

The Design and Testing of a Reaction Calorimeter for Enthalpy Studies on Complex Formation

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For the determination of enthalpy changes accompanying the stepwise formation of metal complexes in solution, a "constant temperature environment" reaction calorimeter has been built and tested. The calorimeter is equipped with a device for the successive addition of known, varying amounts of a solution, containing either a central metal ion or the ligand. The system is electrically calibrated and the temperature is measured by use of a thermistor. After each single experiment, the calorimeter is quickly brought back to the initial temperature by blowing a precooled gas through a built-in cooler.

The temperature sensitivity is $\pm 1 \times 10^{-4}$ degrees, corresponding to an accuracy of ± 0.02 cal or $\pm 0.2\%$ of the heat of reaction, whichever is larger. The time of equilibration of the system is less than 3 min.

The calorimeter has been tested by measuring the heat of neutralization of potassium hydroxide by hydrochloric acid, the heat of solution of potassium chloride and the heat of dilution of hydrochloric acid.

During recent years it has become more and more evident that the formation and stability of complexes between a central metal ion and a variety of ligands are governed to a great extent by entropy factors. This was primarily found from studies of equilibrium constants and their temperature dependence for strong chelates.¹ Even in cases where ΔH° was found to be positive, the complex species could still be rather strong, because of a large positive value of the entropy change. Later, it was found for more complicated systems where more or less weak complexes are successively formed, that this method could give quite erroneous results.²

The enthalpies of formation have also been determined in a direct way by calorimetric investigations and this method should generally be capable of giving more precise results. In most cases, rather crude methods have been

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used, not particularly suitable for the study of not quantitatively formed complexes. An interesting and suitable technique was developed by Sillén and Schlyter.^{3,4} These authors refined the method of thermal titrations, as used by Jordan and Alleman⁵ in studies on chelates. The principal advantages of Sillén and Schlyter's method are that one of the reaction solutions can be repeatedly added in an unbroken series of measurements and that a device was introduced to cool the calorimeter content to the standard reference temperature between each single experiment.

In the present work a reaction calorimeter was designed and tested, in which the mentioned advantages were incorporated together with a number of well-known thoroughly tested constructional features taken over from general reaction calorimetry.⁶⁻⁸

APPARATUS

The calorimeter. The calorimeter is of the "constant temperature environment" type and consists of an outer, nickel-plated brass can with lid and sleeve and an inner glass vessel with gold-plated lid (Fig. 1). The calorimeter was made of an ordinary 250 ml beaker, which was cut to hold approximately 200 ml. A goldplated threaded brass ring was sealed to the rim of the beaker using a thermosetting epoxy-resin (Araldite 103/951). The beaker and its lid were assembled using a thin-walled gold-plated brass sleeve.

The two lids were permanently joined by means of two thin-walled stainless steel tubes. One of the tubes accommodated the central propeller stirrer operating at 500 r.p.m., the second tube carried the device for adding an external solution to a pipette inside the calorimeter (*cf.* Refs.⁹⁻¹⁰). The inner lid also had three short (gold-plated) brass tubes to which were sealed glass tubes with gold thimbles at their ends, accommodating a thermistor, a heater and a cooler, respectively. The cooler consisted

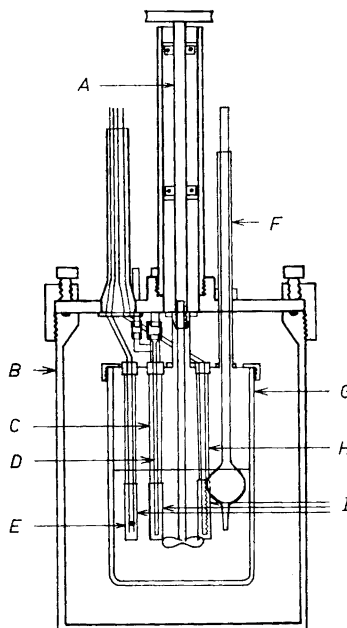


Fig. 1. Calorimeter vessel with jacket. A, stirrer; B, jacket; C, cooler; D, cooling gas inlet tube; E, thermistor; F, pipette; G, reaction vessel; H, heater; I, gold thimbles.

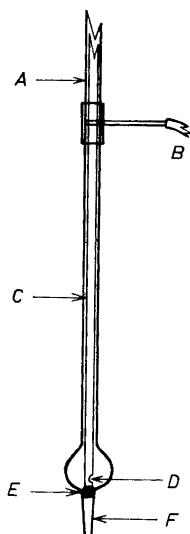


Fig. 2. Pipette. A, connection to the buret; B, connection to rubber bladder; C, inner tube; D, inlet hole; E, ground seal; F, exit tube.

of a central inlet tube through which a pre-cooled gas could be forced to the bottom of the gold thimble, leaving the calorimeter through the outer glass-tube. The inlet and outlet tubes were connected to the outside via metal tubes in the outer lid using short pieces of rubber tubing.

The heater was made from 0.15 mm laquered and silk spun manganin wire, soldered to 0.5 mm copper leads. The total resistance was $21.000 \pm 0.004 \Omega$. The wire was wound on a small piece of glass tube and introduced into its gold thimble which was then filled with silicon oil.

The dispensing device consisted of a silicon treated pipette with a spherical cavity of 2–5 ml volume and a short exit tube (Fig. 2). The exit tube and the cavity could be submerged into the solution in the calorimeter or wholly raised above the surface of the liquid while still being inside the measuring system. A rapid equilibration could be achieved between each added quantity of external solution and the contents of the calorimeter when the pipette was in its lower position. In the upper position it could then be very reproducibly emptied. The pipette had an inner central glass-tube, outer diameter 2.5 mm, bore 1 mm, sealed at its lower end, which was carefully ground to give a leak-proof seal towards an internal seat in the pipette between the cavity and the exit tube. A small hole was drilled in the glass tube just above its lower end. A known amount of external solution could be introduced from a precision all-glass syringe outside the thermostat, connected to the glass-tube, using a few millimeters length of rubber tubing. The plunger of the syringe was spring-loaded and operated from a micrometer screw, each turn corresponding to 0.2 ml. The filling and emptying operations together could be performed with a high reproducibility, the standard deviation in the dispensed volume being only ± 0.0016 ml.

The outer calorimeter can could be wholly submerged in a thermostat, kept at $25.40 \pm 0.005^\circ\text{C}$. An O-ring seal between the lid and the can gave a leak-proof closure. All connections between the interior of the system and the surroundings were carried through metal chimneys extruding above the surface of the thermostat water.

Temperature measuring system. The temperature was measured by use of a 2000Ω thermistor (Stantel F 23), a conventional DC-Wheatstone bridge and a Kipp and Zonen light-spot galvanometer AL 2 (R_i 350Ω , 2.5×10^{-9} A per scale division). At a total bridge current of 0.4 mA, a change of 0.1Ω in the decade box corresponded to 2.3 scale divisions. The galvanometer stability allowed readings reproducible at least to 0.1 scale division.

Electrical calibration system. This was built according to Sunner and Wadsö.¹¹ The potential across a standard resistor of $10.003 \pm 0.002 \Omega$, in series with the heater, was measured by use of a potentiometer bridge (Cambridge Vernier) to within 1 part in 10 000. A 6 V, 190 Ah storage battery was unloaded through a 21Ω dummy for at least one hour before each calibration experiment, to ensure equilibrium conditions in the electrical circuits. The calibration time was measured by an electric contact stop watch (Jaquet 309 d) operated from the dummy-heater-reversing switch. The difference between the true calibration time as obtained from a comparison with a 1000 cycles standard frequency signal by use of a counter, and the time as read on the watch rarely exceeded 0.03 sec. In all experiments, the calibration time was between 2 and 3 min and thus, the time error in the electrical energy supplied to the calorimeter was *ca.* 1 part in 4000.

From the errors in the heater resistance, the current through the heater and the time, a combined probable error in the determination of the electrical energy of 1 part in 2000 is obtained.

Experimental procedure

The calorimeter vessel was filled with 100.0 ml of an aqueous solution (or pure water) at 25°C and assembled. A known quantity of external solution was introduced into the pipette (lower position). Equilibrium was established as found from the time-temperature curve. Then the resistance change during an initial period of 5 min was determined. Two seconds before the start of the reaction period the pipette was raised and opened and the liquid in the bulb was dispensed into the calorimeter liquid. The draining time of the pipette depended on the amount of liquid inside: for 2.0, 1.0 and 0.5 ml it was found to be 12, 8 and 5 sec, respectively. 10 to 20 sec after the pipette had been emptied, a small over-pressure was applied to its interior by pressing twice with 5 sec interval on a rubber bladder connected to the upper tube of the pipette (outside the calorimeter assembly). By this means, the last drops of liquid adhering to the tip of the pipette were removed. At the same time a small amount of moisture-saturated air was blown into the calorimeter. Blanks showed, however, that no detectable heat-effect accompanied this procedure. After one minute the pipette was closed and submerged into the calorimeter liquid.

The temperature at the start of each experiment was so adjusted that the initial temperature of the reaction period could be kept at $24.998 \pm 0.002^\circ\text{C}$. Resistance *versus* time was recorded every minute during the reaction period (duration less than or equal to 4 min) and during the final period. The first reading during the reaction period was taken 2 min after the start of the period. The length of the final period was 5 min.

Provided the reaction had been exothermal, a stream of carbon dioxide, pre-cooled to 0°C, was blown through the cooler until the temperature had reached a suitable value, due allowance being made for the heat transfer from the jacket during the following 30 minutes equilibration period. Thereafter, a calibration or a new reaction experiment could be performed immediately.

The total amount of external solution added could be 20 ml without jeopardizing the necessary requirement that the tip of the pipette must be above the surface of the solution when the pipette is drained.

CALCULATION OF RESULTS

When the temperature rise was less than 0.1°C no significant error was introduced by putting the temperature inversely proportional to the resistance of the thermistor. In checking experiments — heat of neutralization of KOH by HCl and heat of solution of KCl — the temperature rise was above 0.1°C and the approximate function $T_1 - T_2 = -C \log (R_1/R_2)$ was used.⁸ The correction for heat exchange during the reaction period was done according to Dickinson's method.⁶

Several series of calibration experiments were performed on each chemical system with known, equal amounts of external liquid in the calorimeter. The

average values established a linear relationship between the heat equivalent of the system and the total amount of external solution added. Thus, it was not necessary to determine the heat equivalent after each addition (see below).

From the concentrations and amounts of the two solutions, the composition of the liquid phase could be calculated after each addition and thus, the enthalpy change could be referred to defined initial and final states.

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

TESTING OF THE CALORIMETER

Time of equilibration. When using a calorimeter for reactions in which the enthalpy change varies much from experiment to experiment, it is often difficult or at least impractical to perform a series of calibration experiments for each value of ΔT . In order to avoid systematic errors, the calorimeter therefore must respond quickly towards heat generation or absorption and reach equilibrium within a short time. It was found experimentally that the calorimeter reached equilibrium within 3 min after that the calibration current had been switched off, even though the rate of energy generation within the calorimeter exceeded the highest values encountered in any calibration measurements by a factor of seven.

When the calorimeter was cooled, however, it took almost 30 min for the system to equilibrate. Around the entrance and exit tubes of the cooler a cold spot developed which was in rather poor thermal contact with the calorimeter content. Besides, the connections to the outer lid (rubber tubes) only slowly reached equilibrium. This unfavourable property of the calorimeter did not influence upon the accuracy of the measurements but was responsible for the rather slow operation: The time interval between two successive experiments (additions) had to be 45 to 60 min of which *ca.* 50 % was equilibration time after cooling.

Table 1. Calibration experiments. The heat equivalent is expressed in cal. per ohm.

	1 ml	2 ml	10 ml	12 ml
		2.114	2.267	2.457
			2.272	2.459
		2.113		2.468
2.097				2.451
		2.112		2.459
2.096		2.120		2.465
		2.109	2.262	
		2.114		
		2.117	2.269	
Average	2.097	2.114 \pm 0.002	2.268 \pm 0.003	2.460 \pm 0.003
Calculated value	2.095	2.114	2.268	2.460
Difference	0.002	—	—	—

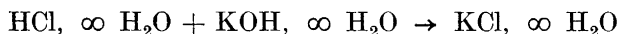
Table 2. Heat of neutralization of KOH by HCl at 25°.

Additions	ΔR ohm	ϵ cal.ohm ⁻¹	$-\Delta H$ cal.mole ⁻¹	$-\Delta H_{\infty}$ cal.mole ⁻¹
1 *	6.090	2.249	13 696	13 385
2 *	5.650	2.427	13 652	13 347
1	6.250	2.202	13 701	13 331
2	6.175	2.229	13 702	13 343
1	6.201	2.219	13 698	13 328
2	6.067	2.265	13 680	13 316
3	5.967	2.295	13 633	13 274
Average				13 332 \pm 11

* These experiments were performed with equivalent amounts of KOH and using 100 and 120 ml of calorimeter solution, respectively.

The reproducibility of the measurements can be judged from the results of several series of calibration experiments (Table 1). For each series new amounts of calorimetric liquids as well as external solution (1, 2, 10, or 20 ml) were used. In all experiments the total change in thermistor resistance was between 1.5 and 1.7 Ω , equivalent to *ca.* 0.03° temperature change. It is seen from the table that the standard deviation for a series of runs using the same amount of liquid is 0.10–0.15 %, which is a very satisfactory figure. The deviations of the four average values from a linear relationship, calculated from the data by use of the least square method, are seen from the last row of the table.

The heat of neutralization of aqueous KOH by HCl. This reaction has been carefully investigated *i.a.* by Pitzer¹² and Rossini.¹³ The calorimeter was charged with 100.0 ml of 0.1000 M KOH. Hydrochloric acid, 0.5000 M, was added from the pipette, each addition being 2.009 ml. By use of the known heats of dilution¹⁴ of HCl, KOH and KCl the result of each experiment was corrected to infinite dilution:



The results of the measurements are found in Table 2. The first column gives the final, total number of 2.009 ml additions of 0.5000 M HCl. The second column gives the change in thermistor resistance, the third the heat equivalent of the system in its final state in cal. per ohm, the fourth and fifth columns give the molar enthalpy change for the real reaction and for the reaction occurring at infinite dilution, respectively.

Table 3 gives a summary of a number of earlier determinations of the same datum. Except for the value found by Papee *et al.* (at very low concentrations) the values are very close to each other, the average being 13 328 cal.mole⁻¹ which is very close to our result.

Heat of solution of KCl. Although the dissolution of KCl in water as a standardizing reaction in calorimetry has been subjected to criticism, it was felt to be of interest to determine this datum for the purpose of comparison. An analytical grade KCl, finely pulverized, dried at 110° and stored in a desiccator above silica gel, was used without further analyses. A small, thin-walled glass

Table 3. Survey of data on the heat of neutralization of strong acid by strong base at infinite dilution and 25°C.

Author	Base-acid	Approx. conc. interval	Obtained values, cal.mole ⁻¹ given recalculated *	
Richards and Rowe ¹⁵	NaOH HCl KOH HNO ₃ LiOH H ₂ SO ₄	0.25—1 M	(13 655 ± 35)**	(13 356 ± 35)
Richards and Hall ¹⁶	Recalculation of Richards and Rowe		13 644 ± 20 **	13 335 ± 20
Rossini ¹³	— » —		13 320 ± 16	13 327 ± 16
Pitzer ¹²	NaOH HCl	0.1—1 M	13 360 ± 16	13 336 ± 16
Bender and Biermann ¹⁷	NaOH HCl	3 M	13 320 ± 20	13 314 ± 20
Papee, Canady and Laidler ¹⁸	NaOH HCl	5.10 ⁻⁴ —3.10 ⁻² M	13 500 ± 50	
Sacconi, Paoletti and Ciampolini ¹⁹	NaOH HCl	0.025 M	13 336 ± 11	13 325 ± 11
Davies, Singer and Staveley ²⁰	NaOH HCl	not precisely given	13 356 ± 11	
This Paper	KOH HCl	0.1—0.5 M		13 332 ± 11

* Whenever possible the recalculation has been done on the primary experimental figures with the values reported by Ackermann ²¹ and Rossini ¹³ (temp coeff.) and Natl. Bur. Standards, SVCTP C 500 ¹⁴ (correction to infinite dilution).

** At 20°C.

bulb was substituted for the pipette and the experiment was started by breaking the bulb towards the bottom of the calorimeter. The results of the experiments are shown in Table 4. Column 1 gives the amount of KCl, columns 2—4 are identical with those of Table 2 and column 5 gives the enthalpy change for the reaction $\text{KCl(c)} + 275 \text{ H}_2\text{O} \rightarrow \text{KCl, 275 H}_2\text{O}$.

About 60 papers have been published on the heat of solution of KCl in water. The results show a most discouraging spread. However, the data have been critically surveyed at the National Bureau of Standards, Washington ²² and by S. R. Gunn, ²³ and the most probable value for KCl, 275 H₂O should be close to 4204 cal.mole⁻¹. Our result is in fair agreement with this value.

Table 4. Heat of solution of KCl at 25°C.

KCl mg	ΔR ohm	ϵ cal.ohm ⁻¹	ΔH cal.mole ⁻¹	$\Delta H_{275 \text{ H}_2\text{O}}$ cal.mole ⁻¹
298.4	7.725	2.171	4 189	4 209
117.3	3.000	2.174	4 146	4 186
168.3	4.329	2.182	4 183	4 213
135.9	3.500	2.173	4 172	4 207
243.8	6.270	2.172	4 165	4 203
177.3	4.560	2.172	4 165	4 194
189.4	4.880	2.168	4 164	4 193
Average				4 201 ± 4

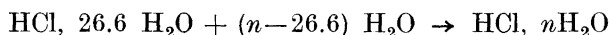
Table 5. Heat of dilution of HCl, 26.6 H₂O to HCl, *n* H₂O at 25°C.

<i>n</i>	ΔR ohm	ε cal.ohm ⁻¹	$-\Delta H$ cal.mole ⁻¹	Ref. ²⁴⁻²⁶	Ref. ¹⁴
1407	1.021	2.216	562.2 \pm 2.0 *	559	564
716	0.880	2.252	527.3 \pm 2.0 *	525	532
487	0.804	2.286	503.7 \pm 2.0 *	502	507

* Average deviation of two determinations.

Heat of dilution of HCl. As a third test on the reliability of the calorimeter, the heat of dilution of 2.000 M HCl was measured. The calorimeter was charged with 100.0 ml of pure water and the hydrochloric acid was added in 2.009 ml portions.

The results of two series of measurements are summarized in Table 5. Column 1 gives the number of moles of water, *n*, per HCl in the final solution, columns 2 and 3 are the same as in Table 2, and column 4 gives the enthalpy change for the reaction



Columns 5 and 6 give the corresponding values, calculated from Sturtevant's measurements²⁴⁻²⁶ and from SVCTP.¹⁴ All values are corrected for the change in vapor pressure due to varying concentrations.

The agreement is not quite as satisfactory as might be expected from the previous checks. However, the discrepancies are tolerable in view of the accuracy of the measurements aimed at and that the values of Sturtevant had to be corrected for a small systematic error, caused by the mixing device.²⁶

CONCLUSIONS

From the above it will seem that the present calorimeter is capable of giving results accurate to within 0.2 % when the total amount of heat evolved is *ca.* 3.5 cal (0.03° temperature rise) and to within *ca.* 0.5 % for 1.8 cal (0.015°).

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