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RECENT DEVELOPMENTS IN MICRO SOLUTION CALORIMETRY

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ABSTRACT

A group of microcalorimetric vessels primarily designed for the dissolution of slightly soluble compounds in water is described. Gaseous and liquid solutes are injected into a flow of solvent and the measurements in these cases are automatized by means of microprocessors. The amount of solute used in each experiment is typically 0.4 ml and 0.5 μl for gases and liquids, respectively. In typical experiments with solids, 1 mg or less of the solute is used in each experiment.

INTRODUCTION

Since the late sixties a significant part of the work in our laboratory has been concerned with investigations of dissolution of simple organic compounds in water. To some extent measurements have also been made with other solvents. These studies have been undertaken primarily because of the need for data of this kind in connection with discussions of biochemical model systems. In particular our interest has been focused on the characterization of hydrophobic hydration, i.e., the interaction between hydrophobic groups and water.

Most of this work has been performed by use of precise "macro" solution calorimeters. However, for slightly soluble compounds - which naturally are of a particular interest in this connection - it has been necessary to develop more sensitive micro-calorimetric methods. Such techniques are also of general interest from the point of view that very small quantities of substances are used. In this report a group of microcalorimetric vessels designed for measurements of enthalpies of solution of slightly soluble gases, liquids and solids is briefly described.

GASES

Thermodynamic data for aqueous solutions of simple hydrophobic gases such as, for instance, argon and methane, have been of fundamental importance in discussions concerning hydrophobic phenomena (refs. 1, 2). However, until very recently such data in all cases were based solely on the results of solubility measurements. It was therefore felt important to carry out direct calorimetric

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measurements on such systems, in particular for the determination of heat capacity data. In cooperation with S. J. Gill, University of Colorado, we have recently developed two flow microcalorimetric vessels (ref.3) which are used with a twin heat conduction calorimeter developed some years ago (ref.4), cf. (ref.5).

In one approach constant flows of gas and solvent are brought together to form a steady-state system of gas dissolution. This method has very recently been further developed by Dec and Gill (ref.6) and has been used on rare gases and hydrocarbons (refs.7, 8). In a second method, the "batch" method, which we prefer to use (ref.9), a discrete quantity of gas is injected into the vessel where it is dissolved by the solvent flow. This method is described below. The experimental arrangement is shown schematically in Fig. 1.

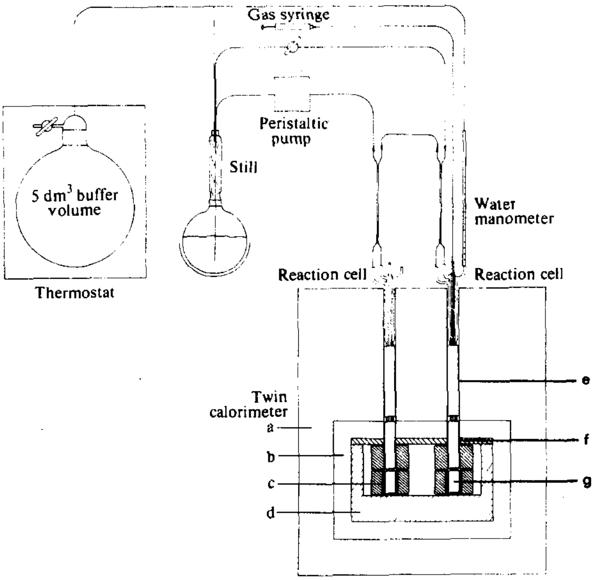

Fig. 1 Schematic view of instrumental arrangement in gas experiments. a, water thermostat; b, steel container; c, thermocouple plates; d, main heat sink; e, f, brass tubes; g, brass cup (dissolution region). From ref. 3.

The gas solution vessel, which has a rod-like shape, is made up of two concentric glass tubes and a brass cup which forms the dissolution region, g. The glass tubes form a counter-current heat exchange system which is fitted with two thermally conducting regions (e, f) made up of brass tubes. These are in thermal contact with the thermostatic bath and the calorimetric block, respectively. A section through the brass cup and the lower parts of the heat exchange system is shown in Fig. 2.

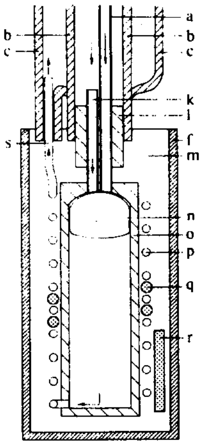

Fig. 2. Section through the gas solution region (g in Fig. 1). a, stainless-steel tube; b, c, concentric glass tubes; f, brass cup; k, stainless-steel tube; l, steel rod; m, Wood's-metal filling; n, gas bubble; o, steel dissolution vessel; p, steel tube; q, r, electrical-calibration heaters; s, solvent outlet. From ref. 3.

Gas is introduced through a hypodermic steel tube (not shown in Fig. 2) which is soldered to the syringe needle. The hypodermic tube is inserted into the steel tube, a, which is positioned in the center of the glass tubes. Gas-free solvent is sucked through the vessel by means of a peristaltic pump, flow rate about 40 ml/h.

The dissolution region (Fig. 2) consists of a stainless steel cylinder, o, which is imbedded in Wood's metal inside the brass cup, f. The gas bubble, n, will be slowly dissolved by the solvent flow. Before the solution reaches the outlet, s, it is thermally equilibrated by passing a steel tube spiral, p.

The inside of the gas syringe and the hypodermic needle are kept wet in order to ensure that the gas is saturated with solvent when it enters the dissolution region. The gas syringe is kept thermostated at 25 ^{0} C for all calorimetric temperatures. During the measurement the system is closed off from the atmosphere (see Fig. 1) in order to secure a constant pressure.

In a typical dissolution experiment, 0.2-0.4 ml of gas is added. Once the syringe has been charged, the measurements are performed automatically. Injections are controlled by a microprocessor which is also used to calculate the power-time integrals. Fig. 3 shows typical results from experiments where 0.4 ml of oxygen is dissolved in water at 25 ^{0}C.

The calculation of ΔH values is based on the measured gas pressure and the volume displaced by the syringe. Corrections are applied for enthalpy of condensation of water vapor and for viscous heating due to the presence of the gas bubble.

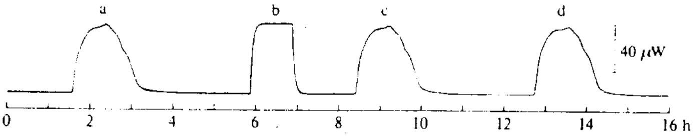

Fig. 3. Typical calorimetric curves from solution experiments with oxygen. From ref. 3.

The instrument is calibrated electrically but we make an extensive use of oxygen as a test substance (refs.3, 9). Our value for solution of oxygen in water at 298.15 K is $\Delta H = -(12.06 \pm 0.04)$ kJ mol^{-1} ($\pm 2\sigma$), which is in agreement with the value derived by Benson et al (refs.10), $\Delta H = -12.02$ kJ mol^{-1}, from their very careful solubility measurements.

We have recently reported enthalpy values determined with this instrument for solution in water of helium, neon, argon, krypton, xenon, methane, ethane, propane and 1-butane at 288.15, 298.15 and 308.15 K (ref.9). So far we have only used the method with water as solvent. However, we believe it can be used with any non-viscous solvent. In contrast to the steady-state method, the batch method can also be used with gas mixtures.

LIQUIDS

Some years ago we developed a flow-calorimetric vessel for the solution of hydrophobic liquids in water (ref.11). The instrument was used for the determination of $\Delta_{sol}H$ and $\Delta_{sol}C_p$ in water for several hydrocarbons (ref.12). Recently (ref.13) this vessel has been modified in order to avoid some possible sources of systematic errors. In addition, the instrument can now also be used for measurements of solution of small quantities of easily soluble liquids in water and in other not too viscous solvents. The same type of twin heat-conduction calorimeter as was used earlier (ref.11) and with the gas calorimeter (ref.3) has also been employed in this case and the general experimental arrangement has some similarities with that used with the gas calorimeter, see Fig. 4.

The calorimetric vessel consists of two concentric glass tubes which, like the gas instrument, have two heat-conducting regions. Below them there is a brass cup which is in thermal contact with the thermopiles. The cup contains a system of spiralized tubes which are embedded in Woods' metal. The spirals form the dissolution region. A section through the brass cup and the lower part of the heat exchange system is shown in Fig. 5.

During an experiment, a constant flow of gas-free solvent is sucked through the vessel by use of a peristaltic pump. A typical flow rate is 40 ml/h. The flow is thermostated during its passage down to the level of the brass cup. The flow is then carried into a thin-walled (0.1 mm) teflon tube positioned inside the stainless steel spiral.

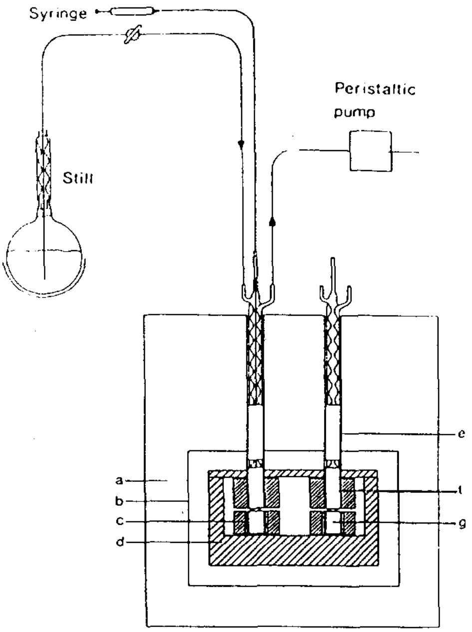

Fig. 4. Instrumental arrangement in experiments with liquid solutes: a, water thermostat; b, steel container; c, thermocouple plates; d, main heat sink; e, f, brass tubes; g, brass cup (dissolution region). From ref. 13.

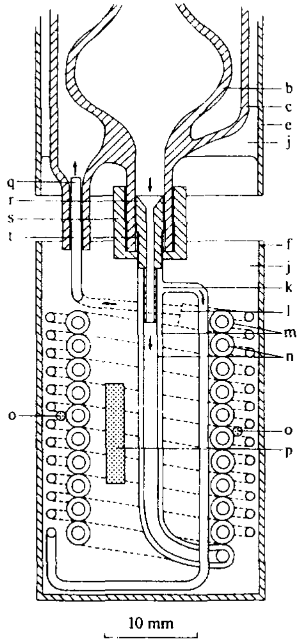

Fig. 5. Section through dissolution region in micro-calorimetric vessel for dissolution of liquids. b, c, concentric glass tubes; e, brass tube; f, brass cup containing the dissolution vessel; j, Wood's-metal filling; k, T-junction;

l, end of steel spiral; m, stainless-steel tube; n, Teflon tube; o, p, calibration heaters; q, connection to solvent outlet from the reaction vessel; r, nozzle; s, brass tube; t, tin-soldered connection between the nozzle and the stainless-steel tube. From ref. 13.

At the end of the spiral, l, the solvent flow will turn back through the annular space between the teflon and the steel tubes. Following the vertical part of the tubes, the flow passes through the T-junction, k, to the narrow steel tube spiral, i, and is delivered to the space between glass tubes at q.

The solute is introduced to the dissolution zone by means of a thin steel tube i.d. 0.15 mm, not shown in Fig. 4), fastened to a Hamilton 100 µl gas-tight syringe. Hydrophobic liquids will adhere to the teflon tube and form a thin film inside the teflon spiral. The solute will thus form a large contact area with the solvent (water) and an efficient dissolution process can take place. Typically, with slightly soluble solutes, 5 µl is added. For easily soluble compounds, similar stepwise additions of very small volumes can be made. Alternatively, for these compounds slow injections (ca 30 nl/s) can be made over longer periods of time. A very low and well-defined final concentration of the solute is then obtained. As for the gas calorimeter, the measurements are made automatically by use of a microprocessor.

It was found that with some volatile solutes a significant leakage can take place through the teflon seal of the syringe plunger. This could be overcome by applying a mercury seal in the syringe, see (ref.13). For easily soluble compounds, a small but significant diffusion can take place through the tip of the injection needle prior to the injection. This diffusion can be corrected for by performing a series of injections with different time increments between the injections, see (ref.13).

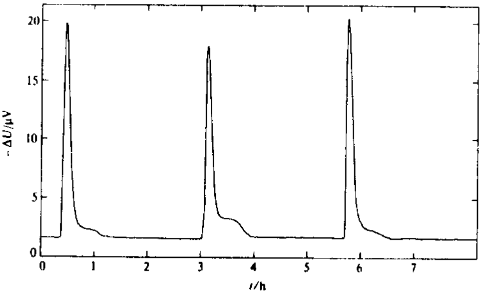

Fig. 6. Typical results for solution of benzene in water. Injection rate was about 30 nl/s and the injection time was 180 s. Water flow rate was 11 µl/s. From ref. 13.

The instrument can be calibrated electrically. However, we have found it to be more accurate to use a chemical calibration, e.g. the solution of 1-

propanol in water. Fig. 6 shows results of typical experiments with benzene.

The value obtained for benzene at 298.15 K is $\Delta H = 2.22 \pm 0.02$ kJ mol ($\pm 2\sigma$), which is slightly more endothermic than the value which we have reported earlier (ref.12), $\Delta H = 2.08 \pm 0.04$ kJ mol.

For easily soluble compounds the precision obtained is typically $\pm$ 0.05 kJ mol ($\pm 2\sigma$). The instrument has recently been used for measurements of solution into water at different temperatures of normal alcohols (C_1-C_8) (ref.14) and of esters, ethylene glycol diesters and glycerol triesters (ref.15).

For some of the very slightly soluble compounds measured, the reaction time was very long (several hours). In such cases it is usually the baseline stability of the calorimeter which is the limiting factor for the precision. We have very recently tested a new version of the dissolution vessel which is used with the LKB BioActivity Monitor (ref.16). The new vessel is a slightly modified version of our perfusion-titration vessel (ref.17). Test results show a significantly improved precision for solutes requiring a long time for the dissolution process (ref.14). Some compounds (e.g. alkylsulphides and some halogenated hydrocarbons) appear to be irreversibly dissolved in the teflon material used in the dissolution region. Work is in progress to overcome this problem.

SOLIDS

Some years ago Gill and Seibold (ref.18) described a flow microcalorimetric method by which enthalpies of solution of small quantities of slightly soluble solids could be measured. However, this instrument does not seem to have been used very widely. A few years ago we built a flow solution vessel by which the enthalpy of solution in water of about 1 mg of a slightly soluble solid compound could be determined to about 2%. The solid sample was contained in a small cavity where it was covered with a saturated solution of water. The sample container was inserted into a solution vessel which was similar in design to the instruments used with gases and liquids. After equilibration, a flow of pure solvent was brought in contact with the sample.

The instrument proved to have some shortcomings and was never reported in any detail, cf. ref.19. However, using the same principle we have now redesigned the sample container (15). It can be inserted into our perfusion-titration vessel (ref. 17) used with the LKB BioActivity Monitor (ref. 16). Test results are very satisfactory.

REFERENCES

1 C. Tanford, The Hydrophobic Effect, 2nd edition, Wiley, New York, 1980.

2 F. Franks and D. S. Read in F. Franks (Ed), Water, A Comprehensive Treatise, Vol. 2, Plenum Press, New York, 1973, pp 323-356.

3 S. J. Gill and I. Wadsö, J. Chem. Thermodynamics 14 (1982), 905-919.
4 I. Wadsö, Science Tools 21 (1974) 18-21.
5 C. Spink and I. Wadsö in D. Glick (Ed), Methods of Biochemical Analysis, Wiley, New York, 1976, pp 1-159.
6 D. S. Dec and S. J. Gill, Rev. Sci. Instr. 55 (1984) 765-772.
7 D. S. Dec and S. J. Gill, J. Soln. Chem. 13 (1984) 27-38.
8 S. F. Dec and S. J. Gill, J. Soln. Chem. In press.
9 G. Olofsson, A. A. Oshodi, E. Qvarnström and I. Wadsö, J. Chem. Thermodynamics 16 (1984) 1041-1052.
10 B. B. Benson, D. Krause, Jr.and M. A. Peterson, J.Soln. Chem. 8 (1979) 655-690.
11 S. J. Gill, N. Nichols and I. Wadsö, J. Chem. Thermodynamics 7 (1975) 175-183.
12 S. J. Gill, N. Nichols and I. Wadsö, J. Chem. Thermodynamics 8 (1976) 445-452.
13 S.-O. Nilsson and I. Wadsö, J. Chem. Thermodynamics, 16 (1984), 317-330.
14 D. Hallén, S.-O, Nilsson and I. Wadsö. To be published.
15 S.-O. Nilsson and I. Wadsö. To be published.
16 J. Suurkuusk and I. Wadsö, Chemica Scripta 20 (1982), 155-163.
17 M. Görman Nordmark, J. Laynez, A. Schön, J. Suurkuusk and I. Wadsö, J. Biochem. Biophys. Meth. In press.
18 S. J. Gill and M. L. Seibold. Rev. Sci.Instr. 47 (1976), 1399-1401.
19 I. Wadsö, Proceedings of the 2nd Australian Thermodynamics Conference, Royal Austr. Chem. Inst., Melbourne, 1981.