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A HIGH PRESSURE DIFFERENTIAL THERMAL ANALYSIS APPARATUS*

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ABSTRACT

A high pressure differential thermal analysis apparatus is described which is capable of operation in the pressure range from 1–600 atm of nitrogen gas and at temperatures from 25 to 500°C. Use of the apparatus is illustrated by the deaquation reactions of $CuCl_2 \cdot 2H_2O$ and $CoSO_4 \cdot 7H_2O$ at pressures from 1 to 69 atm.

INTRODUCTION

High pressure differential thermal analysis (DTA) equipment may be broadly classed into two categories—the first type includes equipment in which the pressure is transmitted to the sample by means of a piston in direct contact with the sample or by hydrostatic pressure. This type of apparatus was used to study liquid phase organic reactions at pressures up to 10 Kbar[1] and also polyethylene transformations at pressures of 5 Kbar[2]. Using a closed system at high hydrostatic pressures, the fusion reactions in the system, CaO–$Ca(OH)_2$–Ca_2SiO_4[3], where studied. The second type of equipment is that in which the pressure is developed in the system by means of an external compressed gas reservoir. One such apparatus, usable at pressures up to 28 atm, featured continuous gas analysis[4]. Other instruments have been described for reduction rate studies of a NiO–Al_2O_3 catalyst at pressures up to 100 atm[5]: shrinkage of leather at pressures to 10 atm[6]; characterization of thermosetting resins[7]; reduction of dinitrotoluene from 1 to 200 atm[8]; and the decomposition of explosives and propellants under controlled atmospheres to 7 atm[9]. The change in the melting point of diopside[10] and the oxidation of several hydrocarbons[11] were also studied using high pressure DTA techniques. Levy *et al.*[12] and Locke[13] have described commercially available high pressure DSC (differential scanning calorimetry) and DTA sample holders and furnaces. The Levy system[12] can be used to a maximum cell pressure of 67 atm and a maximum temperature of 650°C, while the Locke system[13] has a high pressure maximum of 200 atm at a maximum temperature of 500°C.

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The high pressure DTA apparatus described here was constructed for the investigation of metal salt hydrate systems and is capable of operation to a maximum pressure of 600 atm in the temperature range from 25 to 500°C.

EXPERIMENTAL

Description of apparatus

A schematic diagram of the apparatus employed is illustrated in Fig. 1. It consisted of a high pressure DTA cell and enclosure (A) complete with relief valve (D), pressure gauge (F), a furnace temperature programmer (B) and the DuPont Model 900 Recording Module (C).

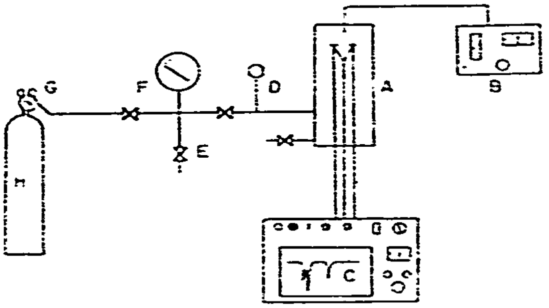


Fig. 1. Schematic diagram of the differential thermal analysis apparatus. A, high pressure DTA cell; B, T & T Controls Company Model No. TPC-2000 temperature programmer; C, DuPont Model 900 Recording Module; D, relief valve; E, valve; F, pressure gauge; G, gas pressure regulator; H, gas cylinder.

The high pressure DTA cell is shown in Fig. 2. It consisted of two 104 mm o.d. cylindrical segments of type 316 stainless steel secured together with six stainless steel bolts, each 13 mm in diameter. The upper portion of the enclosure (A) contained a 26 mm i.d. furnace housed in an insulated body. A threaded opening was provided at the top of the chamber for the heater wire entry through a Conax high pressure connector. The gas tight seal between the upper portion of the chamber and the base (G) was obtained by the use of a Buna-N O-ring (F) contained in a groove cut in the base. The base contained two threaded openings for high pressure gas inlet–outlet fittings (I) and a Conax wire connector (H) for the thermocouple wires. The sample probe (D) consisted of a 5 mm in diameter four-holed ceramic tube containing the differential thermocouple and furnace thermocouple wires. The reference [illegible] sample containers consisted of 1 mm by 2 mm in diameter platinum cups welded t[illegible] thermojunctions of the thermocouples. The top of the probe was enclosed by a removable machined aluminum cap to insure even heat distribution to the sample. The furnace design is the same as that previously described[14].

Operation of apparatus

For all pressures the operating procedure was basically the same and consisted of the following: From 5 to 20 milligrams of a 100–200 mesh powdered sample was

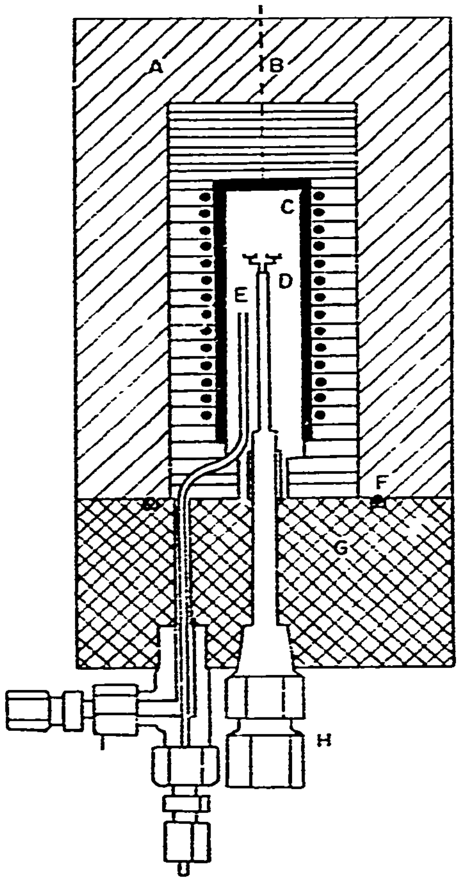


Fig. 2. Schematic diagram of high pressure DTA cell. A, furnace chamber; B, high pressure connectors for furnace wires and thermocouples; C, furnace; D, DTA sample and reference holders; E, gas outlet tube; F, Buna-N O-ring; G, base plate; H, Conax connector for thermocouple wires; I, gas inlet–outlet connector.

placed in the sample chamber and lightly packed by tamping; a similar amount of Al_2O_3 was placed in the reference holder. The outer aluminum cap was then placed over the probe and the furnace body bolted in place to the base plate. The enclosure was then purged with the pressurizing gas and the system pressure adjusted to a predetermined level. Once the system pressure was stabilized, the furnace heating cycle was begun and the differential temperature curve was recorded, as a function of time or temperature, on the Y-axis of the X-Y recorder. A heating rate of 10°C min^{-1} was normally employed. Due to the change of pressure due to the temperature increase, a slight flow of gas was passed through the chamber to maintain a constant pressure in the system.

Calibration and response

The system was calibrated using indium metal; it was found that a 12 mg sample gave a full scale deflection on the recorder. The fusion temperature was found to change by no more than ± 0.4 °C during the repetitive runs. Response of the ΔT thermocouples were found to change inversely with the pressure. The results, as shown in Fig. 3, indicate that as the system pressure increases, the ΔT output signal decreases. The peak area, normalized to the area at one atm, shows that at 126 atm of nitrogen. the area is 56% of the area at one atm of nitrogen. The two curve peaks shown, (A) and (B), are for a sample of indium at 126 atm (A) and one atm of nitrogen (B), respectively. Both the area of curves and the peak heights decrease with an increase in pressure.

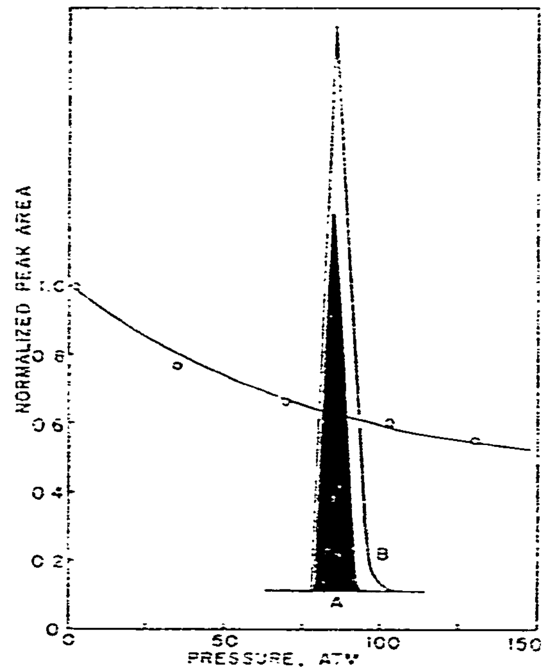


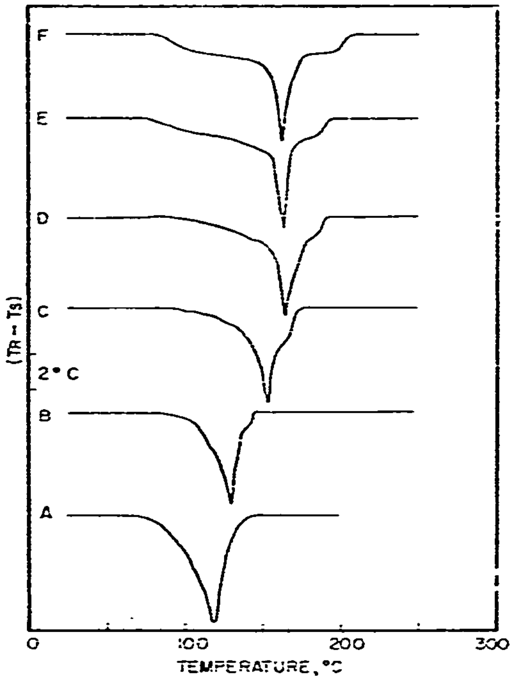
Fig. 3. Change in ΔT output as a function of pressure. Typical DTA curve peaks at 126 atm (A) and 1 atm (B) for a sample of indium; temperature scale not indicated.

RESULTS AND DISCUSSION

Application to metal salt hydrate systems

To illustrate the use of the apparatus in the investigation of metal salt hydrate systems, the DTA curves of $CuCl_2 \cdot 2H_2O$ and $CoSO_4 \cdot 7H_2O$ at different pressures are illustrated in Figs. 4 and 5, respectively.

The DTA curve for $CuCl_2 \cdot 2H_2O$ at one atm of pressure consists of a single endothermic peak at a ΔT minimum temperature of about 120 °C. As the system pressure increases, several changes in the curve are evident. The most prominent change in the curves is the shift in peak temperatures to higher values; this occurs to an extent of about 45 °C on going from one to 69 atm but remains relatively



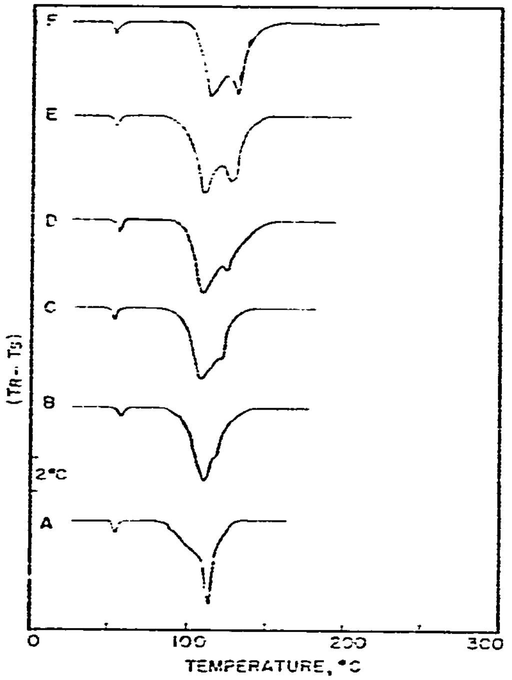


Fig. 4 (left). DTA curves of $CuCl_2 \cdot 2H_2O$ at various nitrogen pressures. A, 1 atm; B, 27 atm; C, 35 atm; D, 69 atm; E, 103 atm; F, 137 atm.

Fig. 5 (right). DTA curves of $CoSO_4 \cdot 7H_2O$ at various nitrogen pressures. A, 1 atm; B, 15 atm; C, 21 atm; D, 28 atm; E, 35 atm; F, 69 atm.

constant above the latter value (up to 137 atm). The second feature is the increase in the prepeak baseline deviation as the pressure is increased. It should be noticed that the initial ΔT baseline deviation is independent of pressure but the ΔT peak temperature is not; hence, the prepeak baseline deviation increases with an increase in pressure.

A somewhat different type of behavior is exhibited by $CoSO_4 \cdot 7H_2O$ (Fig. 5). At one atm of pressure, two endothermic peaks are observed in the DTA curve; a small endothermic peak at a ΔT minimum temperature of 55°C and a large endothermic peak at a ΔT minimum of 115°C. As the pressure is increased, the 55°C peak remains essentially unchanged indicating that it is some type of a phase transition that is pressure independent. The 115°C peak, however, splits into two peaks as the pressure is increased to 69 atm. This peak splitting is thought to be due to the two reactions: (a) deaquation and the evolution of a liquid water phase; and (B) vaporization of the liquid water phase. The first step is independent of pressure while the second step is pressure dependent; this is the behavior that is observed in the curves.

CONCLUSIONS

The examples indicate the use of the DTA apparatus. It is capable of operation up to 600 atm in gases which are noncorrosive to the thermocouple junctions and furnace material. The use of this technique at elevated pressures has revealed new information on metal salt hydrate systems. It also appears possible to determine the heat of deaquation and vaporization in those systems for which good peak resolution is not generally obtained.

ACKNOWLEDGEMENT

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