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On the Design and Efficiency of Isothermal Reaction Calorimeters

S. SUNNER and I. WADSÖ

Thermochemistry Laboratory, University of Lund, Lund, Sweden

A number of isothermal reaction calorimeters have been designed, built and tested. From an initial, very simple Dewar-type calorimeter a system was developed that showed an accuracy of 0.1 % and an equilibration time less than 2 minutes. To check the accuracy of the electrical calibrations, the heat of solution of potassium chloride was measured. The results obtained were compared with those of previous investigators.

In principle, changes in enthalpy accompanying a chemical reaction can always be calculated from heat of formation data, given that these are available for all the participating substances. In most cases this is not so — even the determination of a single heat of combustion value can be a laborious and very time-consuming task. Besides, in some reactions one (or more) of the participants may be too unstable for investigation by the combustion method [1]. A few years ago we therefore began to develop suitable apparatus for reaction calorimetry.

The variety in types of chemical reactions makes it impossible to design a more or less universally useful reaction calorimeter (in the same sense as a bomb calorimeter can be constructed). We therefore restricted the methodological work to calorimetric equipment suited to reactions obeying the following limiting conditions:

1. The reactions should be reasonably fast, the duration of the reaction period not exceeding one hour.
2. The total amount of heat evolved (or absorbed) during the reaction should be 50 cal. or less.

Further, the following conditions should be emphasized:

3. The size of the calorimeter should be *ca.* 100 ml.
4. The calorimeter should be simple in design and easy to operate, and
5. The accuracy achieved should be 0.1 % or 0.05 cal. whichever is larger.

Having these conditions in mind it was felt that a calorimeter of the "constant-temperature environment" (isothermal) type should be adopted. Furthermore, there being no systematic treatise on reaction calorimeters available, it was decided to start by assembling a very simple Dewar-type calorimeter, and from the experience gained with this, to develop a more elaborate apparatus.

Altogether five different calorimeters have been built and tested, and the present paper reports briefly on the experience gained with these.

CALORIMETERS IN THE DEVELOPMENT STAGE

The essential features of design of the calorimeters are shown in Fig. 1. The second earliest type (A) consisted of a silvered Dewar vessel with an inner thin-walled glass-shield (e) and an inner socket standard joint *. All connections were made through the cone-joint: the thermistor (a) (in the beginning a Beckmann thermometer was used); the calibration element (b) and two short glass tubes carrying the stirrer (c) and the ampoule holder (d). A rigid mounting was achieved by use of sheets of cork interspaced by cork crumbs as insulating materials. The inner end of the standard cone-joint was protected against absorption of moisture from the calorimeter liquid by a paraffin wax-poly*iso*butene coating.

The temperature was measured by use of a thermistor (Stantel F 2311/300) in a conventional Wheatstone bridge arrangement. The thermistor was sealed into a glass tube; only the small thermistor bead extruded into the calorimeter liquid. The stirrer hung freely through the glass tube into the calorimeter liquid and was mounted directly on the shaft of a 600 rpm synchronous motor. At the start of an experiment, the Dewar-vessel was completely submerged in a thermostat, the temperature of which was constant to within 0.002°C. After equilibration the measurement was performed in the usual way by observing the temperature during the initial, reaction and final periods. The reaction was started by breaking a sealed glass ampoule on the bottom of the Dewar.

The heat equivalent of the calorimeter was determined by passing a known current through the known calibration resistance for a known length of time.

Although this common type is very easy to build and operate, it suffers from several weaknesses. The reproducibility was not very high, ± 0.5 %. The reasons for this are several. The mounting of the stirrer was not rigid enough to ensure an even heat of stirring. The ampoule, which was positioned very near the stirrer, broke irregularly causing a sudden change in the heat of stirring. The most serious disadvantage, however, was that the time for reaching thermal equilibrium was very long mainly due to the slow equilibration. This calorimeter has been used for several measurements [2,3].

In order to overcome these difficulties a new calorimeter was built (Fig. 1). This consisted of a steel can (B) which could be used together with one of three different surrounding systems — a solid copper block (B 1), a double walled glass flask (B 2) or a single-walled glass flask (B 3).

The calorimeter can was made out of high grade stainless steel and consisted of a thin-walled cylinder to which a lid and a bottom had been soldered. A

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* The first calorimeter built consisted of an ordinary Dewar vessel, volume 150 ml, fitted with a heavy rubber stopper.

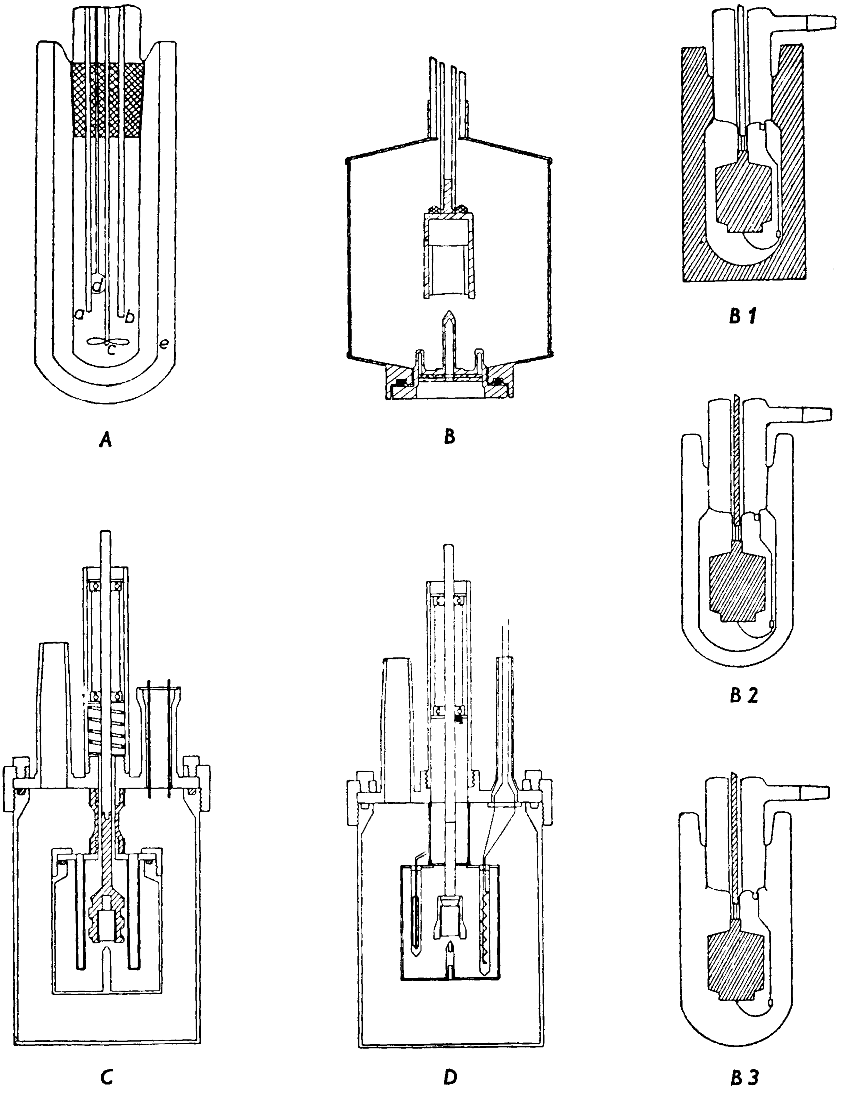

Fig. 1. Principle design of the calorimeters.

plug, machined from one piece of steel and having two wells was screwed into the bottom, and a high-vacuum tight seal was achieved by use of an O-ring gasket. The central well served to house the thermistor and the concentric well contained the calibration heater. This consisted of a 2 mm strip of thin mica on which a 0.15 mm manganin wire was wound (resistance 15 Ω). The strip was inserted into the bottom of the well and insulated from the walls by use of mica. The lower part of the well was closed by a PVC ribbon; further insulation between the heater and the outside of the plug was effected by a PVC disk kept in place by a steel plate.

The calorimeter can was sealed to a tube extruding from a hollow glass stopper. Through the stopper, the space between the calorimeter can and the surrounding flask could be evacuated. The electrical connections were carried from the plug in the calorimeter can to four terminals placed on a strip of phosphor-bronze, and then passed through the stopper to the outside of the calorimeter.

The stirrer was made of steel and shaped like a three-armed clutch grasping the ampoule and provided with small wings for the stirring. It was sealed with sulphur to a short glass tube, the upper end of which was sealed to a steel rod. The stirrer and shaft were precisely centered during the sealing operation. The steel rod was mounted in two ball bearings outside the hollow stopper and could be moved up and down during a run.

At the start of an experiment, the calorimeter was held in an upside down position. The stirrer shaft was moved so that the ampoule holder projected from the can. The ampoule was inserted and the stirrer was moved back to give a leak-proof seal between the lid of the can and the ampoule holder by means of a small rubber gasket. The calorimeter can was filled with 90 ml of solution, the plug was screwed tight and the can was inserted into the jacket, which was afterwards submerged in the thermostat.

This calorimeter can together with the surrounding system (B 1) fulfilled the given conditions reasonably well and was used for several measurements [4-8]. It was, however, not convenient for reactions with a heavy second reaction component (bromine, or certain solids) as the stirring did not affect the liquid in the ditch between the thermistor and the calibration element wells. Further, the stainless steel was corroded by bromine or showed catalytic activity in the reaction $SO_2 + Br_2$ or I_2. Finally, with certain calorimeter liquids, *e. g.* amines, the rubber-gasket did not always give a leak-proof seal due to swelling or dissolution processes.

We therefore built a third calorimeter (Fig. 1, C), of a rather common design (*e. g.* Ref.[9]). This was machined from stainless steel and consisted of a body, a lid with tubes for the thermistor and the calibration element and a screw-nut ring. The high-vacuum seal was made with an O-ring gasket. All inner parts were coated with several layers of teflon, of total thickness 0.12 mm. The stirrer was made from a teflon-rod. The calorimeter can hung from the lid of the surrounding chromium-plated brass can in a tube of teflon.

This calorimeter was tested and immediately rejected because the equilibration was very slow, particularly if the calorimeter can was not completely or almost completely filled by liquid.

THE FINAL CALORIMETER

Finally, a calorimeter (Fig. 1, D), was built according to the main principles of the design of calorimeter B.

A thin-walled (0.5 mm) open can machined from one piece of brass was silver soldered to a brass lid. The bottom had a central rod to support an ampoule-breaking pin. The lid was provided with two thin-walled tubes, and had a central, wide opening surrounded by two concentric thin brass-rings. After being chromium-plated, all interior parts of the can were coated with teflon as described above.

The calorimeter can hung from the lid of a surrounding brass can in a thin-walled (0.7 mm) glass tube which was sealed to the metal parts by Araldite applied to groves between the brass-rings. Thus, a rigid mounting as well as a high-vacuum tight seal were attained. In order to minimize the air gap between the stirring rod and the walls of the opening in the calorimeter can, a snugly fitting teflon coated brass gasket was introduced into the glass tube. The only free space between the gas phase in the calorimeter and the surrounding air was thus reduced to a 0.5 mm air gap around the stirring shaft.

The combined ampoule holder and stirrer was made of teflon-coated stainless steel and fastened to a teflon rod, the upper end of which was screwed on to the steel spindle of the stirring device. The whole stirrer was exactly centered and could be easily unscrewed from the lid of the outer brass can.

The thermistor was introduced into one of the tubes in the calorimeter can. The calibration element was placed in the second tube and both tubes were vacuum-tightly sealed with Araldite. The electrical connections were passed through the outer can by metal-glass seals soldered to the lid of the can.

The interspace was evacuated through a B19 standard cone, using a mechanical rotary pump and a three stage glass mercury pump attached to a liquid air trap. The evacuation was very rapid and a vacuum better than 10^{-4} mm Hg was reached within a few minutes after the start of the pumping.

This calorimeter was very easy and rapid to operate, one experimental cycle being completed within *ca.* 1 h.

Technique of mixing

The reaction period was started by breaking a glass ampoule and mixing the liquid or solid contents with the calorimeter liquid. In order to achieve rapid mixing a modification has been developed of a well-established procedure [9-12], in which the stirrer performs the breaking of the bulb.

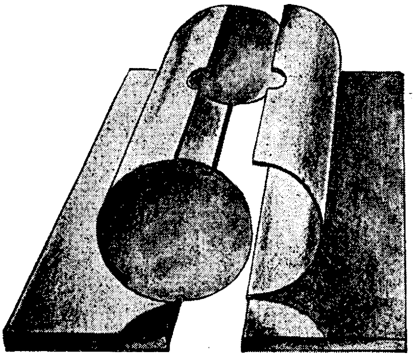

Fig. 2. Ampoule mould.

The ampoules were blown in a mould (Fig. 2) from selected thin-walled glass tubing. The method has two advantages: the ampoules are of uniform and predetermined size, and the end walls are very thin, facilitating the breaking and minimizing possible heat effects. For liquid samples, the ampoule shaft was drawn to a fine capillary as near the bulb as possible and for solid samples, the shaft was only slightly narrowed. When the sample had been introduced, the bulb was placed in a small copper block which was cooled by dry ice and the shaft was sealed very close to the bulb wall with a micro flame. The ampule was inserted centrally in the stirrer which during rotation gave the liquid an upward motion. By lowering the stirrer, a steel or platinum needle was forced to break through the end walls of the ampoule and a rapid mixing was achieved, the contents of the bulb being thrown out into the calorimeter liquid.

Heat effects arising from bulb breaking

Many authors have pointed out that the breaking of a bulb may give rise to one or more small heat effects[11-13]. Principally such a heat effect can be traced back to one or several of the following causes:

1. The heat of stirring is dependent on the environmental situation — other conditions being equal. If the bulb is situated close to the stirrer the heat generated by friction between the liquid and the unbroken bulb might be significantly different from that generated between the liquid and the remaining parts of the broken bulb. This effect is the only one which is dependent on the speed of stirring and can therefore easily be detected by observing the time-temperature curves before and after breaking an empty bulb[12]. By varying the speed of stirring the highest rpm value can be found at which the change in the heat of stirring is insignificant.

It is of course desirable to make the breaking of the bulbs as uniform as possible. This is difficult when using the type of bulb which is very common and which we used in our first apparatus. However, a moulded bulb tends to break very uniformly. In our first calorimeter we found a varying and sometimes quite appreciable heat effect of this kind. It was not detectable in calorimeters B and D.

2. The heat of rupture of the bulb depends on the mechanical properties of the glass: wall thickness, internal strain *etc.* With rather large and rigid ampoules, the heat of rupture may be considerable[11].

In our case, in which the volume of the bulb is only *ca.* 1 ml and the end walls break through for a pressure of about 10 g this effect is negligible.

3. The heat of wetting of the inner surface of the glass bulb is usually a negligible quantity. Only in microcalorimetric measurements of, *e. g.*, heats of adsorption is it necessary to take this effect into consideration[13].

4. Heat effects due to a change of state of one or two of the phases in the calorimeter may or may not be significant depending on the experimental conditions. Bartell and Suggitt[11] have pointed out that the breaking of an evacuated bulb is followed by an evaporation. In the same way, the rupture of a bulb partly filled by a volatile liquid is accompanied by a condensation process.

5. The vaporized reactant in a partly filled ampoule may partly escape the surrounding liquid when the bulb is broken.

The magnitude of both effects 4 and 5 are easily estimated from vapor pressure data and the volume of the gaseous phase in the bulb. With 1 ml bulb they are usually negligible.

Time of equilibration

In high precision calorimeters it is of great importance to minimize the time of equilibration as much as possible. The method of comparative measurements is not rigorously applicable as the heat cannot be generated at the same rate in the calibration experiment as in the actual measurement. Evidently, a simultaenous measurement of the kinetics and exothermicity of a particular reaction also requires a small time lag of the apparatus compared to the total time of reaction.

The time of equilibration was experimentally determined for the different calorimeters by studying the heat transfer constant, K, as a function of time in a calibration experiment. K is defined as

$$K = \frac{| g_f - g_i}{| \Theta_i - \Theta_f}$$

where

g_i is the rate of temperature change during the initial period,
g_f is the rate of temperature change during the final period,
Θ_i is the mean temperature during the initial period and
Θ_f is the mean temperature during the final period.

By chosing different reaction times in one and the same experiment, different values of K were obtained and plotted against the time elapsing from the moment when the calibration current was shut off until the middle of the final period. In such a way the curves in Fig. 3 were obtained.

The following conclusions can be drawn from the results: Any construction which creates an indetermined boundary of the calorimeter system towards the surroundings leads to a slow equilibration. A stopper which is in reasonably good contact both with the calorimeter system as well as with the surroundings and which contains insulating materials (in order to slow down the heat transfer) introduces an appreciable time lag. Also, a radiation shield with a not negligible heat capacity compared to that of the calorimeter increases the time of equilibration. The three-parted calorimeter C was slow, due to the low heat conductivity of steel together with the fact that the lid and the screw-nut ring represent rather heavy masses far removed from the liquid phase. When the amount of liquid in the calorimeter was increased from 90 to 110 ml (the vessel was then almost full), the time of equilibration dropped from 40 to 15—20 min. Both calorimeter B with single glass wall (B 3) or copper block (B 1) as well as calorimeter D reached equilibrium rapidly. Indeed, D equilibrated within 2 min, as is best seen from the curve in Fig. 4.

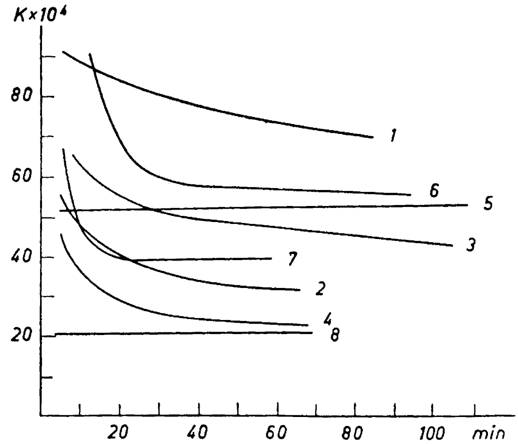

Fig. 3. K-values *versus* time. At time zero the input of *ca.* 50 cal of electrical energy was completed.

1) Ordinary Dewar, fitted with a heavy rubber stopper. 100 ml of water.
2) Calorimeter A. 75 ml of water.
3) Calorimeter B 2. 90 ml of water, 10^{-1} mm Hg.
4) Calorimeter B 2. 90 ml of water, 10^{-4} mm Hg.
5) Calorimeter B 1 and B 3. 90 ml of water, 10^{-1} mm Hg.
6) Calorimeter C. 90 ml of water, 10^{-1} mm Hg.
7) Calorimeter C. 110 ml of water, 10^{-1} mm Hg.
8) Calorimeter D. 100 ml of water, 10^{-4} mm Hg.

Temperature measuring system

The temperature was measured by a thermistor (Stantel F 2311/300) in a conventional D.C. bridge circuit [14]. Instead of using a high current sensitivity galvanometer together with scale and lamp outfit we have used a spotlight galvanometer (Cambridge Spot Galvanometer, 41159/2, sensitivity 0.03 μA/scale division for calorimeters A—C; Sullivan T 2001/D, sensitivity 0.005 μA/scale division for calorimeter D) together with a 40 × microscope. The sensitivity corresponds to a temperature change of the thermistor of less than 0.0001°C. The galvanometer was placed on a heavy iron plate resting on rubber knobs directly on a table. The mounting is simple and sturdy and the galvanometer is reasonably insensitive to vibrational disturbances.

The uncertainty in the determination of a temperature difference is estimated to ± 0.0002°C.

Electrical calibration system

The calibration resistance was wound from 0.15 mm lacquered and silk spun manganin wire on a thin-walled glass tube, coated with an epoxy resin and inserted into a glass or metal tube, which was then carefully sealed. The resis-

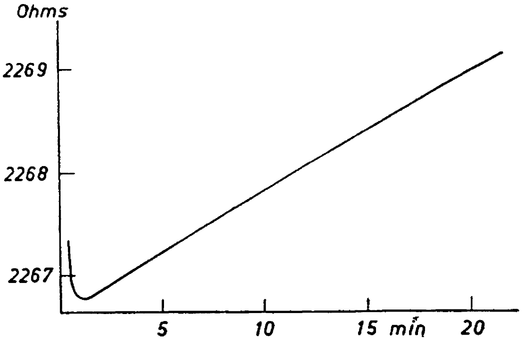

Fig. 4. Time of equilibration for calorimeter D, with water as calorimetric liquid. At time zero the input of *ca.* 50 cal of electrical energy was completed.

tance of the heater was measured between the leads to the heater at the midpoints between the calorimeter can and the outer jacket. The resistance was about 15 Ω (calorimeter B) and 65 Ω (calorimeter D). By separate experiments it was found that the resistance did not change within 0.001 Ω during a run.

The calibration was performed by the substitution method. The current from a 12 V storage battery was passed through a dummy heater, of the same resistance as the calibration resistance. When the current became constant, as found from the potential drop over a standard resistor in series with the dummy heater, the calibration was started by switching over to the calibration heater for a fixed time. The current was measured as above at regular intervals by use of a potentiometer (Leeds — Northrup Student Potentiometer, calorimeters A—C, and Rubicon High Precision Type B Potentiometer, calorimeter D).

The time during which the current was passed through the heater was chosen to equal the time of an actual experimental determination, if possible, the shortest time being *ca.* 240 sec. and the longest *ca.* 1 000 sec. The current was chosen to produce a temperature increase as near to that in an actual run as possible. The total input of electrical energy was usually kept at *ca.* 200 J. The uncertainty of the electrical calibration as calculated from the errors in the determinations of voltage, resistance and time was ± 0.15 % for calorimeters A—C, and $\pm$ 0.05 % for calorimeter D.

All heat quantities are given in thermochemical calories, defined by 1 calorie = 4.1840 abs. joules.

Heat of solution measurements of potassium chloride

Mishchenko and Kaganovich[15] suggested in 1949 the solution of potassium chloride in water be used as a standard process to calibrate reaction calorimeters. The authors critically examined the relevant literature and concluded that the best value for the integral heat of solution according to the equation

$$\mathrm{KCl\ (c)} + 200\ \mathrm{H_2O\ (l)} \rightarrow \mathrm{KCl,\ 200\ H_2O}$$

is $\Delta H_{25°} = 4\,194 \pm 3$ cal.mole^{-1}.

In order to check the reliability of our calorimeters we therefore made heat of solution measurements with calorimeters B 1 and D.

A sample of pure KCl (Merck's pro analysi) was pulverized, carefully dried at 105°C for 2 h and stored in vacuum over phosphorus pentoxide. About 800 mg were weighed out, corresponding to a molar ratio KCl to H_2O of *ca.* 1 to 450. With calorimeter B 1 two sets of calibration experiments were performed (Table 1), one with pure salt and pure water (I) and the second with potassium chloride solution (II). The first set together with the dissolution experiments (Table 2) gave ΔH(soln) at 24.73°C and the second set gave ΔH(soln) at 25.17°C. In calculating the results in Table 2 the average value from Table 1 was used and the heat of solution values therefore refer to 24.95°C.

In Table 1, the first column gives the corrected logarithmic resistance ratio value (which is proportional to the temperature increase), the second column the input of electrical energy in calories and the third column the value of the heat capacity in calories per unit of $\log(R_i/R_f)$. In Table 2, the first column gives the amount of KCl (vacuum weight), the second the corrected temperature increase as above, the third column gives the heat absorbed, the forth

Table 1. Calibration experiments. Calorimeter B 1.

	$10^4 \times \log(R_i/R_f)$	q, cal.	$\varepsilon \times 10^{-2}$
I	64.085	44.046	68.73
	64.450	44.349	68.81
	64.442	44.265	68.70
	64.667	44.340	68.57
	62.114	42.699	68.74
			Mean 68.71 ± 0.03
II	64.621	44.265	68.50
	64.715	44.298	68.45
	63.680	43.614	68.49
	61.123	41.817	68.41
	63.533	43.539	68.53
			Mean 68.48 ± 0.03

Table 2. Heat of solution measurements. Calorimeter B 1.

mg KCl	$10^4 \times \log(R_i/R_f)$	q, cal.	ΔH(soln) cal.mole^{-1}	$\Delta H°$(soln) cal.mole^{-1}
816.73	66.785	45.811	4 182	4 180
829.40	67.975	46.627	4 192	4 190
770.28	63.006	43.219	4 183	4 182
766.78	62.586	42.931	4 174	4 173
645.63	52.880	36.273	4 189	4 190
				Mean 4 183 ± 3

Table 3. Calibration experiments. Calorimeter D.

$10^4 \times \log (R_i/R_f)$	q, cal.	$\varepsilon \times 10^{-2}$
52.148	47.12	90.36
53.097	48.01	90.41
54.733	49.47	90.38
53.535	48.30	90.22
54.259	48.95	90.22
		Mean 90.32 ± 0.05

Table 4. Heat of solution measurements. Calorimeter D.

mg KCl	$10^4 \times \log (R_i/R_f)$	q, cal.	ΔH(soln) cal.mole^{-1}	ΔH°(soln) cal.mole^{-1}
891.78	55.416	50.05	4 184	4 187
871.10	54.041	48.81	4 177	4 180
923.33	57.299	51.69	4 173	4 177
919.06	56.974	51.46	4 174	4 179
889.80	55.378	50.02	4 191	4 184
947.72	58.901	53.20	4 185	4 189
			Mean	4 183 ± 2

column gives the uncorrected heat of solution in cal.mole^{-1} and the last column gives the heat of solution value corrected to KCl, 450 H_2O and 25.00°C. The magnitudes of the corrections were obtained from the literature [16,17].

The same series of experiments were performed with calorimeter D, although only one set of calibration experiments was taken. The results are shown in Tables 3 and 4.

The agreement shows that systematic errors are either absent or equal in the two calorimetric systems. However, the difference between our value and that recommended by Mishchenko and Kaganovich, corrected to KCl, 450 H_2O, 4 196 ± 3 cal.mole^{-1}, is more than twice the sum of the standard deviations and therefore seems to be significant [18].

The recent careful investigation by Coops *et al.*[12] gives a heat of solution value of 4 126 cal.mole^{-1} for KCl, 5 170 H_2O. Corrected [16] to KCl, 450 H_2O this value becomes 4 165 cal.mole^{-1}.

From a comparison of the results given, it is obvious that systematic errors are present in one or more of the determinations. With calorimeters of an expected accuracy of *ca.* 0.1 %, the agreement between values obtained in different laboratories for a standard reaction should definitely be better. For the following reasons we question if the solution of KCl in water is really suitable for calibration purposes:

1. ΔH(soln)/ΔT at room temperature is too high (36 cal.mole^{-1} per centigrade).
2. On a molar basis, the heat of solution of KCl is inconveniently low. It might therefore easily be influenced by impurities, crystal shape and size, and dissolved gases in the water phase.
3. When used in connection with a measured reaction having a large temperature change, a rather large amount of KCl must be used. The con-

centration of the KCl solution will be high and the differential heat of solution for concentrated solutions is high. Thus not only has the temperature to be known with an accuracy of *ca.* 0.005°C but also the concentration must be very well defined in each experiment.

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