# CALORIMETRIC STUDIES OF CHEMICAL REACTIONS USING A THERMAL MICRO-REACTOR[*]

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ABSTRACT

Chemical reactions involving volatilizable substances cannot usually be studied by standard DTA or DSC techniques. However, such difficulties can be overcome by using sealed sample containers as micro-reactors. This work describes the adaptation of a sealed ampoule technique to standard commercial equipment for calorimetric studies of several chemical reactions. The reaction products are then analyzed by other instrumental techniques such as gas chromatography, mass spectrometry, or infrared spectroscopy.

INTRODUCTION

Differential thermal analysis (DTA) and differential scanning calorimetry (DSC) have now been widely used for the study of chemical reactions in all disciplines of chemistry. However, chemical reactions involving volatilizable substances cannot usually be studied with standard equipment. Mechanically crimped "hermetic" or "volatile" sample pans available from instrument manufacturers, e.g. Perkin-Elmer Corporation and Instrument Products Division of DuPont Company, withstand an internal pressure of only ca. 40 psi (276 KPa). Recent attempts to devise sealed sampled cells to extend the pressure range included the use of threaded metal cells[1], bonded aluminum pans[2], blown flint glass ampoules[3], aluminum cylinders with PTFE plugs[4, 5], and stainless steel cells resistance-welded by capacitor discharge[6], adaptable to the Perkin-Elmer DSC, and sealed glass tubes[7, 8] and sealed glass ampoules[9] adaptable to the DuPont Calorimeter Cell. Our experience with the above approaches showed variable successes and some inadequacies. The present work describes a modification of our sealed ampoule technique[9] for routine adaptation to the DSC Cell of the DuPont 990 Thermal Analysis System. A sample introduction device to facilitate analysis of reaction products after calorimetric measurements will also be discussed.

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## EXPERIMENTAL

The glass ampoule used and the sealing technique have been described previously[9]. Such a sealed sample container has been found to withstand an internal pressure of 1800 psi (12,420 kPa), and is suited as a micro-reactor to study most chemical reactions. In order to adapt such ampoules to a DuPont DSC cell, schematically shown in Fig. 1(B), an ampoule holder made from silver or aluminum metal as shown in Fig. 1(A) is used. The ampoules, quite reproducible in weight and dimensions, are disposable. Calibration and operation of the cell are essentially the same as those for normal DSC. Because of the height of the ampoule holder, a silver lid [1.5 in. (3.81 cm) diameter × 0.05 in. (0.127 cm)] is placed on the top of the heater block to replace the original lid in the DSC cell. A similar approach has been reported by Wendlandt[10], using an aluminum holder for capillaries to handle corrosive samples in a Perkin-Elmer DSC instrument.
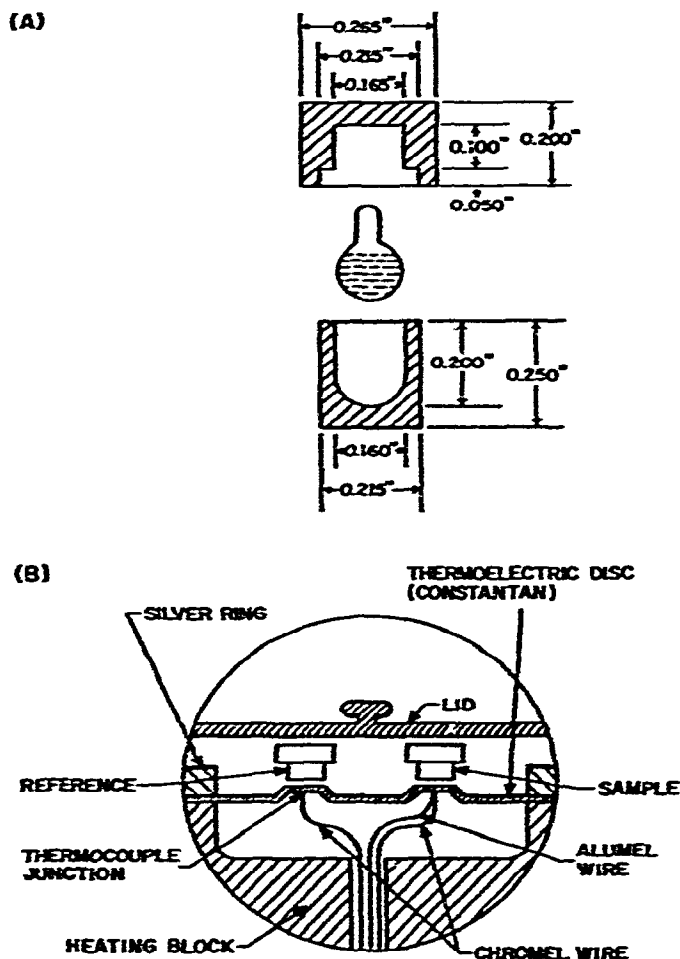
(A)

(B)

Fig. 1. Sealed ampoule DSC. (A) Glass ampoule and ampoule holder. (B) Schematic diagram of DSC cell.
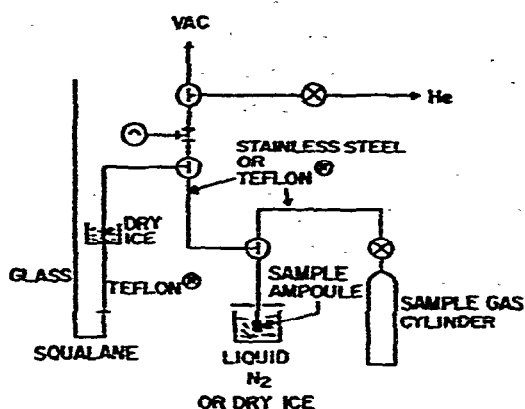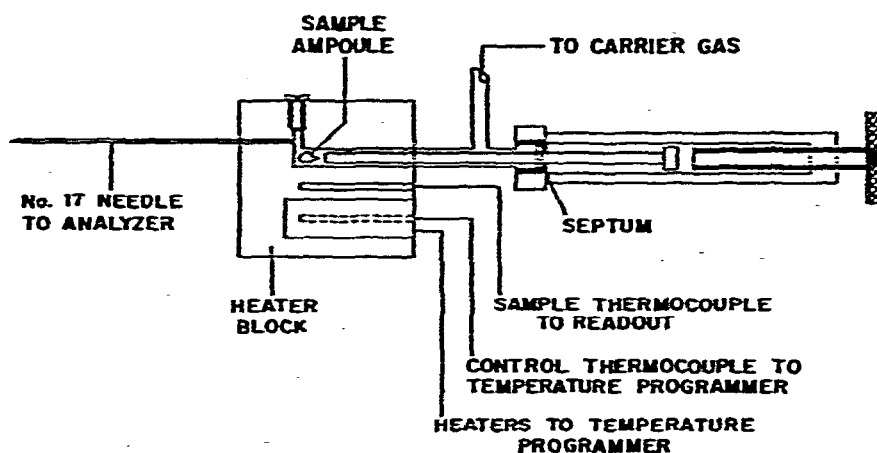
Fig. 2. Gas metering and transportation device.



Fig. 3. Controlled heating device for sample introduction.

Liquid or solid samples can be introduced into the ampoule by a syringe. For gaseous samples, a metering and transportation device shown in Fig. 2 is most useful. The device can be evacuated and filled with inert gas such as helium or the gas to be sampled. A squalane manometer is used to estimate the amount of gas condensed into the ampoule. Squalane is easily frozen by dry ice to facilitate evacuation or other manipulations. Tubing made of Teflon* FEP fluorocarbon resin is used for some sections of the transportation line to permit use of corrosive gases.

After DSC studies, the reaction products or unreacted sample in the ampoule can be conveniently introduced into other instruments for analysis by a device shown in Fig. 3. This controlled heating device is a very versatile tool, mainly for studying thermal reactions, the construction and the applications of which will be discussed elsewhere. In the present use, the ampoule is placed in the heater block, heated to the highest temperature during the DSC studies, and then crushed by turning the screw to release the volatile products into the analyzer. The heater block is connected to the

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* DuPont registered trademark.

analyzer by inserting the needle through the septum of the analyzer inlet such as the injection port of a gas chromatograph. Of course, the reaction products can also be produced by simulating the heating conditions in the heater block without going through DSC operation.

A F&M 810 research gas chromatograph (Hewlett Packard Co., Avondale, Pa.), a Perkin-Elmer Model 457 infrared spectrophotometer (Perkin-Elmer Corp., Norwalk, Conn.), and a DuPont Model 21-104 mass spectrometer (DuPont Co., Wilmington, De.) were used for analyses of the reaction products.

RESULTS AND DISCUSSION

Information on the thermal stability of a volatilizable substance is frequently needed for new product development or process design, but cannot be obtained by typical DTA/DSC or thermogravimetry (TG). The present sealed ampoule technique readily provides such an information. For example, DTA of a perfluorodisulfone, $CF_3CF_2SO_2(CF_2)_6SO_2CF_2CF_3$ in an open capillary showed a melting peak at 58°C and a boiling peak at 232°C as shown in Fig. 4. Decomposition of the sample cannot be reached before evaporation. By the sealed ampoule technique, the sample showed an exothermic decomposition peak at 308°C without boiling. The onset temperature of 265°C is a measure of the thermal stability of this material. If desired, the heat of decomposition can be simultaneously obtained. The decomposition products in the ampoule can also be identified by other analytical techniques through the use of the heater device shown in Fig. 3.

The use of sealed ampoule calorimetry for the determination of heats of polymerization has been demonstrated previously by employing the DuPont calorimeter cell[9]. This can now be performed with the DuPont 990 system equipped with a
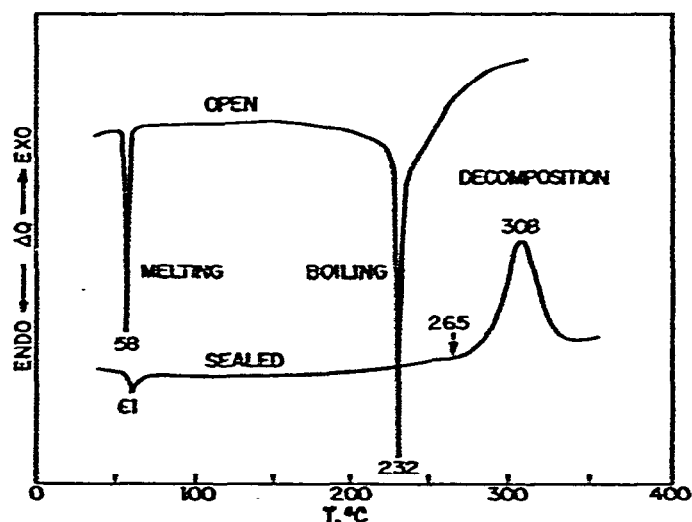


Fig. 4. DTA of a perfluorodisulfone. Open, DuPont DTA cell, 4.0 mg sample in a 2 mm capillary. Sealed, DuPont DSC cell, 3.5 mg sample in ampoule. Heating rate, 15°C/min.
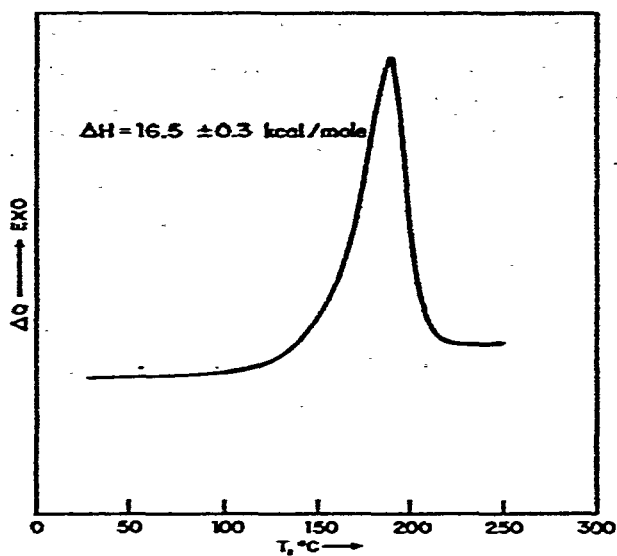
Fig. 5. DSC study of styrene polymerization. 9.8 mg Styrene containing 0.46% di-*tert*-butyl peroxide; heating rate, 2°C/min.; reference, empty sealed ampoule.
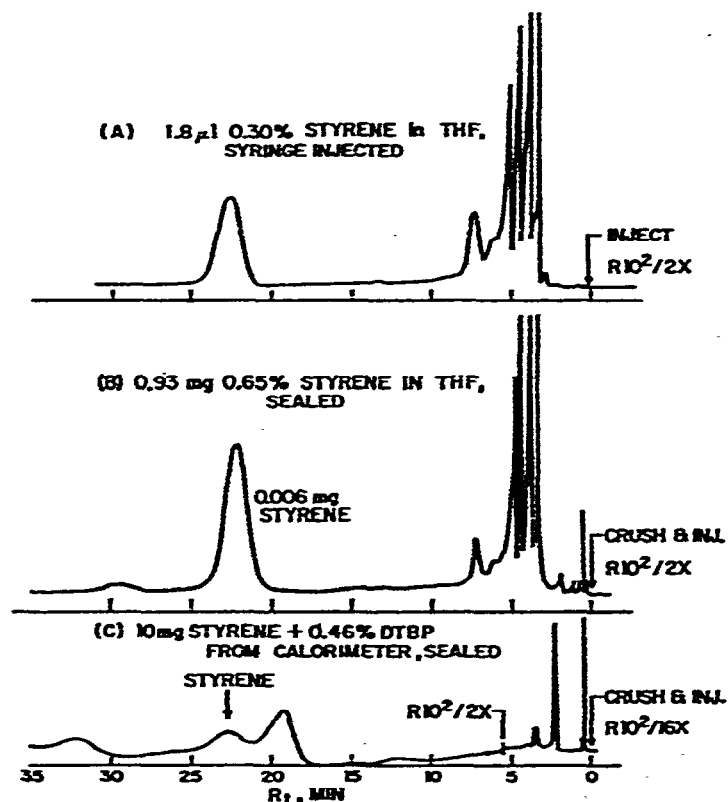


Fig. 6. GC analysis of residual styrene. 9 ft. × 1/8 in. O.D. stainless steel column of 50/80-mesh Porapak Q; injection port, 300°C; flame ionization detector, 330°C; helium flow, 30 ml/min at an inlet pressure of 100 psig; column temperature, 200°C; sample introduction block temperature, 220°C.

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DSC cell. A typical scan is shown in Fig. 5 for the polymerization of styrene. Calibration of the instrument is based on the heats of fusion of pure materials such as mercury (Reliable Chemical Co., St. Louis, Mo.), gallium (Reliable Chemical Co.), stearic acid (Applied Science Laboratories, State College, Pa.), indium (Reliable Chemical Co.), tin (National Bureau of Standards, Washington, D.C.), lead (National Bureau of Standards), and zinc (National Bureau of Standards). Heat of polymerization values of 16.5 $\pm$ 0.3 cal/g were obtained. The residual monomer content was determined by crushing the ampoule in the heater block shown in Fig. 3 and analysis of the evolved styrene by gas chromatography. A typical GC scan is shown in Fig. 6(C), and compared with scans obtained by direct syringe injection of a styrene solution in tetrahydrofuran shown in Fig. 6(A), and sealed ampoule injection of a standard
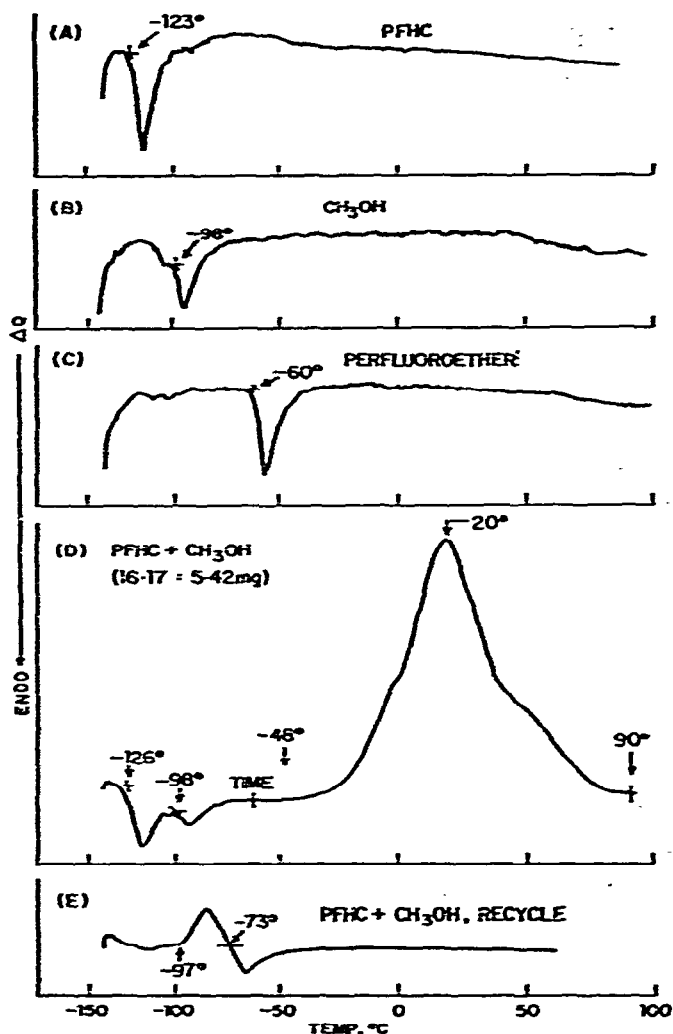


Fig. 7. DSC study of PFHC–methanol reaction. Heating rate, 10°C/min; reference, empty sealed ampoule.

solution for calibration shown in Fig. 6(B). Since the residual styrene content is far less than 1%, no correction of the heat values is necessary.

Many organic reactions can be investigated by DTA/DSC with the aid of sealed ampoules[8]. This capability can be further illustrated by a reaction between a gas, an unsaturated perfluorohydrocarbon (PFHC), and a volatile liquid, methanol. Alcohols are known to add to the double bond of perfluoroolefins to form ethers[11]. Thus PFHC reacts with methanol to form a perfluoroether. In the present study, a weighed amount of methanol was first loaded into the ampoule, and then the metering device shown in Fig. 2 was used to add various amounts of PFHC. As shown in Fig. 7(D), the reaction occurred exothermally in the temperature range from −50 to +90°C. The melting points of PFHC, methanol, and the product ether were −123, −98, and −60°C, respectively [Fig. 7(A)–(C)]. The heat of reaction was measured from the peak area recorded on a time base as indicated on the scan in Fig. 7(D). Heats of fusion of pure materials were used for calibration as described in the preceeding section. Measurements made with various mole ratios of PFHC and methanol indicated the heat of reaction to increase with increasing excess of methanol and level off to a value of 30 kcal/mole (126 kJ/mole) of PFHC in the range of 10-fold excess of methanol (Fig. 8). Still larger excess of methanol resulted in gradual decrease in the heat values, presumably due to heat absorption of the solvent.

The reaction products were analyzed by GC with the aid of the ampoule crushing device shown in Fig. 3. A 20 ft. × 1/8 in. O.D. stainless steel column of 10% Carbowax 1500 on 80/100 mesh Chromosorb P provides good separation among PFHC, methanol, and the ether product. Preliminary results showed significant amounts of PFHC unreacted even with a large excess of methanol. Later, infrared and mass spectrometric analyses of the reaction products by crushing the ampoule directly into a 10 cm infrared gas cell and the mass spectrometer inlet showed the presence of perfluorobutene-2 (PFB-2) which was not separated from PFHC by this column. Successful resolution of PFHC and PFB-2 in the presence of large amounts of methanol and the fluoroether was achieved by using a 10 ft. × 1/8 in. O.D. stainless steel column packed with 80/100 mesh Porapak N in series with the above Carbowax column. Typical GC scans are shown in Fig. 9. Essentially complete consumption of PFHC resulted from the use of more than 10-fold excess of methanol. Thus, no
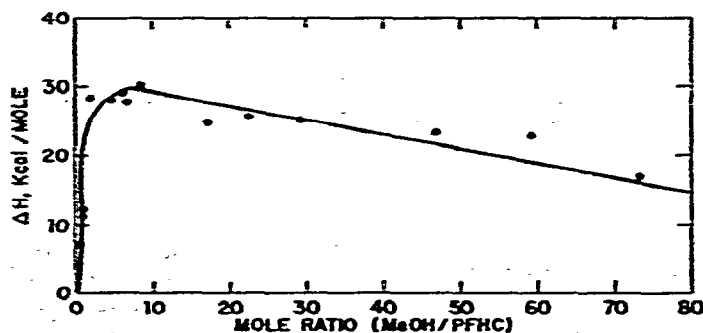


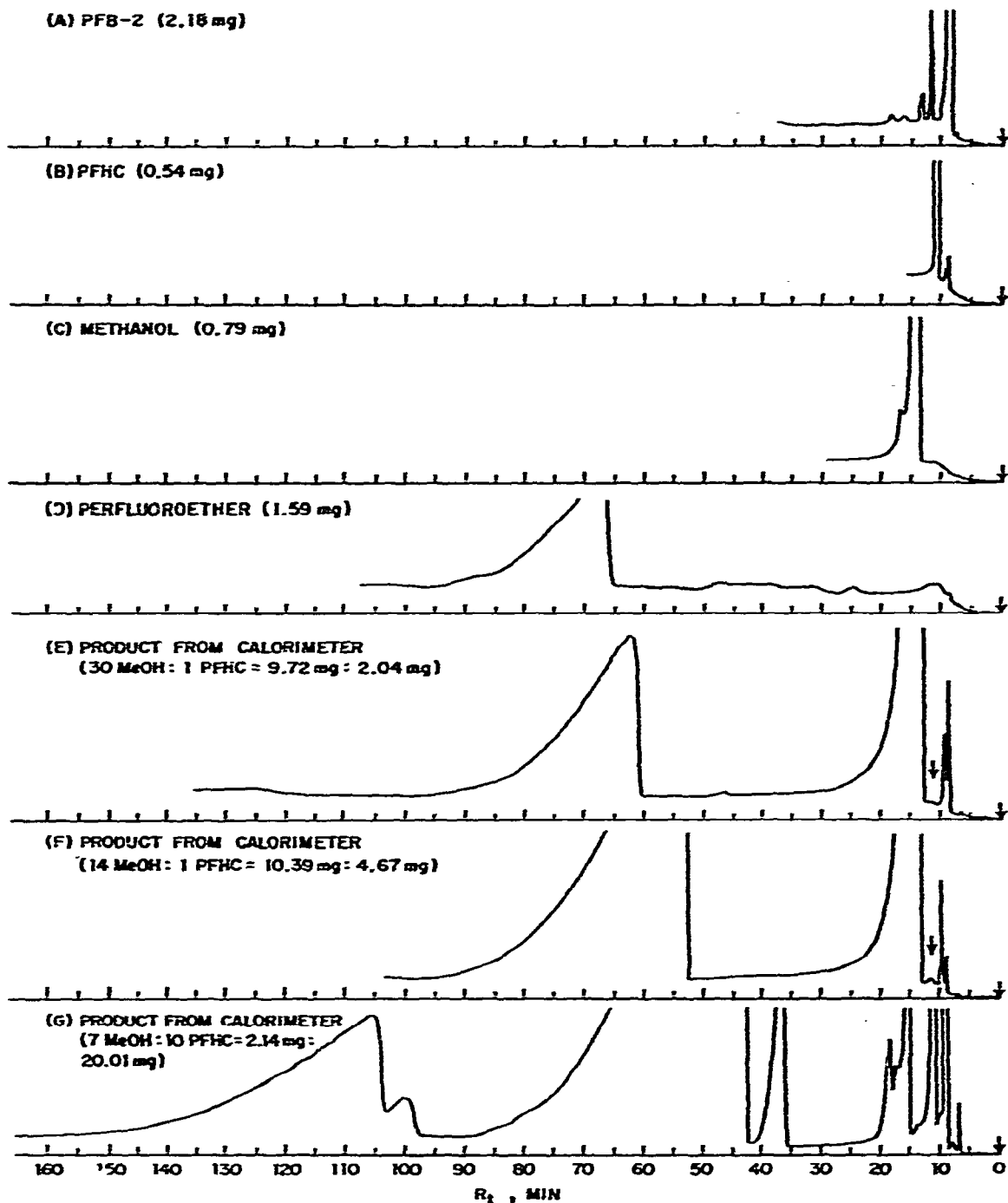Fig. 8. Heat of PFHC–methanol reaction.

Fig. 9. GC of PFHC–methanol reaction product. 20 ft. × 1/8 in. O.D. stainless steel column of 10% Carbowax 1500 on 80/100-mesh Chromosorb P + 10 ft. × 1/8 in. O.D. stainless steel column of 80/100-mesh Porapak N; injection port, 130°C; flame ionization detector, 315°C; helium flow, 30 ml/min at an inlet pressure of 100 psig; column temperature, from 70°C to 130°C at 6°C/min; sample introduction block temperature, 130°C.

correction of the heat of reaction was necessary if a large excess of methanol was used.

In summary, I have described a simple method to adapt a sealed ampoule technique to a commercial DSC instrument for routine calorimetric studies of chemical reactions involving volatilizable substances. A unique controlled heating device has also been shown to be useful in introducing the reaction products to other instruments for analyses so that all analytical results can be correlated on the basis of identical thermal history.

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