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DESIGN AND TESTING OF A MICROTITRATION ASSEMBLY FOR USE WITH AN LKB BATCH MICROCALORIMETER

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ABSTRACT

A twin, automatic microtitration assembly suitable for use with an LKB Batch Microcalorimeter is described. The apparatus, which can accurately and reproducibly deliver volumes as low as 1 μl, permits up to 20 titration additions to be made. It has been tested by the determination of the heat of ionisation of water at 303.15 ± 0.01 K. The value determined compares favourably with the "best" value reported in the literature.

INTRODUCTION

The LKB Batch Microcalorimeter [1,2] employs the twin-vessel, heat conduction principle and has been used extensively for the determination of the heats of reaction of both chemical and biological systems. Its operation is, however, hampered by the lengthy equilibration times required after each loading of the calorimetric vessels. These times are typically 1–2 h which, together with the associated friction and calibration experiments, means that normally only 2–3 experiments are possible in a working day. Thus to determine, for example, the enthalpy change and equilibrium constant for a relatively simple reaction requires several weeks. The use of calorimetric techniques to determine K and ΔH simultaneously has been well reviewed [3].

Determination of enthalpies of solution and dilution of sparingly soluble liquid solutes has been achieved by flow microcalorimetry [4] but lengthy experimentation is again required. Such enthalpies may be determined, after lengthy experimentation, by batch calorimetry. Data of this type would also be more accessible if some titration device were available.

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Talibudeen et al. [5] have recently described a microtitration device upon which our design is based but they did not report any experimental results for a thermochemical test reaction. The design and testing of a versatile microtitration system is therefore described here.

The test reaction selected to assess the accuracy and reproducibility of the titration unit was the heat of ionisation of water: Larson and Hepler [6], reviewing the available data, adopted a "best" value of 54.73 kJ mole^{-1} at 303.15 K.

DESIGN AND ASSEMBLY

The assembly is shown in Fig. 1. It consists of a 6 V d.c. motor (Aidus Supplies, Middx., U.K.) (A) which, through gear boxes (Aidus Supplies, Middx. U.K.) (B) operates the final drive at 6 r.p.m. This whole is mounted on a duraluminium base (C). The motor is connected to a micrometer screw

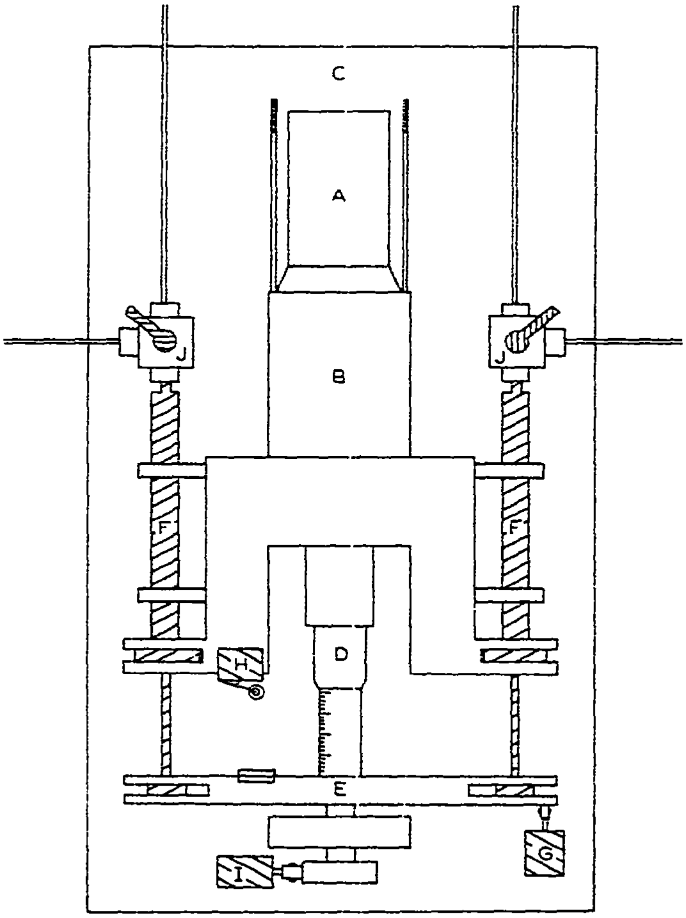

Fig. 1. The microtitration assembly.

thread (D) which in turn is fixed to a slotted arm (E). Rotation of the motor drive shaft will then either depress or withdraw the plungers of two identical gas-tight syringes (Hamilton, 1750 LT). The maximum travel of the micrometer screw is controlled by two microswitches (G and H). Microswitch I automatically halts the syringe drive after one revolution of the motor and thus controls the volume of titrant added. The syringe mountings will accept either 100 or 50 μl syringes, allowing single "steps" of either ~ 5 or 1 μl in titrant addition. An override switch permits multiple injections to be made in one "step". Three-way taps (J) enable the syringes to be filled and discharged without the need for removal from the titration system. The liquid titrants are conducted to the calorimetric vessels via PTFE tubing (Hamilton 0.25 mm i.d.) which is laid across the calorimetric block to ensure temperature equilibration and enter the vessels through the PTFE stoppers.

The whole assembly is attached firmly to the calorimetric unit and counterbalanced by lead weights.

MATERIALS AND METHODS

Pure deionised water (specific conductance less than 10^{-6} mho) and B.D.H. analytical volumetric concentrate of hydrochloric acid and sodium hydroxide were used.

Three separate series of determinations were performed with freshly prepared solutions (0.1 M) using syringes delivering approximately 5 μl. Another series of determinations was performed using approximately 1 μl delivery syringes. A change in volume of the contents of the microcalorimetric vessels of up to 2% did not apparently affect the area under the calibration curves.

Hydrochloric acid and sodium hydroxide solutions were made up at 293 K in 500 ml flasks and the density of the hydrochloric acid calculated from the equation [7]

$$\rho\,(293\,K) = 0.99821 + 1.7906 \times 10^{-2}C - 2.59 \times 10^{-4}C^2 \text{ kg dm}^{-3} \qquad (1)$$

where C is the concentration (molarity) and ρ is the density. Therefore, $\rho = 0.999998$ kg dm^{-3} at 293 K for a 0.1 M solution and 0.1 mole of hydrochloric acid is present in 0.999998 kg of solution. To calculate the enthalpy of ionisation of water per mole, the value obtained per aliquot of 0.1 M hydrochloric acid solution of weight Y kg must be multiplied by the factor $(10 \times 0.999998)/Y$. The delivery from the syringes was measured by weighing. The syringe supplying the reaction microcalorimetric vessel was filled with 0.1 M hydrochloric acid and that supplying the tare vessel was filled with 0.1 M sodium hydroxide. Both microcalorimetric vessels were charged with 6 ml of 0.1 M sodium hydroxide using a 2 ml pipette. Titration of each aliquot of hydrochloric acid was made with simultaneous rotation of the microcalorimetric barrel housing the reaction and tare vessels to ensure rapid and complete reaction.

The enthalpy values obtained were corrected for the relative apparent molal enthalpies of hydrochloric acid and sodium hydroxide [8].

RESULTS AND DISCUSSION

The derived value for the heat of ionisation of water shown in Table 1 is in good agreement with the Larson and Hepler "best" value. Moreover, the

TABLE 1

Derivation of the heat of ionisation of water

	Areas under titration curves (arbitrary units)			
	Run 1 [a]	Run 2 [a]	Run 3 [a]	Run 4 [b]
	119.22	118.44	121.74	23.39
	118.06	124.49	124.70	22.89
	119.67	118.78	123.47	22.79
	120.40	122.01	122.32	23.05
	120.74	125.30	123.30	22.80
	118.54	122.09	121.99	23.18
	119.73	122.64	122.00	23.07
	118.60	122.17		23.49
	117.79			22.81
	121.72			
	120.27			
	120.42			
Calibration current	5 mA for 23 s	5 mA for 23 s	5 mA for 23 s	2.23 mA for 20 s
Area under calibration curve	120.6 ±0.64	122.62±0.07	122.64±0.24	21.12±0.20
Calibration constant (mJ/unit area)	0.237	0.233	0.233	0.234
ΔH^0_{303} (kJ mole^{-1})	54.75±0.46 [c]	54.78±0.16 [c]	55.15±0.49 [c]	54.94±0.63 [c]
	$\Delta H^0_{303} = 54.89 \pm 0.32$ kJ mole^{-1} [d]			

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[a] 5.109 mg delivery of 0.1 M hydrochloric acid.

[b] 0.967 mg delivery of 0.1 M hydrochloric acid.

[c] Corrected for relative apparent molal enthalpies of hydrochloric acid (556 J mole^{-1}) and sodium hydroxide (296 J mole^{-1}).

[d] All limits of error are for a probability level of 0.95

reproducibility obtained (±0.6%) is excellent. The titration system described is, therefore, capable of determining heats of reaction with both good accuracy and reproducibility. The fact that ca. 20 additions may be made in one loading means that a titration curve, for example, may be completed in one experiment instead of 20 separate experiments.

Operation of the microcalorimeter in its conventional manner does not permit dissimilar solvent systems to be used (the two reacting solutions are, initially, separated by a glass divider but share a common vapour space). The use of the titration system will permit dissimilar solvent systems to be used (with a consequent small loss in reproducibility).

A commercial model of this system is now marketed by LKB Produkter AB.

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