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# Testing of the NBS Clinical Microcalorimeter



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E. J. Prosen and R. N. Goldberg

Thermochemistry Section  
Physical Chemistry Division  
Institute for Materials Research  
National Bureau of Standards  
Washington, D. C. 20234

April 1973

Interim Report

Prepared for  
National Institute of General Medical Sciences  
National Institutes of Health  
Bethesda, Maryland 20014

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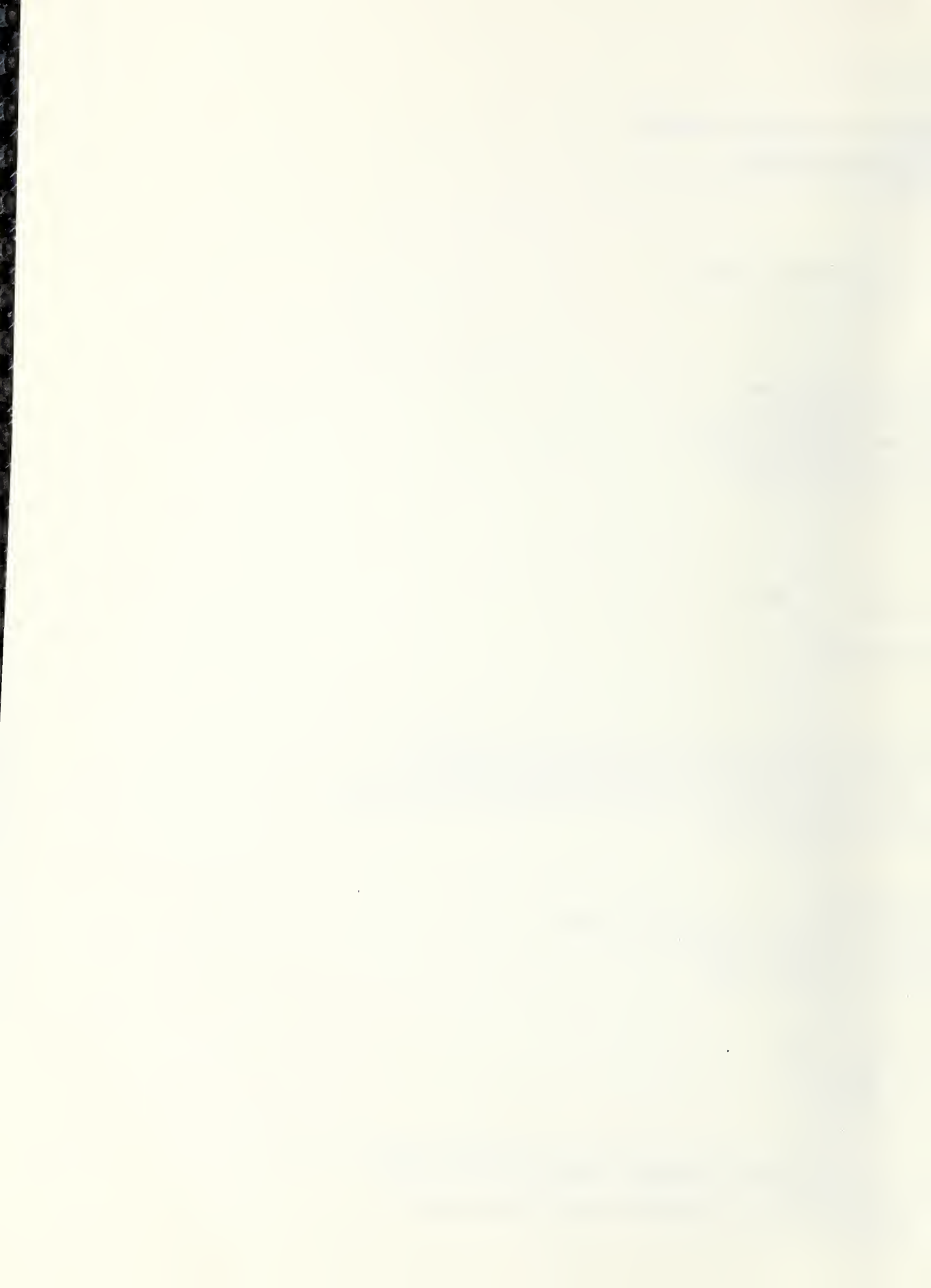
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Prepared for  
National Institute of General Medical Sciences  
National Institutes of Health  
Bethesda, Maryland 20014



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**U. S. DEPARTMENT OF COMMERCE, Frederick B. Dent, Secretary**  
**NATIONAL BUREAU OF STANDARDS, Richard W. Roberts, Director**



## Foreword

The use of clinical laboratory tests of physiological fluids for specific components has been rapidly increasing in the past few years. One aspect of this has been an increase in the number of tests for well-known particular substances for which satisfactory tests are available. Another equally important aspect is the increasing need of the physician and of the research biochemist for ready methods for determining other substances present in varying amounts in normal and pathological states. For this reason, the development of new techniques applicable to problems for which optimum solutions have not been found are of considerable interest in clinical and biological chemistry.

The universal occurrence of energy changes in chemical and physiological processes has caused the calorimeter to be considered as a potential tool for clinical chemical analysis and for observing biological processes for some years. The actual applicability, however, has been limited previously by lack or insufficiency of one or more necessary factors. Such factors include: instrument sensitivity and operational noise levels, instruments adapted to use of small samples, simplicity of instrumental operation and data reduction, and suitable mechanisms for sorting out specific processes from a melange of potential interferences. It was the judgment of the authors and of the National Institute of General Medical Sciences (NIGMS) that the understanding of these factors had developed to a point where a well coordinated attack on the application of micro-calorimetry would now lead to successful results.

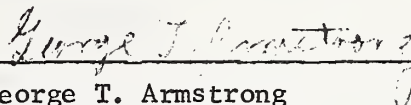
A program was established in the Thermochemistry Section (Physical Chemistry Division, Institute of Materials Research) at the National Bureau of Standards, and after some months was augmented with support from the NIGMS to demonstrate the feasibility of microcalorimetry in some specific areas useful in the Clinical Chemistry Laboratory. Dr. Robert S. Melville is the program officer for NIGMS. Collaborative support has been provided by the Clinical Chemistry Service (Dr. Donald Young, Chief), and by the Laboratory for Technical Development (Dr. Robert L. Bowman, Chief, and Dr. Robert L. Berger).

This is a report provided at the end of the first year of the NIGMS support of this work and summarizes a portion of the



work done. This report is one of four covering different aspects of the NBS Program. For the information of the reader, the titles and NBS Report numbers of the four reports are as follows:

NBS Report	73-178	Microcalorimetric Assay for Glucose in Human Serum and Plasma
	73-179	Design and Construction of the NBS Clinical Microcalorimeter
	73-180	Testing of the NBS Clinical Microcalorimeter
	73-181	Fine Structure in Thermal Growth Patterns of Bacteria by Microcalorimetry



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George T. Armstrong  
Principal Investigator



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Project Leader





## Testing of the NBS Clinical Microcalorimeter

by

E. J. Prosen and R. N. Goldberg

### ABSTRACT

The NBS Clinical Microcalorimeter has been tested for stability, sensitivity, ease of operation, and accuracy. The accuracy was tested by means of electrical calibration and the determination of the heat of neutralization of  $\text{HCl}(\text{aq})$  with  $\text{NaOH}(\text{aq})$ . The heat of this reaction agrees with the best literature value within the precision of the calorimeter. The precision is about 0.6 percent when measuring about 50 mJ of heat of chemical reaction. The accuracy is estimated as 1 percent. The precision of electrical energy determination is about 0.4 percent for energies of from 1 to 1400 mJ.



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## 1. Introduction

This report describes tests of the performance of the NBS Clinical Microcalorimeter. This calorimeter was designed and constructed [1] in order to be able to perform microcalorimetric measurements as part of a program, sponsored by the National Institutes of Health, investigating the applicability of microcalorimetry to clinical chemistry and to biochemistry.

The reader is referred to several books and articles [2, 3, 4] to obtain further background on the subject of microcalorimetry.



## 2. Measurement of Thermopile Voltage

The thermopile voltage of the NBS Clinical Microcalorimeter was amplified using a linear D.C. amplifier<sup>1</sup> (Keithley Model 140), the gain setting of which was generally set at  $10^5$  and only rarely set at  $10^4$ . The rise time of the amplifier was set at 5 seconds and it was not found necessary to use either the amplifier's zero suppression or input filter. Electrical ground for the thermopile signal was established at the input to the amplifier.

Calibration of the amplifier was periodically performed in the following manner: a stable current from a D.C. power supply (Sorensen Model QHS 40-.5) was passed thru four standard resistors (1- $\Omega$ , 10- $\Omega$ , 100- $\Omega$ , and 10-k  $\Omega$ ) in series with each other. The input voltage to the amplifier was then selected to be across one of the lower valued resistors. By measuring the voltage across both the entire voltage divider network and the amplifier's output terminal and by application of a small correction for the amplifier zero, the gain of the amplifier was calculated. The amplifier's gain, as measured in this manner, was found to be within 0.02% of its nominal value on the  $10^5$  scale and stable to within  $\pm 0.006\%$  over a period of one year.

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<sup>1</sup>Certain commercial products and instruments are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the products or equipment identified are necessarily the best available for the purpose.





The amplifier output was recorded both in analog and in digital form. The purpose of the analog record (obtained either with a Leeds and Northrup Speedomax XL-600 or Varian F80 recorder) was to give the calorimeter operator a visual picture of the course of an experiment, while the digital record was used to obtain all numerical results. The analog to digital conversion was accomplished using an autoranging digital voltmeter (Hewlett-Packard Model 3450A,  $\pm 1 \mu\text{v}$  or  $\pm 10 \mu\text{v}$  sensitivity, depending on range). The stability and accuracy of this voltmeter were checked periodically against saturated standard cells calibrated by the National Bureau of Standards. Using this procedure, the accuracy of the digital voltmeter was found to be within 0.0025% at a reading of 1.018 v, and to have a stability of  $\pm 0.001\%$  over a period of one year. During an experiment, a digital clock, having the line frequency as its time base, sent "read" commands to the digital voltmeter every 3 seconds. The time and voltage information was then processed thru a digital coupler (Hewlett-Packard 2547A) and recorded in typewritten form and on punched paper tape.



### 3. Calculation of Areas

In a properly designed heat conduction calorimeter, the thermopile voltage is a measure of the rate of heat transfer between calorimeter vessel and heat sink. A calorimetric experiments thus consists of measuring the thermopile voltage as a function of time continuously (or at 3 second intervals). These readings may be divided into three periods: a fore period, a main period, and an after period. During the fore period, no process heat is being liberated in the reaction vessel. Ideally, the mean of the measured voltages would be zero volts and flucuations about the mean would be due only to Johnson noise. The main period begins with the initiation of the reaction or electrical heating and the accompanying heat effect, which is detectable as a heat flow across the thermopile and a corresponding change in the thermopile voltage. After completion of the reaction or electrical heating, there will be an exponential decay of the voltage to the after period baseline which ideally should be the same as the fore period baseline.



The total heat effect,  $Q$ , to be associated with the reaction is proportional to the area,  $A$ , of the plot of voltage readings,  $E$ , versus time,  $t$ .

$$Q = k \cdot A$$

This area,  $A$ , in millivolt-seconds ( $\text{mv} \cdot \text{s}$ ) is the area of the curve above the extrapolated baseline from time  $t_1$  (at the end of the fore period) to time  $t_2$  (at the beginning of the after period).

To obtain the extrapolated baseline during the reaction period, a straight line was assumed from  $E(t_1)$ , the voltage at the end of the fore period, to  $E(t_2)$ , the voltage at the beginning of the after period.  $E(t_1)$  and  $E(t_2)$  were obtained by a least-squares straight line fit of the fore and after period readings, respectively. The area was obtained by the use of the trapezoidal rule.

All of the above calculations were done on a digital computer utilizing the digital voltage and time readings (taken at 3-second intervals throughout the experiment).

The electrical calibration experiments gave the value of  $k$ :

$$k = Q/A$$

where, in this case,  $Q$  is the electrical energy added to the calorimeter heater.



#### 4. Temperature of the Calorimeter

The temperature of the microcalorimeter was controlled by controlling the current through a heater wound on the inner jacket [1].

A modified Quartz Thermometer [6] was used to check the temperature stability of the inner jacket. In performing this test, the quartz thermometer probe was taped to the inside of the calorimeter's inner jacket, and a temperature record (sensitivity  $\pm 10 \mu\text{K}$ ) was obtained over a 15 hour period. This record indicated a steady drift of 0.00094 K for this entire period, while short term variations in temperature were with  $\pm 0.0002 \text{ K}$ .

The absolute temperature of the inner jacket, as measured with an NBS calibrated mercury-in-glass thermometer and a copper-constantan thermocouple junctioned between the inner jacket of the microcalorimeter and the mercury-in-glass thermometer, was determined initially to be  $29.85^\circ\text{C}$ . Several weeks later an abrupt change in temperature to  $30.80^\circ\text{C}$  was noted. It is believed that this jump was due to a break in a wire that connected a  $20\text{-k}\Omega$  resistor, which had been put in parallel with one of the manganin arms of the wheatstone bridge of the temperature control circuit on the inner jacket. More recently, the temperature of the calorimeter has been observed to be drifting gradually higher to  $31.00^\circ\text{C}$ . This may be attributable to relaxation effects in the resistors comprising the regulation network.





## 5. Time Constant and Speed of Operation of Calorimeter

The half-response time of the microcalorimeter, as determined by observation of the exponentially decaying portion of reaction peaks, was observed to be about 30 to 40 seconds. This corresponds to a time constant of about 50 seconds. This time constant has important implications as regards the speed of operation of a microcalorimeter. For example, it has been empirically found that a wait of twenty half-response times, or 10 minutes, is generally adequate to insure proper thermal equilibration of a calorimetric cell with the calorimeter block and thermopiles when an external heatsink, kept to within a degree of the calorimeter's temperature is employed to pre-equilibrate the reaction cell and its contents before inserting the cell into the calorimeter (pre-equilibration time approximately 5 minutes). The amount of time required to complete a run, following the thermal equilibration period in the calorimeter, is about 15 minutes. This allows sufficient time for both a mix and remix operation with the necessary recording of the fore, main, and after period voltage readings for each. Thus, total time elapsed from the inserting a cell into the calorimeter to end of a run is about 25 to 35 minutes. Using manual methods it is possible to do about 15 separate experiments during the course of an 8 hour day.



## 6. Quality of Baseline

The quality of the baseline or thermopile voltage readings, is an important characteristic of a heat conduction microcalorimeter, and is determined by the absence of electrical or thermal interferences and is ultimately limited by Johnson noise. For measurement of the heat effects accompanying rapid processes, as a consequence of the calorimeter's rapid response time, it is necessary to be concerned about the quality of the baseline over only a 15 to 20 minute interval. Observations of the baseline have indicated that peak-to-peak noise is generally within 30 nv over this sort of time interval. Since the sensitivity of the instrument is  $16.7 \text{ J}\cdot\text{v}^{-1}\cdot\text{s}^{-1}$  (see Section 7), or  $60 \text{ nv}\cdot\mu\text{W}^{-1}$ , this 30 nv peak-to-peak corresponds to  $0.5 \mu\text{W}$  of power peak-to-peak over a 30 second interval. The long term drift of the baseline has been found to be less than 100 nv over a 24 hour period.

It is worthwhile to note that the measured value of the thermopile voltage was generally within  $0.5 \mu\text{v}$  of electrical zero. Occasional severe deviations from electrical zero were attributable to the following causes: (1) water leaks from the reaction cells; (2) a severe thermal disturbance of the calorimeter, such as unscrewing the lids, and (3) an effect believed to be due to a pressure disturbance of the thermopiles whenever a reaction cell was fit too tightly into the silver box of the microcalorimeter. This latter effect was observed, for example, when excess wax, used in sealing earlier cells, was left on the side of that cell.



## 7. Electrical Calibrations

Electrical calibrations of the NBS clinical Microcalorimeter were performed using the permanent resistance heater installed in the silver box which is between the calorimeter thermopiles [1]. Current from a well-regulated D.C. power supply (Sorensen Model QHS 40-.5, stability  $0.0005\% + 50 \mu\text{v}$ ), operated in the constant voltage mode, was passed thru this calibrating resistor and thru a  $1000\text{-}\Omega$  standard resistor in series with it. Measurements of the voltages across the heater and across the standard resistor were made using a digital voltmeter (Hewlett-Packard Model 3450A,  $\pm 1 \mu\text{v}$  or  $\pm 10 \mu\text{v}$  sensitivity, depending on range). The interval of heating was determined [5] by means of an electronic counter (Hewlett-Packard Model 5325B) set to read to the nearest millisecond. Grounding of this calibration circuit was done at the heater connection to the power supply. The saturated standard cells, against which the digital voltmeter was checked, and the standard resistor were intercompared with other standards in this laboratory that had been calibrated by the National Bureau of Standards. The internal oscillator of the counter was checked periodically against the NBS 100 kHz frequency (stability of 1 part in  $10^{11}$ ) and found to be stable to within 5 parts in  $10^7$  over a period of one year. Power input to the calorimeter was calculated as the product of the potential across the heater and the current thru it, with a small correction (0.005%) applied for power generated in the heater leads. In applying this correction, it was assumed that one-half the power generated in the heater leads could be apportioned to the jacket (i.e. the aluminum block) and the other half to the calorimeter vessel. Total heat input to the calorimeter was the product of power



and time interval of heating.

The results of electrical calibrations are given in Tables 1 and 2. The results, shown in Table 1 were obtained when the calorimeter was at a temperature of 29.85°C and were performed (with the exception of run no. 52) with no sample cell contained in the silver box of the micro-calorimeter. In Table 2, the results reported were taken at an assigned calorimeter temperature of 30.80°C and a sample cell, containing approximately 300  $\mu\text{l}$  of water, was contained in the calorimeter's silver box. The calibration constant (units of  $\text{W}\cdot\text{v}^{-1}$  or  $\text{J}\cdot\text{v}^{-1}\cdot\text{s}^{-1}$ ) was calculated as the ratio of the heat input (mJ) to the calorimeter to the measured area (units of  $\text{mv}\cdot\text{s}$ ). A second way of obtaining this calibration constant was by application of a steady state power for a long time (13 to 16 half-response times of the calorimeter). Using this procedure [2], the calibration constant is calculated as the ratio of the steady state power to the steady state deflection of the thermopile voltage from its baseline. The values of the calibration constant, obtained in this manner, are given in parenthesis in Tables 1 and 2.

It will be noted that the calibration constant is the same, within the precision of the measurements, whether we use the integral energies or the steady power-deflection method (values in parentheses). The integral energy results are used since the areas were determined in the same way as in chemical reaction experiments. The calibration constant is thus taken as  $16.67 \text{ W}\cdot\text{v}^{-1}$  at either temperature. Measurements have not yet been made at widely different temperatures. Inspection of the data in Tables 1 and 2 shows no obvious trend with power level from 0.01 to 2.00 mW, time of heating from 10 to 800 seconds, or energy from 1 to





1400 mJ. Below 1 mJ, the area or electrical energy was perhaps not measured accurately enough and runs number 21,24,27, and 209 were omitted in averaging.

The precision of the determinations of the calibration constant with electrical energy can thus be taken as approximately 0.4 percent for energies from 1 to 1400 mJ.

## 8. Procedures Used in Calorimetric Experiments

A calorimetric experiment consists of several distinct operations, the details of which are described in this section.

### A. Preparation of Reaction Cell

Since the Kel-F reaction cells are not yet disposable, it is first necessary to clean a previously used cell by appropriate means. For acid-base experiments, the cleaning procedure employed was to rinse the cell several times with distilled water. After the last rinsing, the water was sucked out using a vacuum line in such a way as to not completely dry the inside of the cell. This procedure, identified as the "wet cell" procedure, was used to facilitate the mixing of the solutions. However, as will be shown, this procedure introduces a heat of dilution which can have serious effects on the accuracy of the results. More recently, it has been found that a "dry cell" procedure, i.e. one where the inside of the cell is completely dry, can be made to mix reliably if the solutions being used contain a trace amount (1 part in  $10^6$ ) of an inert wetting agent such as alkylphenoxy polyethoxy ethanol (trade name, Triton X-100). New cells, which have a hydrophillic surface treatment, do not require the use of the wetting agent nor the "wet cell" procedure. The "wet cell" procedure was used in all experiments summarized in this report.



## B. Cell Loading and Sealing

Solutions were introduced into the reaction cells with syringes. Following the loading of one side of a cell with that solution containing an excess quantity of one of the reactants (solution A), that side of the cell was tilted 90 degrees to the side so that the solution would wet that side of the cell and thus would flow when mixing was desired. The other side of the cell was then loaded carefully with the solution containing the limiting amount of reactant (solution B). Quantities of solutions introduced into a reaction cell were determined by weighing the empty cell, the cell containing solution A alone, and the cell containing both solutions A and B. Care was taken not to wet the "O"-ring seat at the top of a cell.

Cell sealing was done in one of two ways: (1) use of small Kel-F or Teflon plugs that fit into the cell entrance portals and that were sealed over with melted wax and (2) use of no. 2-1 Buna-N "O"-rings that were compressed by means of small Teflon plugs. The sealing process is extremely important, for if a cell is not properly sealed, the heat of vaporization of water, as indicated by a large endothermic voltage signal from the microcalorimeter, will generally dwarf the heat effect being measured and make its determination uncertain. Initial difficulties with the "O"-ring technique necessitated use of method (1) above. However, the use of wax was neither convenient nor desirable in that excess wax left on the side of a cell could adversely affect the thermal sensors (see Section 6). Recent experience with slightly modified cells and "O"-ring plugs has given highly reliable and convenient sealing.



A second possible point of leakage of water from the cell was at the epoxy seal of the top of the cell to the base. If this point of leakage could not be repaired by regluing as was found to be generally the case, the cell was worthless as far as meaningful measurements were concerned. Even more serious, was the case when water from a leaky cell would remain in the silver box of the microcalorimeter. Until evaporation of that water was complete, reliable measurements could not be performed.

### C. Pre-equilibration and Actual Run

Following the sealing of a cell, it was then put into a pre-equilibrator or aluminum block maintained at a temperature within one Kelvin of that of the microcalorimeter. Following a five to ten minute wait, the cell was transferred to the microcalorimeter for final equilibration. This generally took about 15 minutes (see Section 5). The actual run consisted of obtaining a digital and graphical record of the thermopile output as a function of time for the fore period, main period, and after period. The main period was initiated by a 360-degree rotation of the microcalorimeter block and 360-degrees back. After an adequate number of data points had been accumulated in the after period, a remix was performed to ascertain the completeness of reaction. The cell was then removed from the calorimeter and prepared for the next run.



## 9. Blank Heat Effects

A factor which effects the precision and accuracy of the microcalorimeter is reproducibility of the heat effect accompanying the necessary experimental operation of reaction initiation by mixing. The results of measurements of the magnitude of this heat effect are given in Table 3. In performing these runs, the "wet cell procedure", as described in Section 8, was used. The results show that one simple operation of mechanical rotation of the calorimeter block yields an apparent endothermic heat effect of  $-40 \pm 18 \mu\text{J}$  (average deviation). The cause of this effect is not fully understood and may be due to movement of wires during rotation.

The results obtained when solutions are present in the Kel-F reaction cell indicate that the heat effect accompanying the first rotation is always larger than that accompanying the second rotation or remix. The reason for this, in the case of the mixing of water with water, may possibly be attributable to a heat of wetting of Kel-F or to some other surface interaction. However, in the case when hydrochloric acid and sodium hydroxide are mixed with themselves, the effect is due to the "wet cell" procedure used and was the results of the heat of dilution of acid or of base by the pure water on the walls above the solutions in the cell. A series of mixing experiments, employing the dry cell procedure is planned.





## 10. Acid-Base Test Reaction

The heat of neutralization of hydrochloric acid with sodium hydroxide has been used as a test of the accuracy of the microcalorimeter. The hydrochloric acid used in these experiments was obtained from George Marinenko of the Analytical Chemistry Division (NBS) and had been analyzed by him using a coulometric procedure [6, 7]. This stock acid, as received, had a concentration of  $1.99242 \times 10^{-4}$  equivalents  $\text{g}^{-1}$  and was believed to be accurate to within  $\pm 0.02\%$ . This stock solution was used in the preparation by weight of more dilute acid solutions. A saturated stock solution of sodium hydroxide was prepared using Baker analyzed sodium hydroxide pellets and water distilled at the National Bureau of Standards. After allowing this solution to stand for several weeks to permit precipitation of sodium carbonate, a portion of the clear solution was withdrawn from the saturated sodium hydroxide solution and diluted using freshly boiled distilled water. The concentration of this sodium hydroxide solution was determined by titration against potassium acid phthalate (NBS Standard Reference Material No. 84 g). In all calorimetric runs, the sodium hydroxide was used in substantial excess of stoichiometric. The cell loading procedure used was the "wet cell procedure".



The results of calorimetric measurements of the heat of neutralization of hydrochloric acid with sodium hydroxide are given in Table 4. In analyzing these results, a calibration constant of  $16.67 \text{ J}\cdot\text{v}^{-1}\cdot\text{s}^{-1}$  was used (see Section 7). The measured heat (Q), given in Table 4, includes a correction,  $-1147 \mu\text{J}$ , for the blank heat of mixing as determined when  $0.08 \text{ N}$  sodium hydroxide was mixed with itself. This correction is not very satisfactory but until dry-cell experiments are available, this effect is our best estimate of the correction to be applied. It amounts to about 2 percent of the heat of the reaction measured. Corrections for heats of dilution to the standard state [12] were applied using tabulated data [8] for the relative apparent molal enthalpy and heat capacity of the reactants and products. Also a correction was applied [8] to convert the data to  $25^\circ\text{C}$ . The final value,  $\Delta U^\circ$ , is the internal energy change of ionization of water at  $25^\circ\text{C}$ .

No correction was applied for the change in vapor pressure of water above the solutions in the reaction of this space upon reaction. The total estimated effect was  $\sim 0.02\%$ . The vapor pressure before reaction was taken as the average of that of the NaOH and of the HCl and after reaction was that of NaCl and NaOH in water. The change in volume of the liquid phase was taken from Harned and Owen [9], the enthalpy of vaporization of water from Wagman et al [10], and vapor pressures calculated from osmotic coefficients of Robinson and Stokes [11]. Since  $(\Delta PV)^\circ$  is small  $\Delta U^\circ$  is taken as equal to  $\Delta H^\circ$ , the enthalpy of ionization of water.



The resulting values of  $\Delta U^\circ$ , given in Table 4 were averaged (with the exceptions of runs no. 56, 151, 156, and 166) to yield a value of  $\Delta U^\circ = -55.74 \text{ kJ}\cdot\text{mol}^{-1}$  with an average deviation of  $0.33 \text{ kJ}\cdot\text{mol}^{-1}$ . The four runs discarded, out of a total of 22 measurements, all differed from the average of the remaining results by at least a factor of seven times the average deviation. It is believed that these four runs yielded results much lower than the rest due to poor handling of the reaction cell and some attendant pre-reaction of the hydrochloric acid. The result of  $-55.74 \text{ kJ}\cdot\text{mol}^{-1}$  agrees, within the experimental precision, with the "best" literature value of  $-55.835 \pm 0.104 \text{ kJ}\cdot\text{mol}^{-1}$  [8]. At present, new lots of hydrochloric acid sodium hydroxide are being prepared and analyzed by G. Marinenko. Another series of calorimetric acid-base measurements using these materials and the "dry cell" technique is anticipated.

The precision of measurement of the heat of a chemical reaction is thus about 0.6 percent when the heat is of the magnitude of 50 mJ or more. In the present experiments it was necessary to make a 1 mJ correction for the blank mixing effect caused by the "wet cell" procedure. It is estimated that this correction may introduce a systematic error of about one percent in the final result. Thus, at present, we can estimate the accuracy of the calorimeter to be about 1 percent.



## 11. Ease and Reliability of Operation

Various aspects of the ease and reliability of operation of the microcalorimeter have been discussed at various points throughout this report. Difficulties were encountered with sealing the cells and obtaining reliable mixing of the solutions at the appropriate time. Both of these problems now appear to be under reasonable control. As pointed out in Section 5, the speed of operation of the calorimeter itself is such that, at present, a run can be performed once every thirty to forty minutes. The use of automated cell loading and running techniques, automated computation of results, disposable cells, and other devices could in principle greatly improve the reliability, speed of operation, and number of measurements possible in a given period of time.





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### 13. Acknowledgements

We acknowledge the assistance of Ms. Ruby N. Boyd with some of the calorimetric measurements. We thank George Marinenko for providing the coulometrically analyzed hydrochloric acid.



Table 1. Results of Electrical Calibrations (Series I). Temperature is 29.85°C.

Run No.	Power Introduced (mW)	Time of Heating (s)	Heat Input (mJ)	Area (mv·s)	Steady State Deflection ( $\mu$ v)	Calibration Constant ( $\text{W}\cdot\text{v}^{-1}$ )
21	0.010019	20.017	0.2006	0.0118	---	*16.996
22	0.010019	600.125	6.0128	0.3626	0.6066	16.582 (16.517)
23	0.010019	100.254	1.0045	0.0607	---	16.548
24	0.020037	10.457	0.2095	0.0144	---	*14.551
25	0.020037	600.543	12.0332	0.7226	1.2135	16.653 (16.512)
26	0.020037	100.226	2.0083	0.1211	---	16.583
27	0.050117	10.282	0.5153	0.0323	---	*15.954
28	0.050117	599.925	30.0665	1.7993	2.991	16.710 (16.756)
29	0.050117	100.147	5.0191	0.2998	---	16.741
30	0.099820	10.228	1.0210	0.0610	---	16.737
31	0.099820	600.342	59.9263	3.5866	5.986	16.708 (16.676)
32	0.099820	100.227	10.0047	0.5985	---	16.716
33	0.197226	10.379	2.0470	0.1223	---	16.738
34	0.197226	605.393	119.399	7.1509	11.840	16.697 (16.658)
35	0.197226	100.263	19.7745	1.1844	---	16.696
36	0.498069	10.285	5.1226	0.3066	---	16.708
37	0.498069	617.153	307.385	18.4100	29.820	16.697 (16.703)
38	0.498069	99.949	49.7815	2.9821	---	16.693
39	0.998949	10.311	10.3002	0.6185	---	16.654
40	0.998949	600.808	600.177	35.9621	59.824	16.689 (16.698)
41	0.998949	100.151	100.046	5.9948	---	16.689
42	1.99239	10.304	20.5296	1.2304	---	16.685
43	1.99239	600.194	1195.82	71.6537	119.32	16.689 (16.698)
44	1.99239	100.188	199.614	11.965	---	16.683
52 A	0.99901	650.401	649.754	38.8935	59.783	16.706 (16.711)
					Mean calibration constant, $\text{W}\cdot\text{v}^{-1}$	16.682 (16.659)
					Average deviation, $\text{W}\cdot\text{v}^{-1}$	$\pm 0.035$
						( $\pm 0.21\%$ )

\*Omitted





Table 2. Results of Electrical Calibrations (Series II). Temperature is 30.80°C.

Run No.	Power Introduced (mW)	Time of Heating (s)	Heat Input (mJ)	Area (mv.s)	Steady State Deflection ( $\mu$ v)	Calibration Constant ( $W \cdot v^{-1}$ )
110	0.49728	10.979	5.4596	0.3263	---	16.732
111	0.49728	11.570	5.7535	0.3492	---	16.476
112	0.49728	10.227	5.0857	0.3021	---	16.835
128	0.49740	9.981	4.9645	0.2971	---	16.710
140	0.49736	20.428	10.1601	0.6082	---	16.705
209	0.099715	10.220	1.0191	0.0593	---	*17.185
210	0.099715	100.197	9.9912	0.5987	---	16.688
211	0.099715	755.170	75.3019	4.5161	6.039	16.674 (16.512)
212	0.49761	10.457	5.2035	0.3164	---	16.446
213	0.49761	100.210	49.8652	2.9798	---	16.734
214	0.49761	699.751	348.201	20.890	29.79	16.668 (16.704)
215	0.99806	10.477	10.4566	0.6309	---	16.574
216	0.99806	100.256	100.061	5.9993	---	16.679
217	0.99806	809.019	807.446	48.433	59.834	16.671 (16.680)
218	1.99062	10.201	20.3063	1.2276	---	16.541
219	1.99062	100.117	199.294	11.954	---	16.672
220	1.99062	729.464	1452.08	87.119	119.380	16.668 (16.675)

Mean calibration constant,  $W \cdot v^{-1}$  16.655 (16.643)  
Average deviation,  $W \cdot v^{-1}$   $\pm 0.072$   
( $\pm 0.43\%$ )

\*Omitted



Table 3. Blank Heats of Mixing

Simple Mechanical Rotation

<u>Run No.</u>	<u>Area (mv·s)</u>
65	-0.0020
67	-0.0038
68	-0.0006
69	-0.0021
75	-0.0015
76	-0.0045
78	-0.0020

Average Area =  $-0.0024 \pm 0.0011$  mv·s

Q =  $-40 \pm 18$   $\mu$ J

---

Water vs Water

<u>Run No.</u>	<u>Area (mv·s)</u>	
	<u>1st Rotation</u>	<u>2nd Rotation</u>
188	+0.0114	+0.0045
189	+0.0056	+0.0035
190	+0.0150	+0.0000
191	+0.0075	+0.0009
192A	+0.0104	-0.0013

1st Rotation: Average Area =  $+0.0100 \pm 0.0028$  mv·s

Q =  $+167 \pm 47$   $\mu$ J

2nd Rotation: Average Area =  $+0.0015 \pm 0.0020$  mv·s

Q =  $+25 \pm 33$   $\mu$ J



Table 3. (cont.)

0.08 N NaOH vs 0.08 N NaOH (Wet-cell)

<u>Run No.</u>	<u>Area (mv·s)</u>	
	<u>1st Rotation</u>	<u>2nd Rotation</u>
192B	+0.0658	-0.0006
193	+0.0710	+0.0009
194	+0.0782	-0.0004
195	+0.0719	-0.0004
196	+0.0568	+0.0020

1st Rotation: Average Area = +0.0687 ± 0.0060 mv·s

$$Q = +1147 \pm 100 \mu\text{J}$$

2nd Rotation: Average Area = +0.0003 ± 0.0010 mv·s

$$Q = +5 \pm 17 \mu\text{J}$$

---

0.01 N HCl vs 0.01 N HCl (Wet-cell)

<u>Run No.</u>	<u>Area (mv·s)</u>	
	<u>1st Rotation</u>	<u>2nd Rotation</u>
198	+0.0010	-0.0004
200	+0.0046	-0.0025
202	+0.0183	-0.0039
203	+0.0227	-0.0094

1st Rotation: Average Area = +0.0117 ± 0.0089 mv·s

$$Q = +195 \pm 148 \mu\text{J}$$

2nd Rotation: Average Area = -0.0041 ± 0.0027 mv·s

$$Q = -68 \pm 45 \mu\text{J}$$



Table 4. Results of Acid-Base Calorimetric Experiments

Run No.	Temperature (°C)	Mass of acid (g in air)	Mass of base (g in air)	Acid concentration (mol kg <sup>-1</sup> )	Mix Area (mv·s)	Remix Area (mv·s)	Heat** (mJ)	-ΔU (kJ mol <sup>-1</sup> )	Correction Std. State (kJ mol <sup>-1</sup> )	Correction to 25°C (kJ mol <sup>-1</sup> )	-U° (kJ mol <sup>-1</sup> )
52	29.85	0.101753	0.100950	0.010322	3.5720	+0.0003	58.505	55.592	-1.195	1.040	55.437
53	29.85	0.100650	0.100550	0.010332	3.5577	+0.0004	58.268	55.973	-1.198	1.040	55.816
54	29.85	0.094590	0.101715	0.010332	3.3740	-0.0001	55.192	56.415	-1.228	1.040	56.227
56	29.85	0.100865	0.101550	0.010332	3.4084	+0.0081	55.903	53.587	-1.201	1.040	*53.426
59	29.85	0.095260	0.102130	0.010332	3.4000	-0.0053	55.539	56.371	-1.182	1.040	56.184
62	29.85	0.06380	0.104790	0.010577	3.8102	+0.0107	62.657	55.628	-1.172	1.040	55.497
70	29.85	0.101067	0.102005	0.010577	3.6311	-0.0033	59.432	55.539	-1.182	1.040	55.398
71	29.85	0.102465	0.102143	0.010577	3.7063	+0.0031	60.795	56.037	-1.176	1.040	55.901
149	30.80	0.145795	0.153165	0.019669	9.6496	+0.0003	159.81	55.670	-0.859	1.234	56.045
150	30.80	0.149850	0.150615	0.019669	9.8576	+0.0006	163.28	55.341	-0.848	1.234	55.727
151	30.80	0.149341	0.153744	0.019669	8.0123	+0.0003	132.50	45.067	-0.854	1.234	*45.443
152	30.80	0.149345	0.151745	0.0099243	4.9772	+0.0007	81.880	55.187	-1.311	1.234	55.110
156	30.80	0.152340	0.104840	0.0053055	2.4034	+0.2595	43.266	53.476	-1.857	1.234	*52.852
157	30.80	0.149549	0.101190	0.0053055	2.7310	-0.0050	44.319	55.802	-1.841	1.234	55.195
158	30.80	0.145230	0.101675	0.0053055	2.6529	-0.0037	43.038	55.798	-1.874	1.234	55.158
159	30.80	0.149160	0.100730	0.0097799	4.9209	+0.0005	80.938	55.426	-1.114	1.234	55.545
160	30.80	0.150840	0.101715	0.0097799	4.9828	-0.0004	81.956	55.498	-1.113	1.234	55.618
163	30.80	0.148924	0.102438	0.0097799	4.9785	+0.0015	81.915	56.184	-1.124	1.234	56.294
164	30.80	0.150645	0.101251	0.0097799	4.9776	+0.0160	82.142	55.696	-1.112	1.234	55.818
165	30.80	0.147990	0.102026	0.0097799	4.9199	+0.0004	8.920	55.852	-1.125	1.234	55.960
166	30.80	0.148834	0.102352	0.0097799	7.6777	-0.0239	126.51	43.196	-0.748	1.234	*43.681
167	30.80	0.150233	0.102176	0.0097799	9.9808	-0.0013	165.31	55.916	-0.745	1.234	56.404

Base concentration is 0.080856 mol kg<sup>-1</sup> in all experiments.

\* Omitted

\*\* Corrected by -1.147 mJ for "blank" mixing.

Mean of -ΔU° at 25°C, kJ·mol<sup>-1</sup>  
Average deviation, kJ·mol<sup>-1</sup>  
(±0.59%)





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