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An Isothermal Jacket Titration Calorimeter

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One of the main problems in constructing a titration calorimeter is to avoid heat effects due to different temperatures in the calorimeter liquid and the liquid added. In this paper, a modification of the Sunner-Wadsö calorimeter is described, in which the basic principles of the Sillén-Schlyter calorimeter have been incorporated. Any quantity of external liquid can be added to the calorimeter under full temperature control. The total volume of the calorimeter is only 70 ml. Heat quantities of the magnitude 2 cal can be determined reproducibly to within 1 %.

The performance of the calorimeter system was checked by heat of dilution experiments on hydrochloric acid.

In 1959 Schlyter and Sillén [1,2] published a method for quantitative enthalpy titrations, the two main features being that the temperature of the added solution was controlled and that the calorimeter content after each addition of titrant conveniently could be brought back by cooling to the initial temperature, 25°. This calorimeter has since been improved.[3] Gerding, Leden and Sunner [4] describe another calorimeter with a built in pipette that can be repeatedly filled and emptied. For many purposes, however, it would be of value to have available a calorimeter in which the amount of added liquid is not restricted *e.g.* by the volume of a pipette or the thermal capacity of an intermediate buffer volume for the added liquid. Also, it would be of value to have a small calorimeter, as many compounds of interest are not easily accessible in large quantities.

We have therefore modified our ordinary reaction calorimeter,[5] taking advantage of the fact that our calorimeter thermostats are capable of keeping the temperature constant to within $\pm$ 0.001°. The titrant is stored in a Metrohm piston burette of 10 ml volume, delivering a measured quantity of liquid to within $\pm$ 0.002 ml. The burette is equipped with a two-way stop-cock so that it can be refilled from a store bottle. From the burette the titrant flows through a 2 mm capillary tube equipped with a standard joint and a teflon stop-cock

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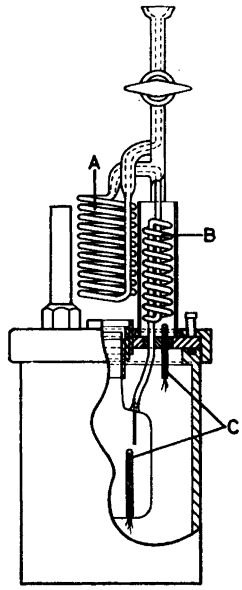

Fig. 1.

into an external, thin-walled glass spiral (A, Fig. 1). The spiral is freely suspended in the thermostat water (to make the construction less breakable, the spiral surrounds the central tube through which the stirrer shaft is carried in ball bearings). The liquid then flows through a second, thin-walled glass spiral, B, immersed in mercury. This serves as a heat buffer, levelling out the small temperature variations of the thermostat (periodicity *ca.* 20 sec.). The internal volume of the outer spiral is 2 ml and that of the inner spiral is 0.56 ml. The glass tube is sealed directly onto a calibrated thin capillary tube (inner diam. *ca.* 0.6 mm), extending into the glass calorimeter vessel and ending below the surface of the liquid. A five junction thermal, C, together with a sensitive galvanometer, is used to control the temperature difference between the mercury and the calorimeter liquid; 1 mm on the galvanometer scale corresponds to 0.001°. Before the start of a series of experiments, liquid is forced through the glass tubes and spirals simply by operating the burette device until the meniscus reaches a point *ca.* 20 mm from the end of the exit capillary tube. (The amount of air left in the capillary, 0.006 ml, is corrected for.)

The stirrer consists of a thin-walled glass tube with a small propeller, fastened to a through-shaft made of a thin-walled stainless steel tubing carried in ball bearings and protruding outside the calorimeter. Cool air can be blown to the bottom of the stirrer by use of a capillary tube. A rapid cooling is achieved and also a rapid thermal equilibration of the calorimeter and its surroundings after cooling. The calorimetric system is electrically calibrated and its temperature is measured by use of a thermistor.

Table 1. Calibration runs.

ml 2.000 M HCl	ε	ε calculated
1.999	5394	5452
2.994	5586	5542
3.999	5681	5633
5.999	5785	5813
6.995	5899	5903

The standard deviation from the least square function is $\pm$ 20.

The efficiency of the thermal equilibration of the external liquid while being added to the calorimeter was simply checked by adding varying amounts of water (external liquid) to the calorimeter (initial charge 60 ml of water) at zero temperature difference between the calorimeter and the mercury. No temperature change of the calorimeter was observed (sensitivity *ca.* 0.01 ohm corresponding to 0.0001°) even at a rate of addition of 5 ml/min.

HEAT OF DILUTION OF HYDROCHLORIC ACID

Initially, the calorimeter was charged with 62.68 ml of water and portions of 2.000 M HCl were added stepwise. Calibration runs (Table 1) were performed after each addition. The dependence of the heat equivalent on total amount of acid added could be described by a linear function, closest fit being obtained by use of the method of least squares:

$$\varepsilon = 90.40_8 X + 5271.4$$

where X is the amount of acid added.

Table 2 gives a comparison between results obtained and values calculated from Ref.[6] The standard deviation of the single experiment is $\pm$ 0.003 kcal/mole.

Table 2. Heats of dilution of hydrochloric acid.

ml 2.000 M HCl	Total amount added	$-\Delta H$/mole	$-\Delta H$/mole SVCTP
2.994	2.994	0.520	0.519
4.001	6.995	0.427	0.422
1.999	1.999	0.538	0.540
2.000	3.999	0.471	0.470
2.000	5.999	0.438	0.436
		Standard deviation	0.003

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