

light-yellow syrup. This material was methylated as previously described and hydrolysed, and the methylated sugars were analysed, as their alditol acetates, by GLC-MS.

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A Reaction Calorimeter

Some Modifications of a Previous System

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A reaction calorimeter of the isothermal jacket type used at this laboratory has been described earlier.¹ The calorimeter has now been in operation for almost five years and the experience gained during this time has led to some modifications of the system. The main principles in the construction have, however, been retained.

The calorimeter. The new calorimeter is shown in Fig. 1 and is very similar to the one described earlier.¹ The most important changes can be summarized as follows:

(a) The mechanical design is much more rugged. (b) The parts included in the reaction vessel, *i.e.* the thermistor, the heater and the stirrer, can all easily be exchanged. (c) The addition capillary tube has been furnished with a spring-loaded valve. This valve provides protection against diffusion, *i.e.* it prevents undesirable reactions in the contact area between the reactant in the capillary tube and the solution in the inner vessel. (d) The transmission between the motor and stirrer (with new precision bearings) is improved by a cog-wheel-cogbelt transmission. (e) The capacity of the heat-exchanger is substantially increased. Solution can be added through the heat-exchanger at a rate of 1 cm³/min during 5 min at a temperature difference of 15 K, without any noticeable heat transfer from the titrant to the solution.

The thermistor circuit and the Wheatstone bridge. The thermistor circuit has been changed in order to allow adjustments of the thermistor current. This is done by the connection of a potentiometer and a standard resistance in series with the bridge. The current is determined by measuring the potential drop over the standard resistance with a digital voltmeter (see below). It is important that this adjustment can be made with good precision as the current causes self-heating in the thermistor. The resistance of the thermistor changes substantially with temperature

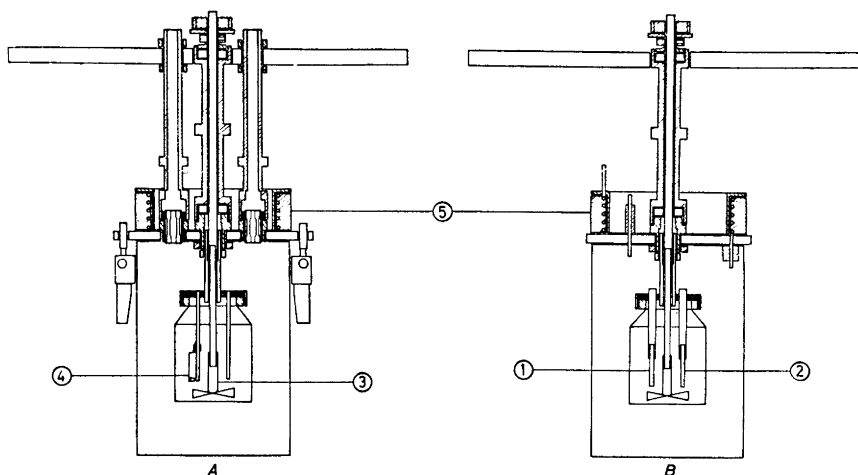


Fig. 1. The calorimeter as seen from two different directions. The parts marked with figures are: 1. Thermistor; 2. Heater; 3. Stirrer; 4. Spring-loaded valve; 5. Heat-exchanger.

causing a variable self-heating if the current is unchanged. The most accurate results are obtained if the power dissipation in the thermistor is kept equal and constant at all temperatures (*i.e.* by varying the thermistor current). The thermistor current used at 25°C is 80 μA , corresponding to a power dissipation of 13 μW .

The bridge ratio is unchanged ($R_D/R_T=5/2$), but improvements have been made in order to prevent fluctuations in the decade resistance, caused by temperature variations in the room. The high-ohm units in the decade have been disconnected and replaced by a non-variable set of precision resistances the magnitude of which is fixed by the thermistor resistance at each temperature. This set is immersed in an air thermostated oil bath. The variable part of the decade left outside the oil bath has a total resistance of 1110.10 Ω . By this arrangement, the variations in the room temperature during a calorimetric measurement cause changes in the decade resistance which are well within the error limits of the experiment as a whole.

The calibration circuit. The calibration resistance is designed in the same way as described before.¹ However, the accuracy in the determination of the amount of energy added has been improved considerably. The calibration resistance has

been connected to the calibration circuit using a four-lead system, which means that the potential drop over the resistance can be measured simultaneously with the addition of current without losses in accuracy. The potential drop is measured by a digital voltmeter with a large input resistance. (Type SE, SM213, MK 2. The same instrument is used for the adjustment of the thermistor current.) The calibration current is supplied from a constant

Table 1. The calibration constant ϵ at 25.0°C. $V=100.054 \text{ cm}^3$ of H_2O . The energy input in each run was 11.639 J.

$\Delta R/\Omega$, $\epsilon\Omega/\text{J}$:	4.992, 2.3315; 4.990, 2.3325;
	4.994, 2.3306; 4.991, 2.3320; 4.990, 2.3325;
	4.993, 2.3311.
	$\epsilon_{\text{Mean}}=2.3317 \pm 0.0008 \text{ J}^{-1}$.

Table 2. The calibration constant ϵ as a function of the volume V at 25.0°C. The data refer to a 1.00 M NaClO_4 solution.

V/cm^3 , $\epsilon\Omega/\text{J}$:	80.00, 1.8326; 80.00, 1.8213;
	81.54, 1.8623; 83.04, 1.8967; 84.04, 1.9264;
	84.54, 1.9322; 86.04, 1.9632; 87.00, 1.9870;
	87.58, 1.9975; 89.08, 2.0305; 90.00, 2.0544;
	91.08, 2.0711; 92.00, 2.1046; 93.13, 2.1234;
	94.04, 2.1506; 95.13, 2.1669; 96.00, 2.1992;
	97.13, 2.2142.

Table 3. The heat of neutralisation (NaOH + HCl) and the heat of protonation (T + H⁺; $I \approx 0.01$ M) at 25.0°C.

Mean values:		Neutralisation	$\Delta H_{\infty}^{\circ} = -55834 \pm 20$ J mol ⁻¹		
		Protonation	$\Delta H_{\text{corr}} = -47424 \pm 54$ J mol ⁻¹		
Neutralisation			Protonation		
Run No.	$-\Delta H$ J mol ⁻¹	$-\Delta H_{\infty}^{\circ}$ J mol ⁻¹	Run No.	$-\Delta H$ J mol ⁻¹	$-\Delta H_{\text{corr}}$ J mol ⁻¹
1	56448	55854	1	47854	47389
2	56448	55854	2	47950	47485
3	56402	55808	3	47979	47515
4	56435	55841	4	47854	47389
5	56405	55812	5	47900	47435
			6	47854	47389
			7	47828	47364

current source of type Fluke 351A. The measurement of the calibration time is made by a digital clock, which also operates the opening and closing of the current circuit. The clock is of the type Elesta CPT (equipped with a quartz oscillator ZB51/12S).

The reproducibility. The modifications described in both the calorimeter and the bridge unit have given a system with a much higher precision (reproducibility) than before. This is clearly demonstrated by the electrical calibration experiments made at 25.0°C. The results in Table 1 show that the reproducibility in the modified system is about five times higher than before. This increased precision is also verified by the results obtained from calibration experiments made with different volumes of solution in the reaction vessel. The calibration constants can be fitted very well to a straight line, $\varepsilon_v = a + bv$, where $v = V_0 - 80.00$ cm³, which shows that the high reproducibility is independent of the volume in the range 80–100 cm³. The results from this experiment are given in Table 2. A least-squares refinement of the data gives: $a = 1.8276 \pm 0.0017$ J Ω^{-1} and $b = (2.275 \pm 0.019) \times 10^{-2}$ J Ω^{-1} cm⁻³.

The accuracy. The accuracy of the calorimeter (especially the titration unit) has been tested at 25°C by determinations of the enthalpy changes for two standard reactions; neutralisation of NaOH (9.947 mM) with HCl (100.62 mM) and protonation of THAM (tris(hydroxymethyl)amino-methane ($C_T = 19.96$ mM, $C_{\text{TH}^+} = 10.04$ mM) with HCl (100.62 mM). The enthalpy

changes for both the reactions proved to be in agreement with our previous results.¹ The data for the reactions are given in Table 3. Corrections for the dilutions have been made according to SVCTP.^{2,3}

Concluding remarks. The calorimeter has now been incorporated in several other systems, both automatic^{4,5} and non-automatic (Department of Inorganic Chemistry at the Royal Institute of Technology in Stockholm) and the evaluation of precision, accuracy and ease of operation confirm our own findings.

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