

Note

A modified DTA cell to study small-scale reactions

A. DYER* AND T. R. NOWELL

Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT (Gt. Britain)

(Received 14 December 1977)

A modification to a standard Du-Pont 900 DTA cell has been developed to study heterogeneous systems in which the ratio of liquid to solid is high. Crystallization processes producing various solid phases from reaction liquors or melts were monitored by heat content change by use of a small-scale reaction vessel accommodated in the heating block of a standard DTA apparatus. The modified apparatus required a calibration procedure and the heat of fusion (ΔH_f) of benzoic acid was suitable for the determination of a calibration coefficient (E).

EXPERIMENTAL

A Du-Pont 900 standard DTA cell (cat. No. 900 270) was altered as follows. The sample and reference positions of a silver heating block, for the DTA cell, were drilled to a depth of 325 mm and a diameter of 4.1 mm [Fig. 1(a)]. A re-usable reaction cell was made from Pyrex glass, and had the following dimensions: length 40 mm, internal diameter 3 mm, and external diameter 4 mm. It was sealed by a tight-fitting removable fluorinated rubber plug. A hole (1/1000 in.) drilled through the vertical centre of the plug provided access for the sample thermocouple whilst retaining a satisfactory seal. The cell was provided with a curved side-arm to which was fitted a female B5/13 Quick-Fit ground glass joint. A miniature Liebig condenser, of Pyrex glass, was fitted to the side-arm via the B5/13 joint. The condenser was cooled by water from a closed reservoir. The water was circulated by peristaltic pump through small-bore PVC tubing [Fig. 1(b)]. A reference cell was constructed, of similar materials, with a sealed thermocouple but without the side-arm and condenser. The sample and reference cells were placed in the drilled heating block and covered with a removable aluminium foil shield (Fig. 2) to minimise heat losses from the cells. The whole assembly was encased in a specially designed bell jar provided with holes to carry the PVC tubing to and from the condenser. The assembly is shown in Fig. 2.

* To whom correspondence should be addressed.

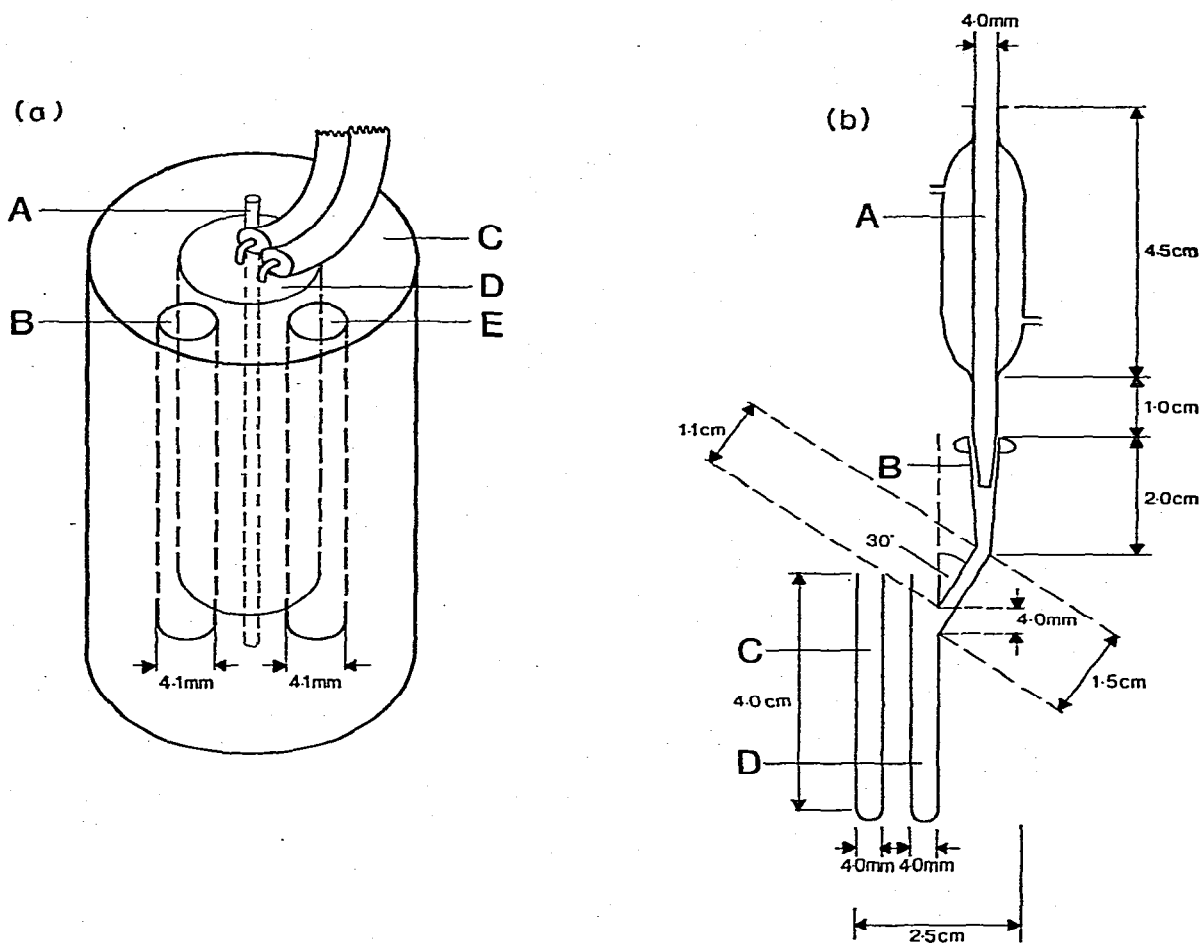


Fig. 1. (a) Modified standard silver heating block. A, control thermocouple; B, modified reference thermocouple well; C, heating block; D, heater; E, modified sample thermocouple well. (b) Position and design of condenser unit. A, condenser unit; B, B5/13 cone and socket; C, modified reference holder; D, modified sample holder.

RECORDING OF RESULTS

Experimental $T/\Delta T$ results were recorded directly on the X - Y recorder of the thermal analyser. An auxiliary Washington curvilinear amplifiable recorder (400 MDI) linked to the output circuit of the thermal analyser monitored time or temperature as needed. The experimental procedure followed the standard instructions for both dynamic and isothermal experiments.

CALIBRATION

Analyses of Analar benzoic acid samples were carried out using the modified cell with the thermal analyser operating in the DSC mode to record the results on the X - Y recorder of the instrument. The reference holder contained α -alumina. An

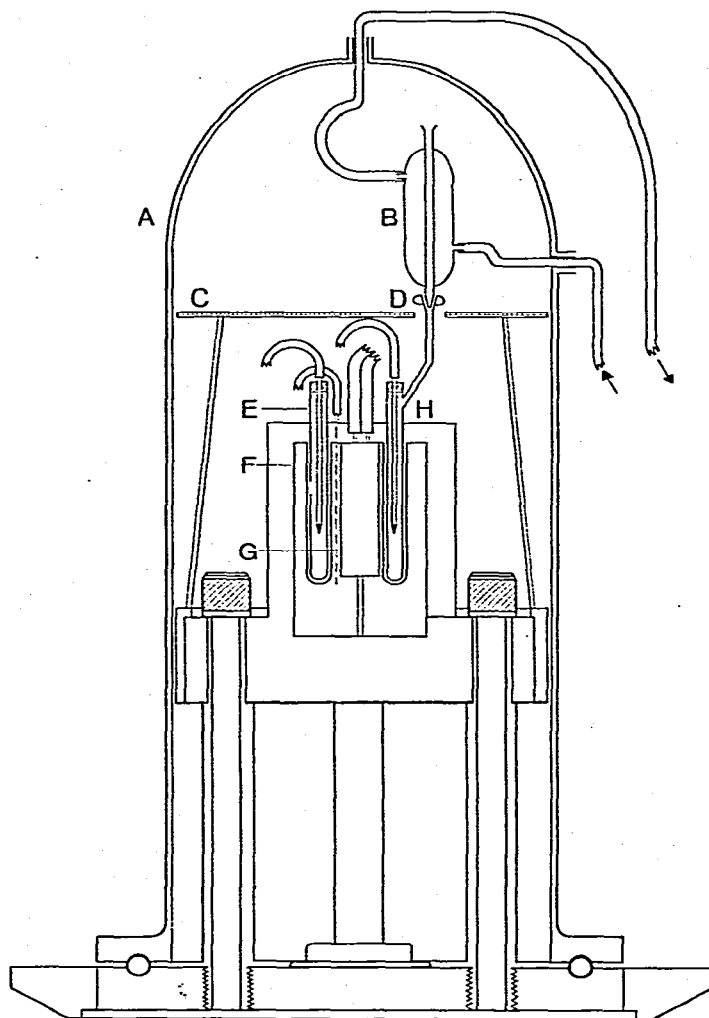


Fig. 2. Modified Du-Pont standard cell showing complete assembly. A, modified bell jar; B, condenser fitted with small bore PVC tubing; D, B5/13 joint; E, reference and thermocouple with fluorinated rubber seal; F, heating block; G, control thermocouple; H, sample and thermocouple with fluorinated rubber seal.

example of the trace recorded is shown in Fig. 3. The peak area was determined by weighing and a calibration coefficient (E) obtained from¹

$$E = \Delta H M \alpha / A \Delta T_s T_s \quad (1)$$

where, ΔH = latent heat of fusion of benzoic acid² (mcal mg^{-1}); M = sample mass (mg); α = heating rate ($^{\circ}\text{C min}^{-1}$); A = peak area (in.^2); ΔT_s = Y -axis sensitivity ($^{\circ}\text{C in.}^{-1}$); T_s = X -axis sensitivity ($^{\circ}\text{C in.}^{-1}$).

Typical calculation

$$\Delta H = 33.89 \text{ mcal mg}^{-1}$$

$$M = 113.55 \text{ mg}$$

$$\alpha = 5.0^{\circ}\text{C min}^{-1}$$

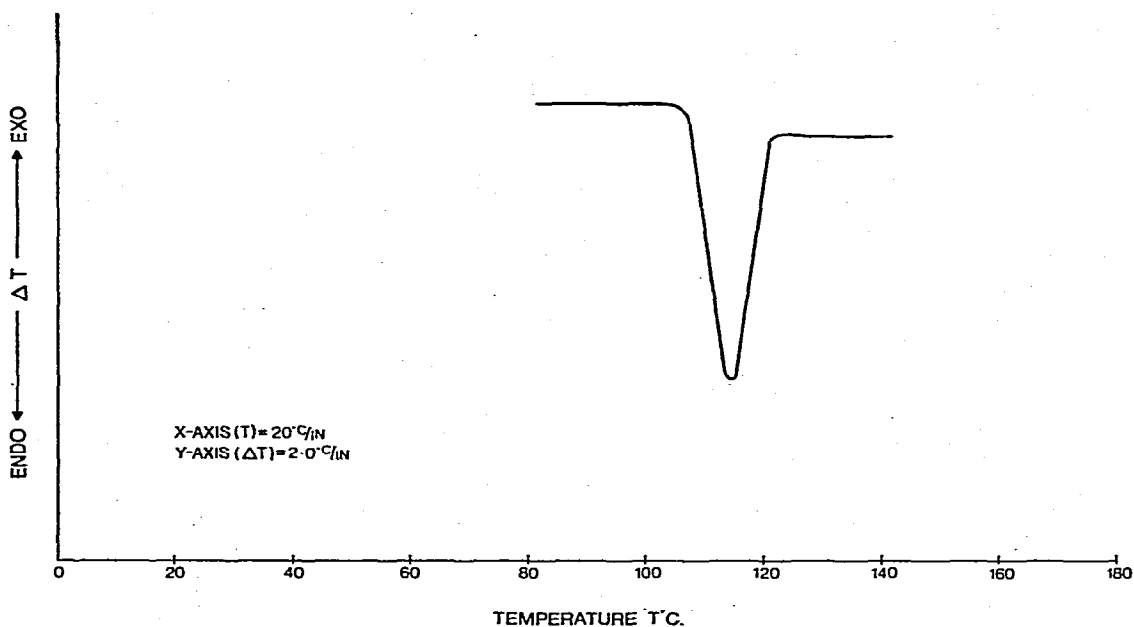


Fig. 3. Determination of calibration coefficient.

$$A = 0.7574 \text{ in.}^2$$

$$\Delta T_s = 2.0^\circ\text{C in.}^{-1}$$

$$T_s = 20.0^\circ\text{C in.}^{-1}$$

$$E = 639 \text{ mcal K}^{-1} \text{ min}^{-1}$$

An average of three determinations gave $E = 642 \pm 3 \text{ mcal K}^{-1} \text{ min}^{-1}$.

CONCLUSION

The Du-Pont 900 was compatible with the modification described. After calibration the instrument has proved valuable in the study of crystallization phenomena.

ACKNOWLEDGEMENTS

We thank Dr. F. Wilburn (Pilkington Bros. Ltd.) for his advice on the use of an auxiliary recorder.

REFERENCES

- 1 Du-Pont Instruments, *Instruction Manual 900 Thermal Analyser and Modules*, Sect. 9, 1968.
- 2 *Handbook of Chemistry and Physics*, R.C. Weast, 55th edn., 1974/1975, p. C718.