

## A Calorimetric Method for Determination of $\Delta C_p$ in Chemical Reactions

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A novel calorimetric procedure for the determination of  $\Delta C_p$ -values in chemical reactions is outlined and exemplified. Results indicate that  $\Delta C_p$ -values for reactions in dilute solutions (0.05 M) and over a small temperature range (0.3°) can be determined with an accuracy of better than 0.5 cal/deg-mole.

Heat capacity data for components in solution ( $\varphi C_p$ , apparent heat capacity;  $\overline{\varphi C_p}$ , partial molar heat capacity, and corresponding  $\Delta C_p$ -values) have recently attracted increasing interest as they have been shown to reflect solute-solvent interactions ("medium effects"), particularly in aqueous solution systems.

There is also a general need in thermochemistry for  $\Delta C_p$ -data, which are used when temperature corrections are made on enthalpy values, *cf.* eqn. (1)

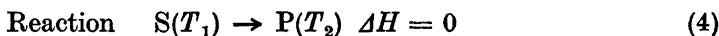
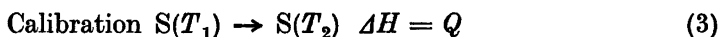
$$\frac{d\Delta H}{dt} = \Delta C_p \quad (1)$$

At present there are very few calorimetrically determined  $\Delta C_p$ -values available, particularly for solution systems. This paper reports a novel method which is a useful complement to the common procedure for deriving  $\Delta C_p$ -data from  $\Delta H$ -values determined at different temperatures, *cf.* eqn. (1).

If a non-isothermal calorimetric system is calibrated both before and after the reaction has taken place,  $\Delta C_p$ -values can be calculated from the heat of reaction value and the difference between the two calibration constants. This principle ought to be known among thermochemists although hitherto no practical use has been made of it.

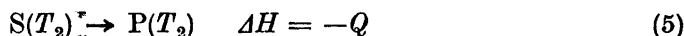
Suppose we are studying a process where the starting system is S and the product system is P and the calibration experiment prior to the reaction has taken place. The experiments are made between temperatures  $T_1$  and  $T_2$  (corrected for heat exchange). We have

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It may be noted that in the calibration experiment there has been an enthalpy increase equal to the calibration heat ( $Q$ ) introduced to the system, whereas in the reaction experiment there has been no enthalpy change.

From eqns. (3) and (4) we obtain for the isothermal process



In practice  $T_1$  and  $T_2$  cannot normally be made exactly identical and therefore proportionality expressions are used ( $\varepsilon$  = calibration constant):

$$Q = \varepsilon \cdot \Delta T_{\text{calibration}} \quad (6)$$

$$Q_{\text{ideal}} = \varepsilon \cdot \Delta T_{\text{reaction}} \quad (7)$$

Calibration values derived from experiments on the *initial* system will thus refer to  $\Delta H$  at the *final* temperature. Similarly, if the calibrations are performed on the final system the enthalpy change will refer to the initial temperature. From the difference between the two enthalpy values and from the corresponding temperature difference one can thus calculate the  $\Delta C_p$ -value for the reaction (at the mean temperature of the calorimetric experiment).

$$\frac{\Delta H_{T_2} - \Delta H_{T_1}}{T_2 - T_1} = \Delta C_p \quad (8)$$

The method was tested on the "THAM-test reaction"<sup>1</sup> employing an LKB precision reaction calorimeter in which the thermistor had been calibrated in °C by means of a platinum resistance thermometer.

Measurements were made on a sample of THAM (= trishydroxymethylaminomethane) purified as described in Ref.<sup>1</sup> The calorimeter was charged with 100 ml of 0.1 M hydrochloric acid and a weighed quantity of THAM was contained in a sealed glass ampoule. Calibrations were performed twice before the reaction run and twice after it. The temperature was adjusted to the starting point either by cooling with dry air or by electrical heating. Electrical heat input in the calibration experiments and ampoule-breaking in the reaction experiments were automatically initiated at a pre-set thermistor resistance value. The starting temperature was therefore the same in all experiments. In the calibration experiments the final temperatures were consistently close because the energy supplied was always the same. Possible errors in bridge, heat exchange corrections and in temperature-thermistor resistance relationships almost cancel themselves by this procedure and very high precision is attainable in repeated calibration experiments.

Results of the experiments are summarized in Table 1.  $\varepsilon_i$  and  $\varepsilon_f$  are the calibration constants for the system before and after the reaction, respectively.  $\varepsilon$ -Values are given in units of calories per unit of thermistor resistance change expressed as  $\Delta R/Rm$  (cf. Ref. 2).

It may be noted that there is a slightly larger difference between calibration constants from the separate experiments than between duplicate calibrations runs. This is due to small variations in heat capacity of the system

as a result of the nonreproducibility of the volumetric filling technique and of slightly different sample weights.

$\Delta H$  in Table 1 is the heat of reaction calculated using the mean value of  $\varepsilon_i$  and  $\varepsilon_f$  and is corrected to refer to 25.00°C. The  $\Delta H$ -value obtained is in agreement with that recently reported,<sup>3</sup> -7111 cal/mole, *i.e.* slightly more negative than the mean value given in Ref. 1 (-7104 cal/mole).

Table 1.

THAM mmoles	$\varepsilon_i$	$\varepsilon_f$	$-\Delta H(25^\circ\text{C})$ kcal/mole	$\Delta C_p$ cal/mole-deg.
4.20484	2637.61	2642.42	7.1135	(47.1)
	2637.77	2642.58		
4.46589	2636.89	2641.40	7.1051	41.0
	2637.05	2641.40		
4.11005	2637.04	2641.40	7.1106	41.5
	2637.48	2641.84		
3.77854	2637.55	2641.48	7.1135	41.4
	2637.85	2641.48		
3.79174	2640.32	2644.13	7.1121	41.4
	2640.52	2644.29		
3.99461	2640.62	2644.82	7.1194	42.7
	2641.02	2645.10		
		Mean:	7.112 ± 0.002	41.6 ± 0.3

Calibration experiments were performed between 24.8 and 25.2°C and derived  $\Delta C_p$ -values thus refer to this small temperature interval. It is shown in Table 1 that the first  $\Delta C_p$ -value falls markedly outside the rest of the series and this value was therefore not included in the calculated mean value,  $\Delta C_p = 41.6 \pm 0.3$  cal/mole-deg. (The uncertainty units are the standard deviation of the mean.) A slightly lower value was reported earlier,<sup>1</sup> 40 cal/mole-deg., evaluated from reaction calorimetric measurements performed at 20, 25, and 30°C.

The present method requires very precise calibration experiments, although it may be noted that the actual heat of reaction value does not have to be determined very accurately. This is important if precise calorimetric measurements, which are pre-requisite for the procedure based on heat of reaction determinations at different temperatures (eqn. 1), cannot be performed. Another valuable feature of the present method is that usually only a very small number of reaction calorimetric experiments need be made, and this is of value when work has to be done on expensive materials.

## REFERENCES

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