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A NEW MEMBRANE CELL FOR THE DETERMINATION OF HEATS OF IMMERSION USING THE SETARAM C–80 MICROCALORIMETER

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A novel experimental cell for the determination of heats of immersion has been designed and constructed for use with a Setaram C–80 microcalorimeter. The cell contains a replaceable aluminium membrane which is used to separate the immersion liquid from the degassed solid. A membrane system considerably eases the problems associated with sample preparation. The construction and features of the cell which are essential for successful operation are discussed. Calibration experiments using *n*-heptane have been carried out. The heat associated with events such as membrane breaking and liquid evaporation has been minimised and represents around 1% of the heat changes involved in a typical immersion experiment.

The heat associated with immersion of a solid in a liquid can be used to characterise a number of surface properties [1]. These include (i) the chemical nature of the surface eg its polarity or (ii) the microporosity of the material which can be determined using different size molecules to probe the pore structure.

To determine a heat of immersion it is necessary to bring degassed solid into contact with degassed liquid inside a calorimeter cell. Conventionally this has been achieved by containing the solid within a thin glass bulb which is then broken under the surface of the liquid by a plunger operated from outside the cell [2]. In addition to the heat of immersion, various other thermal effects are observed which need to be independently determined and then corrected for. By careful experimental design these effects can be minimised or at least made as reproducible as possible. The various effects have been previously summarised by Rouquerol [3] and Everett [4]:

Mechanical Heat – If a plunger is used to break the glass bulb then, to maintain vacuum, it must enter the cell through a gas tight o-ring seal. Movement of the plunger can then lead to frictional heat being generated. One method of overcoming this is to locate the o-ring seal remote from the calorimeter cell [5]. Another approach, which removes the need for the plunger completely [4] involves fitting the glass ampoule into a metal holder which is then held in a raised position by a permenent magnet external to the cell. Raising this magnet causes the ampoule to drop and break against the bottom of the cell.

Breaking the glass ampoule itself may also involve significant heat changes.

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Everett et al.[4] reduced this to a minimum by employing capillary tipped ampoules. Breaking this fine tip evolved as little as 0.2 mJ of heat. However, to construct and seal these thin glass ampoules reproducibly can be both technically difficult and time consuming. An alternative approach is to use metal foil membranes to separate the solid from the liquid [6]. It is this principle which is utilised in the cell described in this paper.

Evaporation and Pressure Changes – The immersing liquid will evaporate to fill the evacuated free space in the chamber containing the solid. In a sealed system additional endothermic contributions come from irreversible expansion of any gas in the cell, and the consequent decompression of the liquid. These effects cannot be eliminated from the measurement, but it is important to make them as reproducible as possible by ensuring that the cell is tightly sealed to prevent ingress of air or loss of liquid. Everett et al.have obtained a precision of ca ± 3% in the correction factor for most volatile solvents [4].

The amount of liquid which evaporates and the size of any pressure change are dependent on the volumes of liquid and solid used. In practice, the volume of liquid is kept constant, therefore it is necessary to obtain a correction factor as a function of the evacuated free in the chamber containing the solid.

Description of the immersion cell

The cell, together with the degassing unit, is shown in Figure 1. It is composed of two chambers, one for the liquid, one for the solid, separated by an aluminium membrane. Epoxy resin is used to bond the membrane to a stainless steel carrier. To evacuate the chamber containing the solid, the cell is first inverted, to prevent solid blocking the needle valve, and then pushed into the degassing unit. The stainless steel needle valve is then opened and the solid evacuated. This valve is then closed under vacuum before removal of the cell from the degassing unit. The cell is similar in concept to one designed by Setaram, however the Setaram cell was not fully developed and is not commercially available [7]. Novel features are the method of holding the membrane, and the use of an all stainless steel needle valve to seal the chamber containing the degassed solid.

A needle is attached to a rod which passes through an o-ring seal in the cell ca 4 cm above the sensing thermocouples of the microcalorimeter. A movement of only 3 mm is necessary to pierce the membrane and allow liquid to flow into the evacuated chamber.

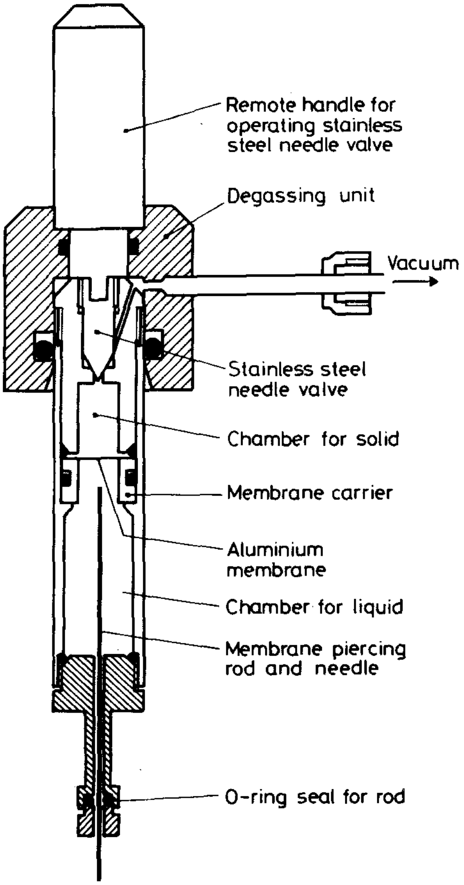

Fig. 1 – Heat of immersion cell mounted in degassing unit with needle valve closed.

Evaluation

Mechanical Heat – Movement of the rod generated no observable heat. The only mechanical heat which needs to be corrected for is the energy involved in breaking the membrane. This was determined five times using an air filled cell and was highly reproducible, albeit larger than from a glass capillary tipped ampoule; the mean value was –7.2 ± 0.5 mJ.

Evaporation and Pressure Changes – To assess the reproducibility of the correction factor required in a typical immersion experiment a series of calibrations was carried out using 2.0 ml of *n*-heptane as the liquid and various weights of inert glass spheres as the solid. *n*-heptane was chosen as a typical volatile liquid adsorbate. The heat observed as a function of evacuated free space, is shown in Figure 2. When working with a volatile solvent such as heptane, it is important to thermostat carefully the calorimeter, as even small changes in temperature (< 0.1°) can cause evaporation and condensation of solvent. These appear as cyclic perturbations of the baseline.

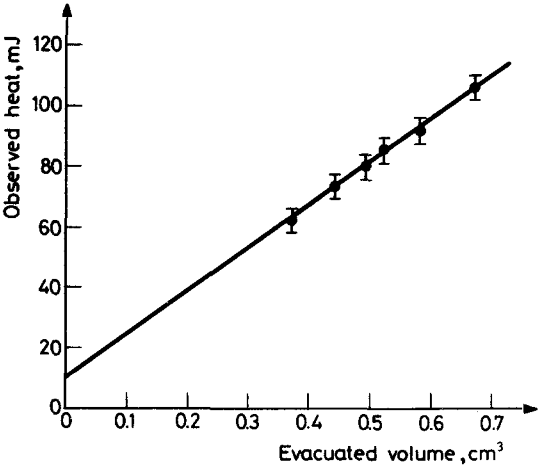

Fig. 2 – Calibration experiments for *n*-heptane.

The calibration curve obtained was a straight line of gradient 145 ± 5 mJ/cm^3. A surprising result is that the intercept is positive (endothermic) when it would be expected to be negative and equal to the energy of breaking the membrane (i.e.–7.2 mJ). This has also been observed for volatile liquids by Everett *et al.* [4] and, at present, there is no obvious explanation. However, since actual immersion experiments are carried out under similar conditions to the calibration runs, the experimentally determined intercept should be used.

For a typical heat of immersion of ca 100 mJ/m^2 [4] with 200 mg of solid of surface area 20 m^2 g^{-1} the uncertainty in the correction factor to be applied to the observed heat of ca 400 mJ amounts to ± 3.0 mJ, or around 1%. This compares with an uncertainty of ca ± 2.0 mJ obtained by Everett *et al.* [4] for *n*-heptane. Therefore the membrane cell combines the precision obtainable with glass ampoules with the ease of preparation of aluminium membranes.

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Zusammenfassung – Eine neue Messzelle zur Bestimmung von Immersionswärmen mit dem Setaram-Mikrokalorimeter C 80 wurde entwickelt und konstruiert. Die Zelle enthält eine austauschbare Aluminiummembran zur Trennung der Immersionsflüssigkeit von dem entgasten festen Adsorbens. Durch dieses Membransystem werden die Probleme mit der Probenvorbereitung wesentlich vereinfacht. Die Konstruktion und die für den Betrieb entscheidenden Merkmale der Zelle werden diskutiert. Eichversuche wurden mit *n*-Heptan durchgeführt. Die mit der Zerstörung der Membran und dem Verdampfen der Flüssigkeit verbundenen Wärmeeffekte wurden minimiert und betragen etwa 1% des Wärmeumsatzes bei einem typischen Immersionsexperiment.

РЕЗЮМЕ — Описана новейшая экспериментальная ячейка для определения теплот погружения и использование ее в сопряжении с микрокалориметром Сетарам С—80. Ячейка содержит заменяемую алюминиевую мембрану, используемую для разделения жидкости погружения от дегазированного твердого тела. Мембранная система значительно облегчает проблемы, связанные с получением образца. Обсуждены конструкционные и измерительные характеристики ячейка. Калибровочные измерения проведены с *н*-гептаном. Тепловые эффекты, обусловленные такими явлениями как разрыв мембраны и испарение жидкости, сведены до минимума и составляют около 1% всех тепловых изменений, наблюдаемых в типичном эксперименте погружения.