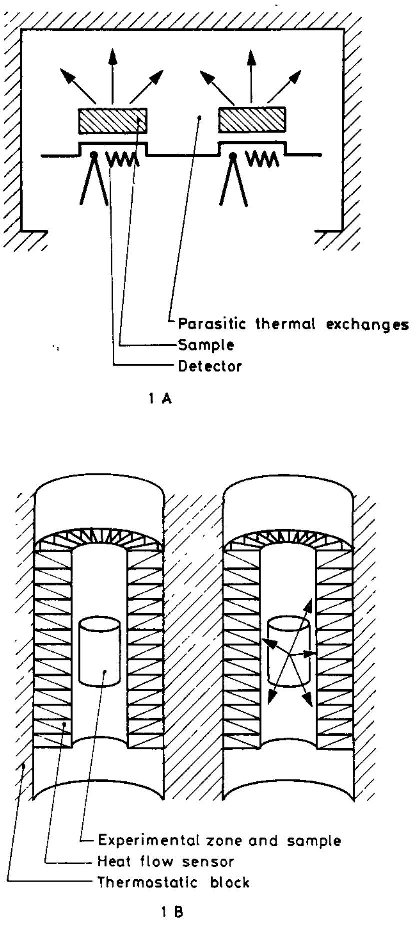

Fig. 1. Comparative schemes: A: Differential thermal analysis; B: Heat flux calorimeter

thermostatic chamber or between the sample and the outside without disturbing the measurements too much.

Used at a scanning temperature with an isolated sample, the calorimeter operates as a precise quantitative differential thermal analyzer.

Used with a sophisticated system, open to the outside (gaseous connection for instance) or closed, the calorimeter operates as a mini chemical reactor with controlled thermal exchanges. According to the experimental requirements, the "mini reactor" operation may occur at fixed temperature, at constantly variable temperature, or at step-by-step variable temperature.

Description (Fig. 2)

The calorimeter itself is set in an external parallelepipedic chamber connected to a work desk by a movable arm. This chamber is closed; access to the useful zone of the calorimeter is given by two pipes passing through the calorimeter.

On the left side we can see the holes into which the tubes open. Most of the time the calorimeter is set in the horizontal position, as shown here. Tipping of the arm sets the tubes in the vertical position and lifts the calorimeter up. The operation is unchanged. The empty space under the calorimeter can be used for auxiliary device implantation for the introduction or extraction of the sample (for example for quick drop in a quench bath). Behind the work desk there is an electronic panel for thermostatic block temperature regulation and programming, as well as the

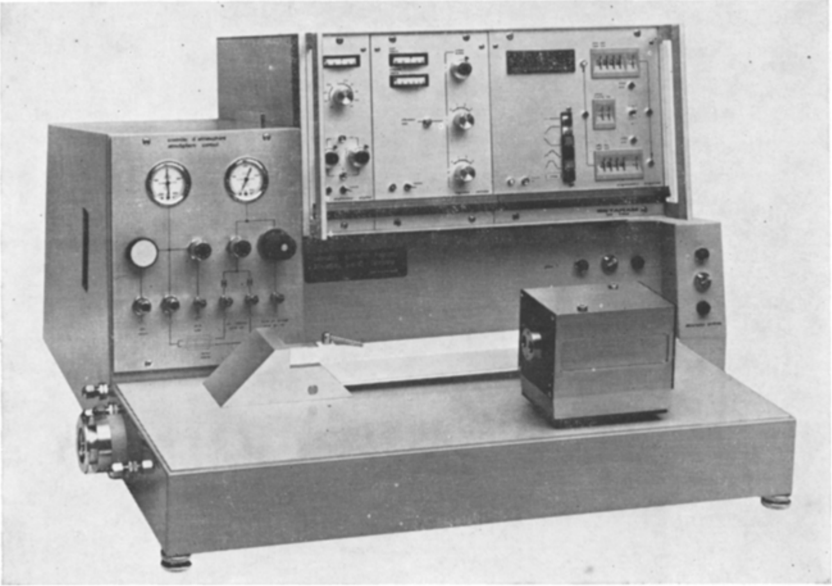

Fig. 2. Calorimeter, general view

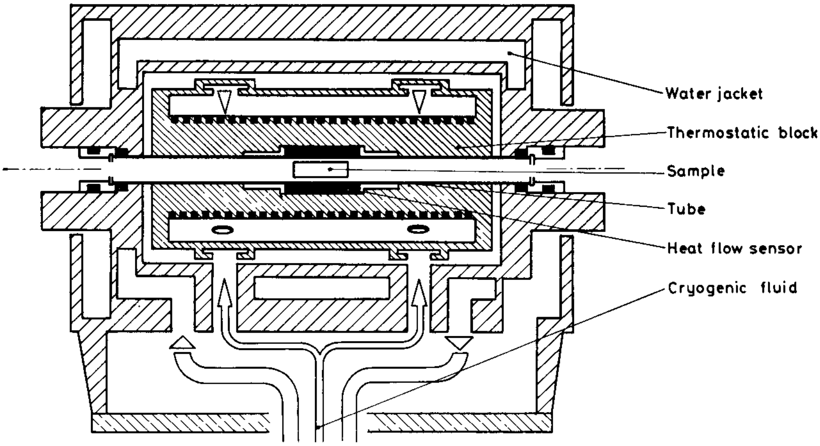

Fig. 3. Schematic calorimeter cross-section

signal amplifier. This panel can be completed by a digital unit connected to a computer.

On the left side there is a gas supply unit used for experimental zone atmospheric control: vacuum pumping or sweeping with inert or active gas under a controlled flow rate.

This atmosphere control may be improved by special accessories, for example for work under high pressure. The digital design of the temperature programmer gives a very high reproducibility of the temperature runs. An original arrangement of the temperature control allows a precise measurement of the heat capacities of the sample.

Figure 3 is a scheme showing the internal arrangement of the calorimeter. The thermostatic block heated by resistors takes up the main part of the apparatus, in order to surround widely the useful space. It is itself surrounded by the external enclosure which is a water-jacket. For subambient operation a cryogenic fluid is introduced in a circuit overlapped in the thermostatic block. The Figure shows one of the tubes traversing the apparatus and allowing access to the useful zone. This open tube permits the direct introduction or even the transit of the sample; it allows gas flowing and sweeping. There are in fact two identical tubes side by side. One contains the sample (the small rectangle in the Figure), and the other the reference. The output signal is the differential signal obtained by a connection in opposition of the "sample" heat flow sensor and the "reference" heat flow sensor. Each heat flow sensor is a set of radial thermal conducting thermocouples connecting the thermostatic block and the central part of the tube forming the experimental zone. The surrounding shape of the heat flow sensor ensures the calorimetric accuracy.

The samples are put direct in the sensitive zone or are inserted in open or tight containers. The useful volume in the middle part of the tube is 7 mm in diameter and 10 mm in length. This important volume gives a very high specific sensitivity (sensitivity corrected for the sample volume). This volume permits too the use of various crucibles. Some crucibles can work under high pressure (more than 100 bars), without any change in stability and sensitivity.

The stability secured by the thermostatic chamber and the high sensitivity of the calorimeter are suitable either for the measurement of the very low powers obtained during isothermal or pseudo-isothermal experiments (very low scanning rates) or for the measurement of large thermal effects evolved during fast scanning rates (a few degrees per minute).

This property is very important, because the study of a fundamental process may be done with all the more facility and accuracy as the studied system is maintained closed to its thermodynamic equilibrium; the more the equilibrium is required, the slower must be the change of the control parameters like pressure and temperature. The digital programmer achieved allows very slow rates, to one degree per hour.

"Open system"

The access to the sensitive zone has two aspects:

1 – The mechanical accessibility is an experimental convenience as previously stated for sample transfer, including during calorimeter operation, installation of mechanical, pneumatic or electric connections.

2 – The general accessibility is especially a new thermochemical ability: The "studied system" is no longer limited to an isolated sample; the sample located in the calorimeter may be only a part of a thermochemical system extending to the outside.

For instance, Fig. 4. shows a study possibility in heterogeneous catalysis. The sample is the catalyst alone. The system includes the reactive gases under flow and pressure controlled from the outside.

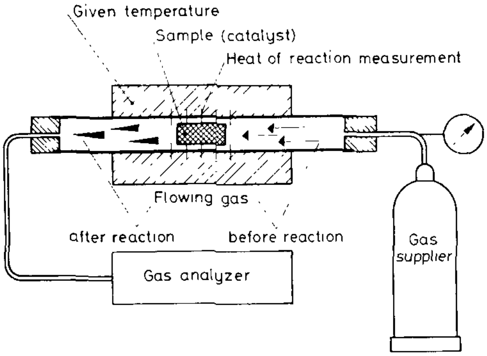

Fig. 4. Schematic setting for catalysis study

Applications

Calibration

The calorimetric calibration of the apparatus is made by the Joule effect: a well-known electric power is applied to a resistor set in a container simulating the experimental crucible. This method is possible thanks to the possibility of access to the sensitive zone which allows connection adaptation (Fig. 5).

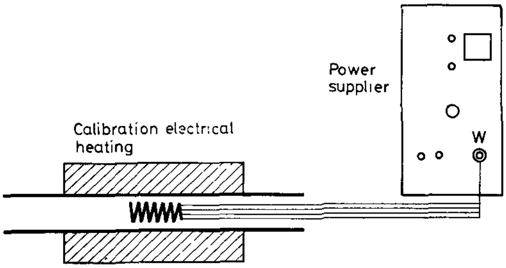

Fig. 5. Electrical calibration arrangement

The Joule calibration is carried out at any temperature. A special design of the calibration source allows the application of repeated electrical impulses during temperature scanning. The resulting square signal is shown in Fig. 6. The automatic integration of the successive areas, and the "base line" interpolation by the computer give as many calibration points as there are impulses. This method is very fast. It has been checked that the calibration does not depend on the scanning speed.

Figure 7 represents a calibration curve obtained after analytical calculation. The sensivity is written in a polynomial form with indicated coefficients $a_0 \ldots a_4$. The mean deviation between the analytical curve and the experimental points is less than 0.3%.

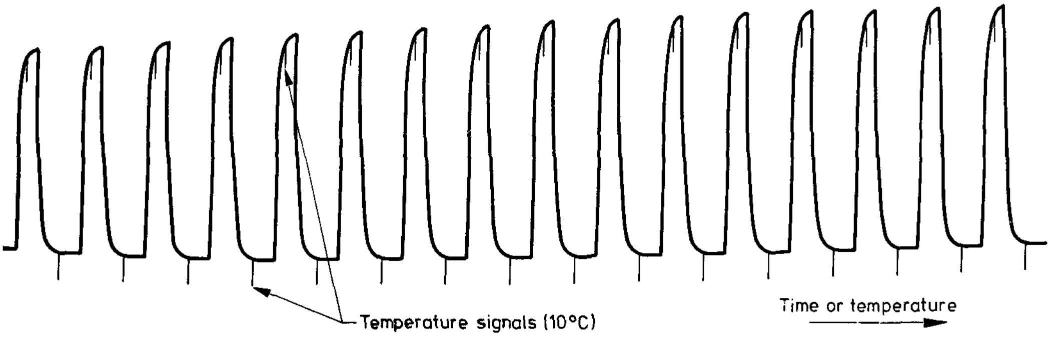

Fig. 6. Automatic calibration "square signal"

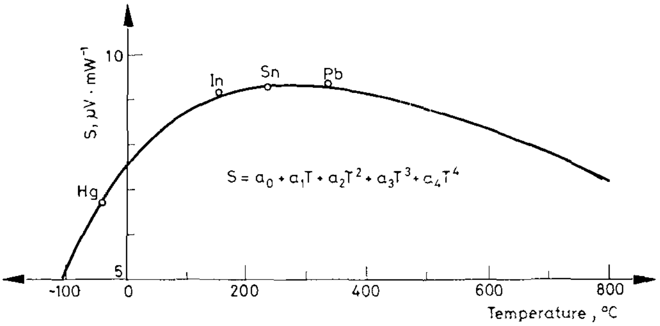

Fig. 7. — Joule calibration curve; — Metal melting calibration

It has been checked that the sweeping or switching-off of gas flow inside the tubes in one or the other direction do not modify the calibration. Nor is the calibration affected by the nature of the gas inside the tubes. (The lateral shifting of a 10 mm long sample crucible does not involve a significant sensitivity change for a shifting smaller than 2 mm; a sensitivity drop of about 1% for a 3 mm shifting.)

Calibration checking by metal melting

The calibration has been checked by melting of pure metals: mercury, indium, tin and lead. The melting heat takes as references where respectively:

Hg: 11.64 In: 28.4 Sn: 60.6 Pb: 23.0 $J.g^{-1}$

The corresponding points are marked in Fig. 7. Successive tests performed on several apparatuses led to a coincidence between the Joule effect and melting calibrations better than 1%.

Figure 8 shows a tin melting diagram. The linear form of the peak rise side is characteristic of a pure compound. Weight 51.4 mg.

Glass transition experiment (Isolated sample arrangement)

Figure 9 is obtained by heating of methyl polymethacrylate from 40 to 170°. The calorimeter is loaded with two identical crucibles, but one of them is empty, while the other contains the sample. The starting-up of the temperature scanning involves an initial shifting of the curve proportional to the sample heat capacity. Stopping the scanning leads to a return to the base line with a deflection proportional to the final heat capacity: a high variation of the specific heat is noted between the following limit values:

$$C_p\ 40^\circ = 1.64\ J.g^{-10}\ \text{degree}^{-1}$$
$$C_p\ 170^\circ = 2.31\ J.g^{-1}\ \text{degree}^{-1}$$

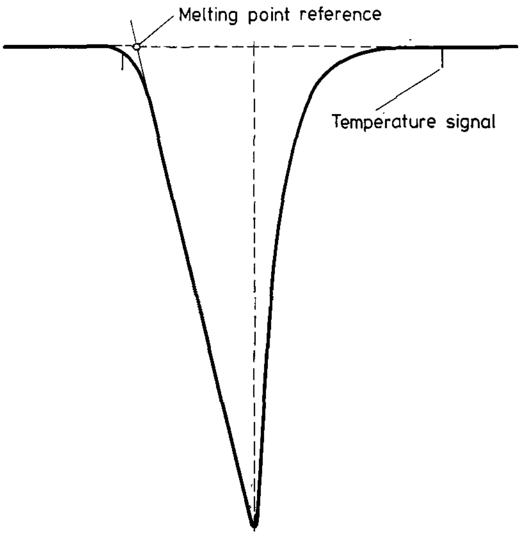

Fig. 8. Tin melting diagram

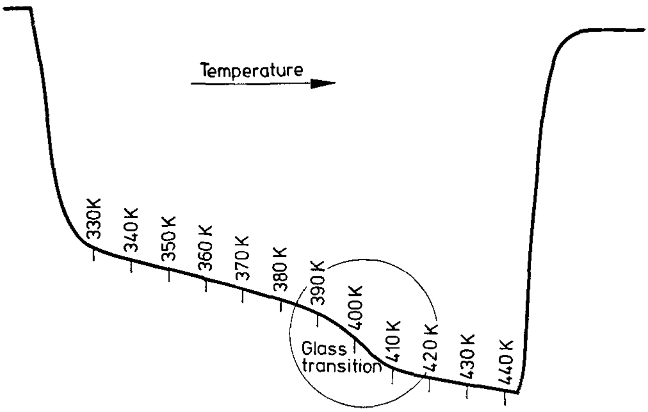

Fig. 9. Methyl polymethacrylate heat capacity. Glass transition

These values are determined from the measured amplitudes taking into account the calibration for the involved temperatures. A glass transition is observed in a 20° gap, centered on the value 120°. The variation of the corresponding specific heat is 0.290 $J.g^{-1}$ $degree^{-1}$. One can see too that the variation of the specific heat as a function of the temperature is higher below the glass transition than above.

Isothermal polymerization at 140° under sealed crucible (styrene + 7% butadiene) (Fig. 10)

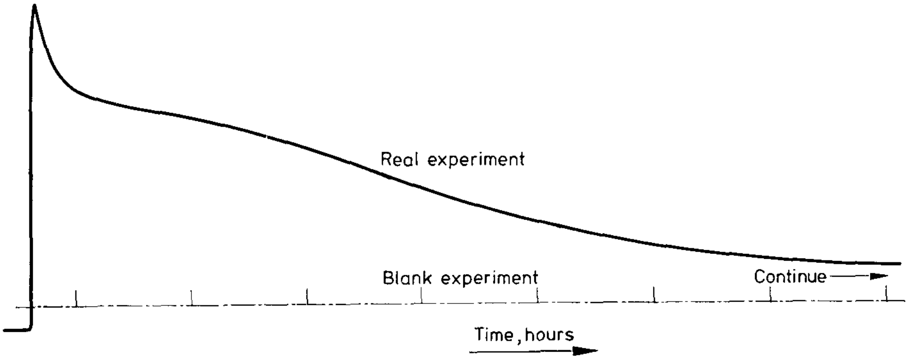

Fig. 10. Styrene-butadiene copolymerization. Isothermal experimentation

This measurement uses two possibilities of the calorimeter. Direct introduction during experimentation and use of thick-walled crucibles resisting high pressure.

Two sealed crucibles are introduced simultaneously. One is empty, and the other contains the monomer. The transition time is very short, as the calorimeter operation is not stopped. The polymerization reaction is at first rather fast. Then during a few hours it proceeds with slowly decreasing heat power. The measured polymerization heat is 63 kJ · mole^{-1}.

Polycondensation of a phenolic resin (1) and a furanic resin (2) (Fig. 11)

Test performed with temperature scanning, in a "high-pressure" sealed crucible. The pressure is not controlled. It is high because of the presence of water, whose steam pressure at 250° (maximum temperature of the test) is 40 bars.

As with the tests of Fig. 9, we work here without reference sample. That is why the scanning shows up an endothermic signal proportional to the sample heat capacity. In curve (1) after this initial shift we can see a significant exothermic peak corresponding to the polycondensation; then the signal comes back to a new stable endothermic value proportional to the new heat capacity. At the end of scanning, the signal returns to the base line. In the case of sample (2), the beginning of the experimentation is the same, though the polycondensation peak has a different shape, showing a quick acceleration of the reaction and a rough stop by reactive consumption. Then the signal comes back to a level not so negative, which could let us suppose a small specific heat. In fact the scanning stopping shows that the specific heat retains a significant value (strong shifting) but shows too that an exothermic phenomenon is superimposed on the polycondensation. This signal slowly decreases with time, probably due to a determination of the product.

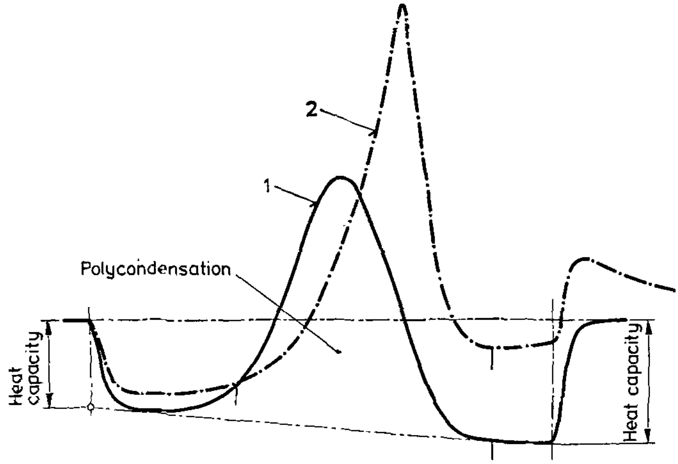

Fig. 11. Polycondensation of 1, phenolic and 2, furanic resin

Measurement of the polycondensation residue of a phenolic resin (Fig. 12) (Check in plant of the non-polycondensed residue).

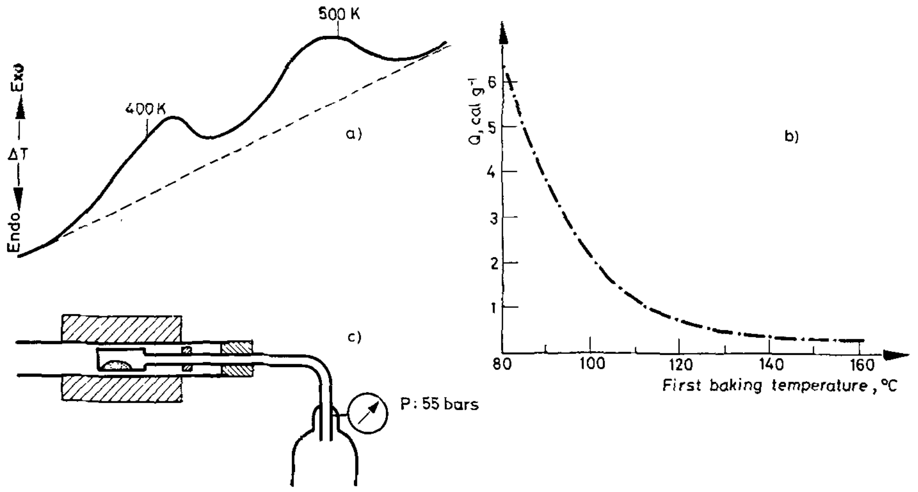

Fig. 12. Polycondensation residue control a) Thermal curve; b) Heat of residue polycondensation: function of first baking temperature; c) Schematic experimentation arrangement

Different lots of phenolic resin are prepared by monomer heating during 3 hours at different temperatures, from 83 to 160°. Then thermal analysis of samples from the lots is performed. The thermal curve is shown in Fig. 12/*a*. The first peak does not vary. The second peak amplitude varies with the first heating temperature: it comes from the polycondensation of the non condensed residue during the heating of preparation; its amplitude is the smaller, the stronger this first baking.

This thermal effect is very slight as only one small non-polycondensed quantity is active. The experiment is performed in a high-pressure crucible adapted with a connection pipe to the outside, connected to a gas volume under pressure (helium, 55 bars).

This setting is indispensable to avoid the evaporation of the residual water, evaporation which could completely hide the small observed thermal effect. Thermal analysis in an isolated and tight crucible is impossible: the set under pressure must be independent of the steam pressure and must be applied before heating.

Curve (*b*) shows the relation between the observed peak area and the temperature of the first baking. The result agrees with that at residue analysis by acetonic extraction, but it is obtained more easily and more quickly. The determination is more precise for the low polycondensation residues. Scheme (*C*) indicates the original setting of the pressurized crucible fitted in the calorimeter.

These examples show the diversity of use of the facilities of the new heat flow scanning calorimeter.

RÉSUMÉ — Description d'un nouveau Calorimètre Différentiel Programmable, de type fluxmétrique. La disposition enveloppante du détecteur de flux thermique rend la sensibilité indépendante des caractéristiques de l'échantillon: dimension, nature et type du container, nature et débit des gaz en présence. Application aux expériences sous haute pression.

La disposition permet l'accès direct de la zone sensible depuis l'extérieur: introduction directe de l'échantillon; possibilité de mise en place de connexions électriques, mécaniques, pneumatiques, etc; application à l'étude de systèmes chimiques ouverts (réactions gaz-solide).

Exemples d'application: chaleurs de transformation (fusion); chaleur spécifique; transitions vitreuses; polymérisation sous haute pression; catalyse hétérogène, etc.

ZUSAMMENFASSUNG — Das beschriebene Kalorimeter ist ein fluxmetrisches Differentialinstrument. Durch die umhüllende Anordnung des Wärme -Flux-Sensors ist die Empfindlichkeit von den Charakteristika der Probe, wie Grösse, Behältertyp, Art der Gase, usw., unabhängig. Der Einsatz bei Hochdruckversuchen wird kurz beschrieben.

Die generelle Anordnung ermöglicht einen unmittelbaren Zugang zur empfindlichen Zone von Aussen: direkte Einführung der Probe; elektrischen, mechanischen oder pneumatischen Anschluss; Einsatz zur Untersuchung "offener" chemischer Systeme (Gas-Festkörper-Reaktionen). Anwendungsbeispiele werden gegeben.

Резюже — Описанный калориметр является поточномерным, дифференциального типа. Вследствии близлежащего расположения теплового поточного сенсора, чувствительность его не зависит от характеристик образца: размеры, тип приёмника, тип газа и т. д. Описано применение его в экспериментах с высоким давлением. Общее расположение дает прямой доступ в зону чувствительности с внешней стороны: прямое введение образца, регулирование электрических, механических или пневматических узлов, применение для исследования «открытых» химических систем (реакции газ-твердое тело). Даны примеры его применения.