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Use of a Microcalorimeter for Determining Reaction Enthalpies in Solution

Calorimetry is a useful technique for the determination of thermodynamic quantities characterizing physicochemical systems. It was used rather early (*1*) and allowed numerous tables of experimental data to be established. At present, sophisticated measuring devices are available on the market, allowing researchers, not only to work on small amounts of substance (microcalorimetry), but also to obtain great accuracy on the quantities experimentally measured.

Use of microcalorimetry for teaching purposes is still a rare matter, owing to the necessity for working with skilled hands on such expensive and complex devices. However, because of its large scope of interest, we have worked out an experiment performed by students in our laboratory (Physical chemistry, 1st year, ENSCP). They can first measure transformation enthalpies (melting, phase transition . . .) and then neutralization or mixing enthalpies.

The apparatus is simple and accessible to students.

Apparatus

A differential microcalorimeter of the MCB type (*2*) sold by ARION society was used for the experiment. It is an inexpensive device appearing as a base unit (Fig. 1) and comprised of

a furnace containing the two cells of 1.7-ml capacity (Fig. 2)
a mechanical shaking system involving rocking of the furnace
a temperature regulating and programming system permitting either a programmed furnace temperature rise, or a temperature regulation (±0.01°C)
a calibration device involving a 120.0-Ω (at 25°C) resistance with 0.1% and 0.01 s accuracy for current intensity and time, respectively

Fitted with a recorder (SEFRAM Servotrace PES type millivoltmeter for instance), this base unit will allow several studies with varying temperature to be made. Our students can thus determine melting enthalpies for substances usually considered as temperature standards by measuring peak areas (see: section on Interpreting the Results).

A few results obtained by our students appear in Table 1.

On the other hand, adapting the base unit is compulsory if isothermal measurements (necessary to study mixing or neutralization enthalpies) are to be made. In fact, liquid mixing ($S_1 + S_2$ for a mixture, acid + base for a neutralization) must take place inside the microcalorimeter cell without destroying its thermal equilibrium, which raises many technological problems we tried to solve.

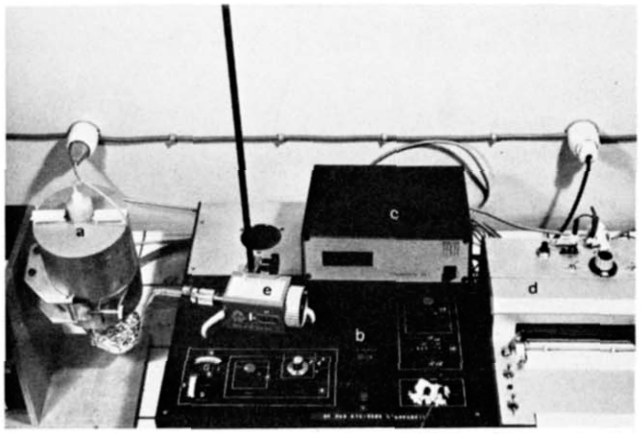

Figure 1. Comprehensive view of the apparatus; (*a*) microcalorimeter (*b*) control and calibration system (*c*) digital thermometer (*d*) recorder (*e*) microburet.

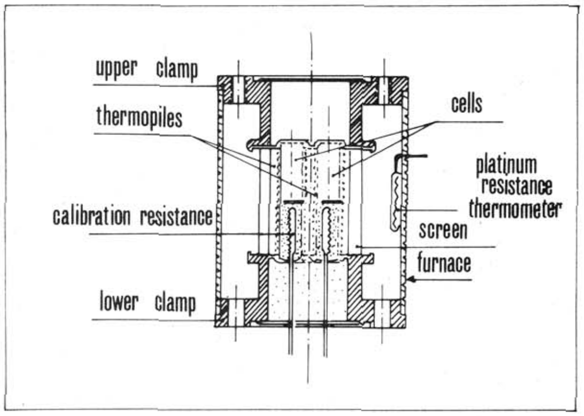

Figure 2. MCB-Type microcalorimeter.

Table 1. **Student Results on Determinations of Melting Enthalpies**

Sample	Melting point °C	ΔH_1	ΔH_2	ΔH_3	ΔH (mean)	ΔH (*4*)
azobenzene	95.2	29.04	28.69	28.76	28.83	28.91
m-nitroanilin	114	40.22	41.31	40.54	40.69	40.97

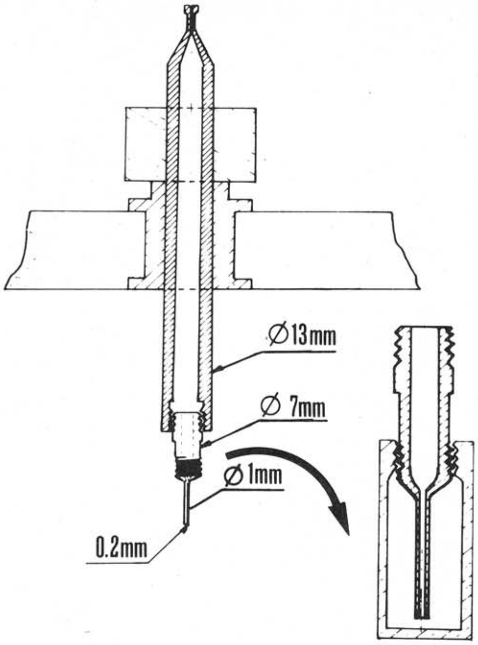

Figure 3. System of reagent injection.

The system of reagent injection (Fig. 3) developed in this laboratory and tested by our students meets the following requirements

1) From furnace and cell conception, it is necessary to work on small volumes of sample
2) A given amount of reagent can be added in the working cell
3) Mixing of the liquids should occur neither before nor after reagent injection, even when rocking the calorimeter
4) None of the calorimeter materials is liable to react with the liquids
5) No thermal loss should be detected along the injector
6) The injected liquid must have the same temperature as the substance in the working cell

The injector (made of KEL-F), linked to the furnace cover by a tightening-ring, is connected by means of vinyl tubing to an E 457 METROHM microburet. The volumes delivered in this way lie in the range 1–2000 ± 0.5 μl. To avoid over-pressure, on injecting, inside the working cell, which would prevent the liquid from running, the screw thread is scratched to allow air to leak out without losing any liquid. Two steel rods guide injector and furnace cover on top of the furnace.

Measuring a Neutralization Enthalpy: Titration of a Base by an Acid

Method of Procedure

The advantage of this experiment lies in the fact that students can both measure a reaction enthalpy and obtain, from the acid-base titration, the concentration of their reagents, thereby verifying the quantity of solution injected.

All experiments were performed at 25°C.

In both cells, the same amount of base to be titrated was introduced (150 μl for instance) so that it can be neutralized by 1/2 to 1/5th its volume of acid (30–75 μl).

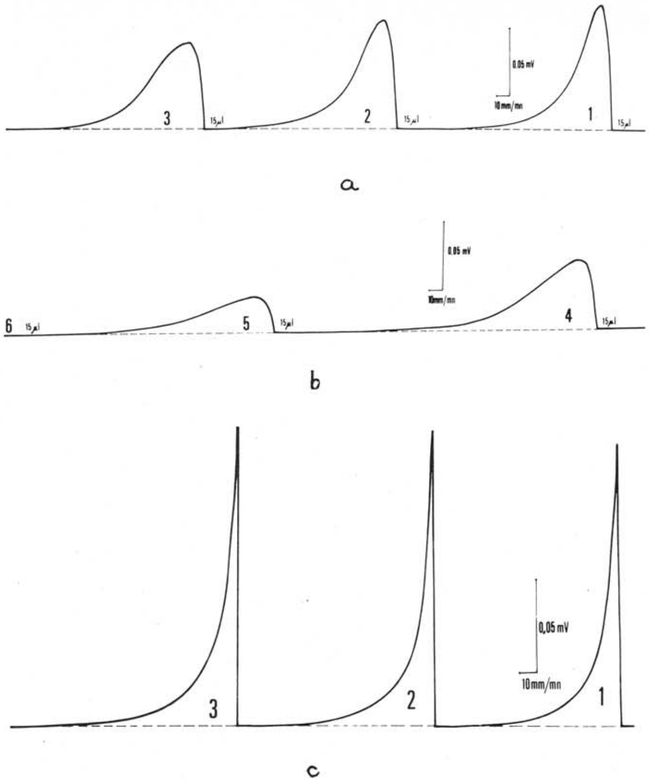

Figure 4. Typical enthalpogramms; (*a*, *b*) peaks corresponding to reagent injections (*c*) calibration peaks.

The working cell was screwed up on the injector, and the whole assembly introduced into the calorimeter. The agitation was then set up.

When thermal equilibrium was reached, a series of acid injections was made (15-μl increments for instance). Each injection appears on the recorder as a peak (Fig. 4), the area of which is proportional to the amount of heat given out by the reaction. Waiting for thermal equilibrium restoration usually took 10 min. In order to estimate the contribution of mixing enthalpies (acid + base medium), a few portions of acid were added after the reaction endpoint.

Several peaks were measured for standardization by means of the Joule effect (Fig. 4), while rocking the calorimeter and modifying, if necessary, both time and current intensity parameters.

Interpreting the Results

Several measurements were made for peak areas with a planimeter, so as to obtain an additional proportion value in

Table 3. Values Calculated From Figure 4

	1	2	3	4	5	6
S planimeter	285 284 285	293 294 295	292 292	269 270	151 153	0
S (mean)	285	294	292	270	152	0
ΔH_n (cal)	0.070	0.073	0.072	0.067	0.0375	0
× H^+ (μl)	15	15	15	15	15	15

Table 2. Results Obtained From Figure 4

	1st peak	2nd peak	3rd peak	Error
I current intensity (A)	0.020	0.020	0.020	2×10^{-5}
t time (s)	3.68	3.88	4.28	0.01
W energy (cal)	0.0422	0.0445	0.0491	10^{-4}
S areas read on planimeter	171; 171; 171	179; 181; 180	198; 197; 198	2 divisions
S mean	171	180	198	
$P = \frac{W}{S}$ (cal)	2.468×10^{-4}	2.472×10^{-4}	2.480×10^{-4}	2.5×10^{-6}

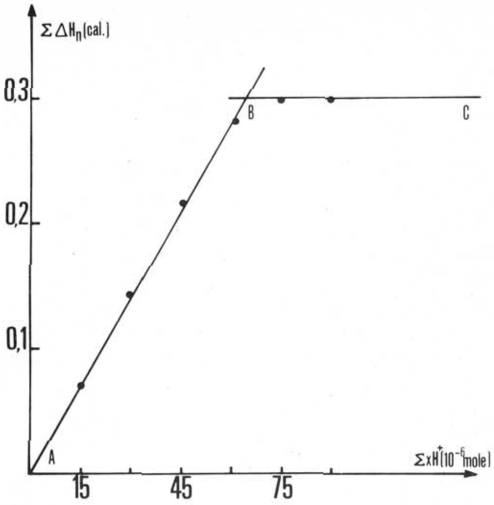

Figure 5. Dependence of $\sum\Delta H$ on number of added protons.

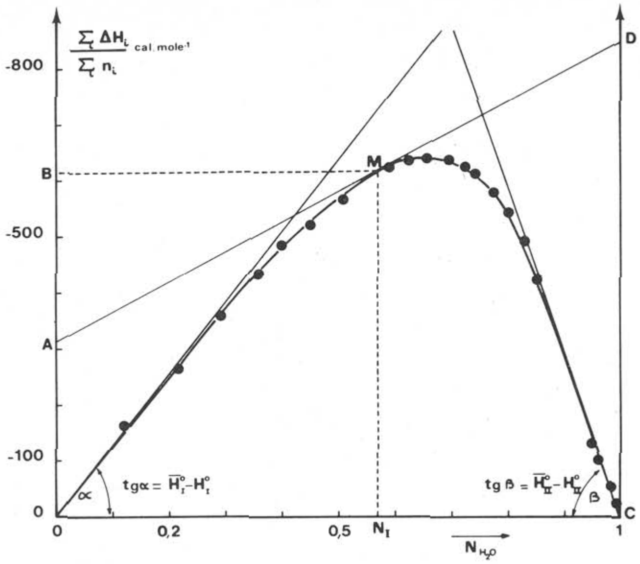

Figure 6. Dependence of $\sum_i\Delta H_i/\sum_i n_i$ on molar ratio of water.

$$AB = N_I \frac{\partial X}{\partial N_I} = N_I(\bar{H}_I{}^i - H_I{}^0) - N_I(\bar{H}_{II}{}^i - H_{II}{}^0)$$

$$OA = X - N_I \frac{\partial X}{\partial N_I} = \bar{H}_{II}{}^i - H_{II}{}^0$$

$$CD = \bar{H}_I{}^i - H_I{}^0$$

the ratio $P = W/S$ of energy given out in the cell to peak area. From Figure 4, Table 2 results were obtained. The error for $\Delta P/P$ may be estimated within 10^{-2}. Reaction enthalpies are obtained from acid injection areas.

Assuming x H^+ ions for each injection, the heat given out in the cell can be expressed as $\Delta H = x\Delta H^0$ for an excess of base (ΔH^0 being the normal standard ionization enthalpy for BH^+).

The heat corresponding to the endpoint is generally smaller owing to only a portion of added protons being consumed. The technique for ΔH^0 calculation is therefore straightforward.

1) The neutralization heats are evaluated for each injection, including those following the endpoint (the latter, being very small, can generally be neglected). Table 3 shows the values calculated from Figure 4 (neutralization of 0.15 ml of 0.44 *M* pyridin by 1 *M* HCl; 15 μl HCl for each injection).
2) From these values the student can plot the curve $\sum\Delta H_n = f|\sum(xH^+ \text{ injected})|$ (Fig. 5). The curve is made up of two straight lines: (a) the line *AB* refers to base neutralization; its slope is $\sum\Delta H_n/\sum x = \Delta H^0\sum x\ /\sum x = \Delta H^0$ which gives the normal standard enthalpy of acid BH^+ ionization by direct means. (b) the line *BC* corresponds to mixing heats for acid and neutralized base. All values obtained in the course of our experiments give a horizontal straight line. The slope could be slightly positive or negative if the injected liquid had a temperature slightly different from the base in the cell, or if the added reagent, having an important dilution enthalpy, was used at a high concentration level. A correction for each value of ΔH should then be made. (c) The abcissa of *B* refers to the endpoint for the acid-base titration and is a check for possible losses of acid (for Fig. 5 the correct concentration is 0.440 *M* against 0.425 *M* found from the curve).

Several systems were studied by our students, whose results appear in Table 4.

Measuring Mixing Enthalpies: Water-DMSO (Dimethylsulfoxide) System

Mixing enthalpy measurements with conventional calorimeters usually means rather long operations since each mixture must be treated separately. The injection system which we developed, obviously not reaching the outstanding possibilities of high level microcalorimeters (Picker type, for instance (*8*)) enabled our students to approach a simple, continuous, fast, and accurate method of measurement.

The solvents we use in the course of this experiment are mainly water and DMSO, the mixing of which is favorable on account of a large amount of heat available for measurement. Other studies are still comtemplated with water, acetonitrile, methyl alcohol . . .

Method of Procedure

About 150 μl DMSO are introduced in both cells. The injecting system is fed with water; the total assembly is mounted as previously on the microcalorimeter.

After waiting for thermal equilibrium, a series of injections are made (from 5- to 10-μl increments) up to 200 μl water. A larger amount of reagent (maximum 350 μl) in the working cell would result in a lack of homogeneity of mixtures with an overflowing hazard. Each injection gives out an amount of heat measured from the area of the corresponding peak on the recorder.

Table 4. Systems Studied by Students

Systems	ΔH° (kcal mole^{-1})	ΔH_1°	ΔH_2°	ΔH_3°	ΔH_4°	ΔH_5°	ΔH_6°
HCl + NaOH	found	13.4	13.5	13.2	13.3	13.5	. . .
1 *M* 0.2 *M*	mean			13.4			
	published (*4, 5*)			13.4			
HCl + Pyridin	found	5.0	5.0	5.1	4.9	5.1	5.0
1 *M* 0.4 *M*	mean			5.0			
	published (*6*)			5.0			
HCl + Anilin	found	6.0	6.1	6.1	6.2	6.1	. . .
1 *M* 0.2 *M*	mean			6.1			
	published (*7*)			from 6.5–7.4			

Table 5. Comparison of Values Obtained and the Literature

N_I	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1
ΔH_{cal}	0	−130	−250	−375	−490	−580	−630	−635	−550	−290	0
ΔH_{cal} (*9*)	0	−128	−258	−385	−515	−637	−710	−697	−580	−360	0
ΔH_{cal} (*10*)	0	−125	−256	−385	−504	−600	−655	−650	−558	−352	0

Interpreting the Results

The following symbols are used

I sub-index for water, II sub-index for DMSO
n_0 moles of DMSO in the assay (constant value)
$n_1, n_2, \ldots n_i$ moles of water added after 1st, 2nd, ... ith injection
N_I and N_{II}, respectively, indicating water and DMSO molar ratios in the mixture
$\bar{H}_I{}^i$ and $\bar{H}_{II}{}^i$ for partial molar enthalpies of water and DMSO after ith injection
$\bar{H}_I{}^0$ and $\bar{H}_{II}{}^0$ for mixing partial molar enthalpies, respectively, referring to water and DMSO for infinite dilution in DMSO and water
$H_I{}^0$ and $H_{II}{}^0$ for molar enthalpies of pure water and DMSO

The first injection mixes n_1 moles water with n_0 moles DMSO. The corresponding amount of heat is equal to

$$\Delta H_1 = n_1(\bar{H}_I{}^1 - H_I{}^0) + n_0(\bar{H}_{II}{}^1 - H_{II}{}^0)$$

The second injection means mixing n_2 moles of pure water with the previous mixture

$$\Delta H_2 = (n_1 + n_2)\bar{H}_I{}^2 - n_1\bar{H}_I{}^1 - n_2H_I{}^0 + n_0(\bar{H}_{II}{}^2 - \bar{H}_{II}{}^1)$$

Therefore

$$\Delta H_2 + \Delta H_1 = (n_1 + n_2)(\bar{H}_I{}^2 - H_I{}^0) + n_0(\bar{H}_{II}{}^2 - H_{II}{}^0)$$

Thus, after the ith injection

$$\frac{\sum_i \Delta H_i}{\sum_i n_i} = N_I\,(\bar{H}_I{}^i - H_I{}^0) + N_{II}(\bar{H}_{II}{}^i - H_{II}{}^0)$$

and this equation allows all results to be obtained: the student measures each area, deducing all ΔH for partial mixings, and plots the curve

$$\frac{\sum_i \Delta H_i}{\sum_i n_i}$$

against N_I (from $N_I = 0$ to $N_I = 0.85$).

The curve obtained with water and DMSO is shown in Figure 6 (the last values from $N_I = 0.95$ to $N_I = 1$ were obtained from a second experiment, on introducing water in the cells and DMSO in the injecting system).

In Table 5 the values obtained in this laboratory are compared with those published by J. Kenttämaa and J. J. Lindberg (*9*) and by F. Rallo, F. Rodante, and P. Silvestroni (*10*).

The classical treatment of the preceding curve (Fig. 6) by drawing the tangents at each point means, for the student, plotting the quantity $\bar{H} - H_0$ for both solvents against N_I (Fig. 7).

Three main areas will thus appear

1) from $N_I = 0$ to $N_I = 0.15$ (Zone I). Water behaves as a solute ($\bar{H}_I = \bar{H}_I{}^0$) in DMSO ($\bar{H}_I{}^0 - H_I{}^0 = -1270 \pm 50$ cal mole^{-1}). Water obeys the laws of infinitely diluted solutions, whereas DMSO behaves as a pure solvent ($\bar{H}_{II} = H_{II}{}^0$), which is furthermore a consequence of Gibbs-Duhem equation.
2) from $N_I = 0.15$ to $N_2 = 0.9$ (Zone II). Water and DMSO are together a mixed solvent whose characteristics can be compared to neither pure substance.
3) from $N_I = 0.9$ to $N_I = 1$ (Zone III). DMSO behaves as a solute ($\bar{H}_{II} = \bar{H}_{II}{}^0$) and water as a pure solvent ($\bar{H}_I = H_I{}^0$). The value $\bar{H}_{II}{}^0 - H_{II}{}^0 = -2930 \pm 100$ cal mole^{-1} has been found.

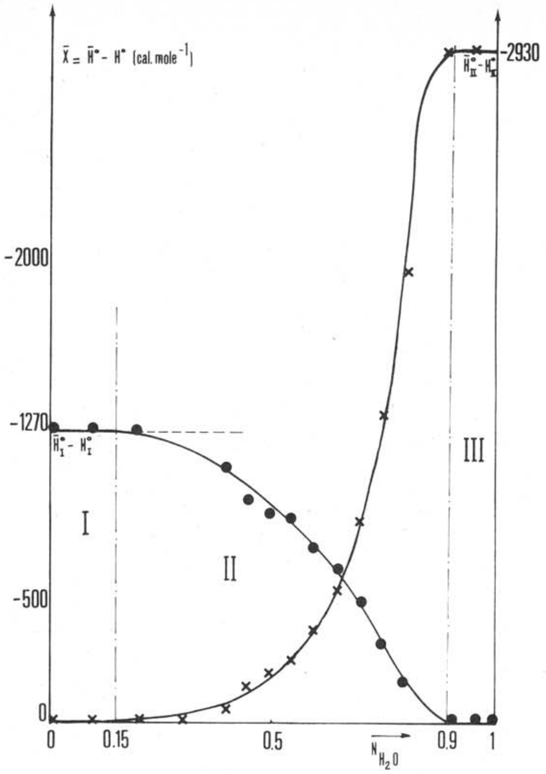

Figure 7. Dependence of $X = \bar{H} - H^0$ on molar ratio of water.

As it stands, this experiment allows the student to simply realize the idea of partial molar value. The results he obtains also bring him to observe various behaviors of water and DMSO, the former being solvent, the latter solute, and vice versa. Thus the choice of standard states, infinitely diluted or pure substance, can be clearly understood for all problems dealing with solution chemistry.

Conclusion

The results obtained by our students very closely agree with those published by various laboratories for which calorimetric measurements are a routine. Nevertheless, this experiment chiefly aims at introducing the students to this rather new technique which shall develop owing to a lack of experimental data, especially for ionization in hydro-organic mixtures.

It also allows students to become aware of the physical significance of various quantities introduced in their lectures on chemical thermodynamics.

Acknowledgment

We are indebted to D. Deville for technical assistance.

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