

The Enthalpy of Reaction of Tris(hydroxymethyl)-aminomethane With Hydrochloric Acid

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The enthalpy of reaction of tris(hydroxymethyl)aminomethane with 0.1 *N* HCl has been measured using an isoperibol solution calorimeter, employing a modified quartz thermometer and an automatic digital data acquisition system. The enthalpy value obtained at 298.15 K is $245.93 \pm 0.26 \text{ J} \cdot \text{g}^{-1}$. Particular attention was given to possible sources of systematic error in the electrical calibrations.

Key words: Enthalpy of reaction; solution calorimetry; standard reference material; tris(hydroxymethyl)aminomethane; thermochemistry.

1. Introduction

This study was undertaken to establish the precision and accuracy of measurements that can be made with an isoperibol (isothermal jacket) solution calorimeter constructed for future work on the thermochemistry of calcium phosphates. The test reaction selected for this purpose was the reaction of tris(hydroxymethyl)aminomethane (hereafter referred to as TRIS) with 0.1 *N* HCl. The samples of TRIS employed in the test reaction were parts of the preparation issued as NBS Standard Reference Material No. 724a (NBS-SRM 724a).

A summary [1]¹ of values of high precision for the TRIS-HCl reaction reports interlaboratory variations in the enthalpy for this test reaction greater than 0.4 percent. The majority of these values have been measured in isoperibol solution calorimeters and are slightly lower than the value reported in this work. The results of this study are in close agreement with those obtained in an adiabatic calorimeter used in the certification of NBS-SRM 724a [1].

2. Materials

SRM 724a was used in all experiments. Prior to filling the sample ampoules, the TRIS was stored in a desiccator over a saturated aqueous solution of magnesium nitrate which gives 50 percent relative humidity. This procedure follows the recommendations of the NBS Standard Reference Material Certificate [7].

The HCl solutions were prepared using ACS reagent grade concentrated hydrochloric acid (37–38%) which was diluted to the desired concentration with freshly boiled distilled water. No special precautions were taken to exclude carbon dioxide during the filling of the calorimeter. The acid concentrations were determined by titrating the HCl solutions with sodium hydroxide solutions that were standardized with potassium acid phthalate (SRM 84h) using phenolphthalein as the end point indicator. The acid concentrations were 0.0996 *N* (Expt. Nos. 9 to 12) and 0.1011 *N* (Expt. Nos. 13 to 18).

The TRIS sample was introduced *via* a small glass funnel into cylindrical glass ampoules with very thin-walled ends. The ampoules hold a volume of 1.0 cm³ and are manufactured by the LKB Company.² Before filling, the ampoules were rinsed with ACS reagent grade acetone followed by distilled water and then dried in an oven. After filling, the ampoule was closed with a small rubber stopper which had been presoaked in HCl, rinsed with distilled water and dried. The stopper was sealed with warm beeswax and the ampoule submerged in 0.1 *N* HCl to check for leakage. It was then rinsed, dried and mounted on the stirrer-ampoule holder of the calorimeter.

3. Calorimetric Apparatus and Procedure

The calorimeter vessel, jacket and constant temperature water bath were manufactured by the LKB Company [2]. However, all auxiliary equipment, including the electrical energy and temperature meas-

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¹ Figures in brackets indicate literature references at the end of this paper.

² Certain commercial materials are identified in this paper in order to adequately specify the experimental procedures. Such identification does not imply recommendation or endorsement by the National Bureau of Standards.

uring apparatus, were assembled from other sources and are described below. As this investigation proceeded several changes were made in various components of the apparatus and these will be described as well.

3.1. The Calorimeter

The isothermal jacket of the calorimeter, a can of nickel-plated brass, is immersed in a stirred-water bath whose temperature is regulated by means of a proportional controller. A test of the temperature stability of the bath, as measured at one point in the well-stirred bath, indicated that it was maintaining a constant temperature to within ± 0.0015 K over a 15 hour period.

The first calorimeter vessel was constructed of thin-walled glass and held a volume of 100 cm^3 . As received from the manufacturer the vessel contained three glass wells. One of the wells was specially added for installation of a quartz-oscillator probe. The other two glass wells held the electrical calibrating heater and a thermistor; the thermistor was not used in this work. The vessel is suspended from the lid of the submarine jacket by means of a screw connection and O-ring-seat at the top of its glass neck. The original glass vessel was broken in an accident following Expt. No. 11 and a second calorimeter vessel was constructed in the NBS glass blowing shop. It differed from the original in that its volume was 110 cm^3 and it was more nearly spherical than the original cylindrical vessel. The thermistor well was omitted and the walls of the heater and thermometer wells were made of thinner glass. The use of the new vessel (Expt. Nos. 12 to 18) had no observable effect on the value of the calorimeter heat leak modulus, the value of which was approximately $1.03 \times 10^{-4} \text{ s}^{-1}$. A photograph of the second vessel is shown in figure 1.

Venting in the original calorimeter was only through the stirrer shaft bearings and housing. Since adequate venting of the calorimeter was desired, following Expt. No. 15, additional venting was provided by drilling a 1-mm diam hole through the bottom and the top of the housing for the stirring shaft and inserting a syringe needle through these two holes. This needle provided direct venting from above the calorimetric liquid to the atmosphere.

The gold-plated combination stirrer-ampoule holder was driven at a constant speed of approximately 300 rpm by a synchronous motor through an O-ring belt and pulley arrangement. This replaced the original cable drive system.

3.2. The Calibrating Heater

The original heater consisted of 50- Ω of manganin wire wound bifilarly on a phenolic form located in the bottom of the heater well of the vessel. A light oil covered the heater. Insulated copper leads were soldered to the manganin wire and were passed through two thin polytetrafluoroethylene (PTFE) disks that were separated with a layer of Wood's metal. The Wood's metal provided thermal tempering of the leads

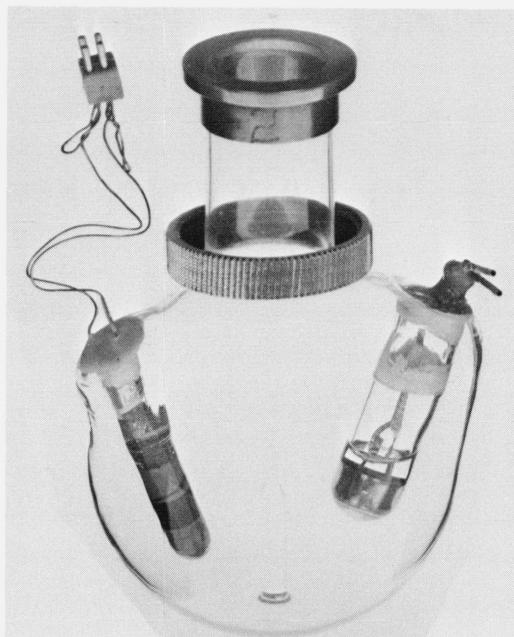


FIGURE 1. Calorimeter Reaction Vessel.

Calibration heater in left well and quartz-probe in right well, central glass pin is for breaking ampoules.

to the vessel. The copper leads, after passing through a second layer of Wood's metal, terminated at the top of the well where they were soldered to two small gold-plated connectors imbedded in an epoxy cement that sealed the heater well. Two short copper wire leads went from the connectors at the top of the heater well to a two-pin connector in the jacket lid. Current and potential leads were attached to each pin of the jacket connector.

After the original vessel was broken, the original heater was installed in the new vessel following the above method employed by the manufacturer as closely as possible and used in experiments 15 and 16. However, a new heater was constructed prior to Expt. No. 17. It was bifilarly wound with 82 Ω of enamel-insulated manganin wire (#40 AWG) onto a piece of thin-walled stainless steel tubing that had been coated with insulating varnish and baked. Approximately six inches of PTFE-insulated copper wire (#30 AWG) was soldered to the manganin wire and then coiled and pushed down into the heater well. As in the original heater, a light mineral oil covered the heater and the thermal tempering and the sealing of the leads to the well of the calorimeter vessel was the same as described earlier. However, the two copper leads (#26 AWG, Formvar insulated) soldered to the PTFE-coated wire went directly to a four-pin connector. The four pins of the connector were shorted pair-wise at the connector to form the branch points for the current and potential leads (see fig. 1). The "thermal stationing" of the heater leads at the jacket was modified by removing the original connector and fitting a brass plug with a smaller hole, and placing a small four-pin feed-through connector into this hole.

3.3. Electrical Energy Measurements

A schematic diagram of the electrical calibration circuit is shown in figure 2. The current through the heater and the potential drop across the heater were obtained from measurements of the potential drop across the 1- Ω standard resistor and across a 2-k Ω resistor in the 20-k Ω volt box. Appropriate corrections were made for the current through the volt box and the leads connecting it to the branch points of the heater. As indicated in figure 2, the circuit was always grounded only at one point, namely, at the power supply (Princeton Model 602R) which was operated in the constant voltage mode. (Note that the measuring resistors are near ground potential. Otherwise the circuit was found to be isolated from ground by at least 100-M Ω .) Voltages were measured on a Leeds and Northrup type K5 potentiometer (error limit of $\pm 0.005\% + 0.03 \mu\text{V}$) which was standardized against a Weston unsaturated standard cell. The standard cell was periodically compared with a bank of NBS certified Weston saturated cells and all measuring equipment was calibrated and compared with other standards in this laboratory. Time measurements were made by inserting a timing circuit, consisting of an electronic counter (HP 5325 B) with a resolution of 1 ms, parallel to the electrical calibration circuit (point A in fig. 2). Current flowing through this parallel circuit has no effect on the measurement of the heater current and voltage since it is outside of the measuring circuit.

The above circuit and apparatus were used in Expt. Nos. 13 to 18. In Expt. Nos. 9 through 12 a completely separate electrical circuit was used. It differed from the above in that (1) there was no volt box across the heater, (2) a digital voltmeter (Hewlett Packard 3450A; input resistance $> 10^{10}\Omega$, sensitivity of $\pm 1\mu\text{V}$) was used to measure the potential drops across the heater and a standard resistor (0.1 Ω) in series with the heater, (3) a different power supply (Princeton 602CR) was used, and (4) a mercury relay was used to switch between the ballast resistor and the heater side of the circuit.

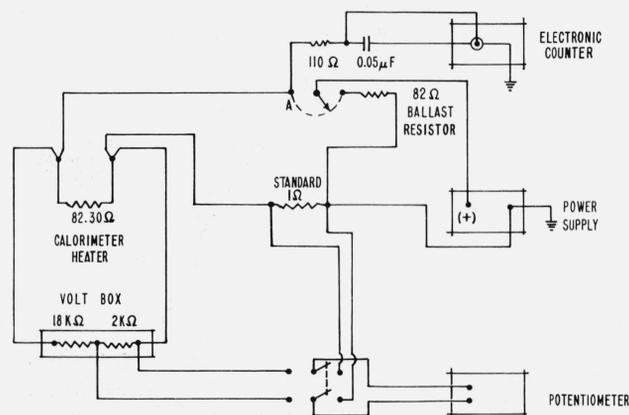


FIGURE 2. Diagram of circuit used for electrical energy equivalent determinations.

The total electrical energy was calculated from the product of the current through the heater, voltage across the heater and time interval of heating. It was assumed that the heat generated in the heater leads between the calorimeter vessel and jacket was apportioned one-half to the calorimeter vessel and the other half to the jacket. The resistance of the leads between the jacket and the calorimeter vessel was 0.04 percent of the resistance of the calibration heater; therefore, a correction of 0.02 percent was applied to the measured electrical energy for the heat lost to the jacket.

It was observed that the heater resistance, as determined from the current and potential measurements, was dependent on the power level applied to the heater. This effect is attributable to the change in resistance of the heater wire as the temperature in the well rises, and became significant at power levels approaching 2 W. Power input during the TRIS experiments was maintained below this level and by measurement of the current through and the potential drop across the heater under load conditions, any change in heater resistance was automatically accounted for in the electrical calibrations.

The power input was 1.18 W, in Expt. Nos. 9 through 16, 0.95 W in Expt. No. 17, and 0.13 W in Expt. No. 18. The time interval of electrical heating was varied from approximately 100 to 1000 s.

In order to test for possible errors associated with the electrical calibrations, a second, temporary heater with a resistance of 87 Ω was placed directly into the water of the solution vessel. This heater was coated with Apiezon "W" wax and no electrical leakage was detectable using the high impedance scale of a volt-ohm meter (the electrical resistance was estimated to be greater than 100 M Ω). Several centimeters of the leads from this heater were coiled and submerged with it in the water to insure good thermal tempering. The two current leads were then passed through the 1-mm vent holes of the housing for the stirrer shaft, and were stationed at the top of the shaft-housing where potential leads were attached. Repeated determinations of the calorimeter electrical energy equivalent, alternating between the permanent heater in the well and the temporary heater in the water of the solution vessel, gave a difference between the means of three determinations with each heater of 0.006 percent, with none of the deviations from each of the means being greater than 0.009 percent. In calculating the heater-lead correction for the temporary heater the calorimeter boundary was chosen to be one-half the distance between the surface of the water in the vessel and the jacket lid. The heater lead correction was approximately equal to that for the permanent heater.

3.4. Thermometry and Data Acquisition

The temperature of the calorimeter vessel was determined by means of a Hewlett-Packard quartz-oscillator thermometer [3]. The TO-5 transistor case containing the temperature-sensitive quartz crystal was removed from its original stainless steel capsule,

placed in the bottom of the glass well in the solution vessel, and covered with light mineral oil. The leads from the quartz crystal were thermally stationed to the calorimeter vessel by passing them through a layer of dental amalgam which was contained between two thin PTFE disks. At the top of the well the leads were soldered to two small, gold-plated pin connectors which were imbedded in the epoxy cement that sealed the well (see fig. 1).

The temperature dependence of the frequency of the quartz probe is nominally $1000 \text{ Hz} \cdot \text{K}^{-1}$ [3], and by counting for 100-s, a temperature resolution of $10 \mu\text{K}$ is obtained. In order for this resolution to be meaningful, it is necessary that the reference oscillator in the quartz thermometer chassis be stable to within 3 parts in 10^{10} during an experiment. It was found by one of us (EJP) that this stability was obtained by replacing the ceramic trimmer-capacitor in the oscillator circuit of the reference oscillator with an air capacitor. To check this stability the reference oscillator frequency was monitored against a standard frequency available at NBS which is reproducible to 1 part in 10^{11} .

The digital output from the quartz thermometer and from a digital clock with 0.1-s resolution, went to a digital coupler and then to a teletype where the time and temperature data were logged both on punched paper tape and in typed form.

The absolute temperature of the quartz thermometer from 295 to 303 K was obtained to within $\pm 0.003 \text{ K}$ by comparison with a platinum resistance thermometer that had been calibrated by NBS (NBS 1948). In performing the comparison, the platinum thermometer was placed in the stirred-water jacket of the calorimeter and its temperature was compared with the quartz oscillator temperature by measurement of the voltage of a differential copper-constantan thermocouple between the vessel and the jacket. One of the thermocouple junctions was cemented to a thin, insulated silver tab cemented to the side of the solution vessel, the other wax-coated junction was located in the bath near the platinum thermometer. Throughout this procedure the water in the solution vessel was stirred and the calorimeter was maintained near its convergence temperature to minimize the temperature difference between the calorimeter and the jacket.

3.5. Experimental Procedure

All weighings were done on a single-pan microbalance with a sensitivity of one microgram. The balance was calibrated against a set of Class M metric weights that had been calibrated by the Mass Section of NBS. Corrections to vacuum were made using a density of $1.35 \text{ g} \cdot \text{cm}^{-3}$ for TRIS. The density of air was determined by daily observations of the temperature, pressure and humidity and corrections were applied as described by Bowman et al. [4]. Care was taken, employing uranyl nitrate in the balance chamber, to avoid electrostatic charge effects that might interfere with the weighings. A molecular weight of $121.1369 \text{ g} \cdot \text{mol}^{-1}$ TRIS was assigned on the basis of the 1969 table of atomic weights [5].

Each calorimetric experiment included three parts, an electrical calibration, the TRIS-HCl reaction, and finally a second electrical calibration. Each part consisted of approximately 30 data points (each point being recorded at 101.6-s intervals) which included an initial rating period, a main period, and a final rating period. Following each part, dried, cold air (introduced *via* a stainless steel tube temporarily inserted through a hole in the lid of the jacket) was blown over the exterior surface of the vessel in order to cool it. The electrical heatings and chemical reaction were thus carried out over the same temperature interval (within a few hundredths of a kelvin). In all experiments the final temperature of the calorimetric vessel was 0.05 to 0.17 K below the convergence temperature.

4. Calculations

4.1. Corrected Temperature Rise

The following treatment to obtain the corrected temperature rise was developed with the help of R. L. Nuttall, NBS Thermochemistry Section.

The corrected temperature rise (ΔT_{corr}) was calculated [6a] using eq (1),

$$\Delta T_{\text{corr}} = (T_f - T_i) - k \int_{t_i}^{t_f} (T_\infty - T) dt, \quad (1)$$

where T_i and T_f are, respectively, the temperatures at t_i , a time during the initial rating period, and t_f , a time during the final rating period. In eq (1), k is the calorimeter heat leak modulus or cooling constant, and T_∞ is the convergence temperature. The time, t_i , was chosen as the time just before heat, either electrical or chemical, was introduced into the calorimeter; the time, t_f , was chosen as any one of several points in the final rating period. The quartz thermometer is an integrating device and will automatically evaluate a part of the integral in eq (1), as indicated below in eq (10). To utilize this feature of the quartz thermometer over the entire main period the times t_i and t_f must be, and were, chosen at the end points of integration periods of observed quartz thermometer readings. During the rating periods the rate of temperature change is given by eq (2).

$$\frac{dT}{dt} = k(T_\infty - T). \quad (2)$$

The integrated form of this equation is

$$T = T_\infty - (T_\infty - T_0)e^{-k(t-t_0)}, \quad (3)$$

where T_0 is temperature at the time t_0 , any selected time in the particular rating period used. It is convenient to select t_0 in eq (3) as equal to t_i in the initial period and equal to t_f in the final period. This has been done in eqs (7) and (8) below.

Since the quartz thermometer is an integrating device the reading, θ , displayed by the quartz ther-

momenter is the time-average temperature over the integration interval, λ , as given by eq (4) and was referenced to the midtime of the interval:

$$\theta = \frac{1}{\lambda} \int_{t-\lambda/2}^{t+\lambda/2} T dt. \quad (4)$$

Substitution of T from eq (3) into eq (4), results in the following expression for θ during rating periods:

$$\theta = T_{\infty} - (T_{\infty} - T_0) e^{-k(t-t_0)} \left[\frac{e^{\frac{k\lambda}{2}} - e^{-\frac{k\lambda}{2}}}{k\lambda} \right]. \quad (5)$$

By defining two new constants, $\theta_{\infty} = T_{\infty}$ and

$$\theta_0 = T_{\infty} - (T_{\infty} - T_0) \left[\frac{e^{\frac{k\lambda}{2}} - e^{-\frac{k\lambda}{2}}}{k\lambda} \right]$$

we get:

$$\theta = \theta_{\infty} - (\theta_{\infty} - \theta_0) e^{-k(t-t_0)}. \quad (6)$$

Thus, we have for the initial and final rating periods, respectively, the following equations:

$$\theta_r = \theta_{\infty} - (\theta_{\infty} - \theta_i) e^{-k(t_r - \lambda/2 - t_i)} \quad (7)$$

$$\theta_f = \theta_{\infty} - (\theta_{\infty} - \theta_f) e^{-k(t_r - \lambda/2 - t_f)} \quad (8)$$

where t_r 's are the times at the end of the thermometer integration periods at which time the readings θ_r appear on the read-out, t_i is the time at the end of the initial period, and t_f is the time at the start of the final period. Equations (7) and (8) were fitted to the time-quartz thermometer data (θ_r , t_r) of the initial and final rating periods as a single set of data by using a nonlinear least squares procedure [8]. From this fit the parameters k , θ_{∞} , θ_i , and θ_f are obtained. The observed temperature rise, $T_f - T_i$, can then be shown to be given by

$$T_f - T_i = (\theta_f - \theta_i) \left[\frac{k\lambda}{e^{\frac{k\lambda}{2}} - e^{-\frac{k\lambda}{2}}} \right]. \quad (9)$$

The last factor in eq (9) depends on k and λ . In this calorimeter $k \cong 0.0001 \text{ s}^{-1}$ and $\lambda \cong 100 \text{ s}$. Thus

the factor has the value 0.999996 and can almost be neglected.

The correction to the observed temperature rise, i.e., the integral in eq (1), can be written as

$$k \int_{t_i}^{t_f} (T_{\infty} - T) dt = kT_{\infty}(t_f - t_i) - k \int_{t_i}^{t_f} T dt. \quad (10)$$

The integral on the right side of eq (10) was evaluated in two parts: (1) an integral over the thermometer integration time which, for the n th time interval is equal to $\lambda\theta_n$; (2) an integral over the dead time (the fraction of a second during which the counter is transmitting data to the coupler) which is evaluated by assuming a linear temperature change between adjacent data points.

Equation (1) can also be written in the form,

$$\Delta T_{\text{corr}} = (T_f - T_i) - u(t_f - t_i) - k \int_{t_i}^{t_f} (T_j - T) dt \quad (11)$$

where T_j is the constant jacket temperature, and u represents energy contributions from constant power sources such as stirring and the temperature sensor. Values of u were calculated from the relationship, $u = k(\theta_{\infty} - \theta_j)$ and are listed in table 1 with θ_{∞} , θ_j , and k for the TRIS-HCl reaction portion of each experiment. It was found that u was negative and thus contributed a positive correction to the observed temperature rise. Since the energy dissipated by the quartz-probe oscillator is small, $10 \mu\text{W}$ [3], u would then be primarily a function of the stirring energy, but its contribution is also positive. However, negative contributions to u could arise from evaporation of liquid from the top of the vessel, or heat conduction up the stirrer shaft to the cooler room environment.

In an attempt to limit evaporation electrical heating experiments were conducted with a light film of oil on the surface of the calorimetric liquid. Negative values of u were still observed. We presume, therefore, that heat leakage *via* the stirring shaft results in a small negative power contribution to u . Although a positive value of u is desirable, the values of u in table 1 are seen to be small and reasonably constant, thus indicating that no inconsistency exists that would adversely bias the calorimetric measurement in any way.

The behavior of the u was evaluated in a more direct manner by plotting values of $d\theta/dt$ (the average slope

TABLE 1. Calorimetric parameters for the TRIS-HCl experiments

Expt. No.	$k \cdot 10^4$	T_j	T_{∞}	$-u \times 10^4$	$-u(t_f - t_i) \times 10^4$	$k \int_{t_i}^{t_f} (T_{\infty} - T) dt$
	s^{-1}	$^{\circ}\text{C}$	$^{\circ}\text{C}$	$\text{K} \cdot \text{min}^{-1}$	K	K
9	1.027	25.0449	25.0272	1.399	18.863	0.010388
10	1.031	25.0513	25.0289	1.379	16.088	.010275
11	1.035	25.0486	25.0274	1.317	17.856	.012646
12	1.045	25.2225	25.1913	1.956	29.813	.013539
13	1.019	25.2070	25.1873	1.199	16.246	.012193
15	1.019	25.2064	25.1849	1.314	22.264	.014371
16	1.045	25.2198	25.2006	1.204	20.396	.012241
17	1.042	25.2155	25.1968	1.169	15.840	.010955
18	1.033	25.2163	25.1976	1.164	21.687	.012027

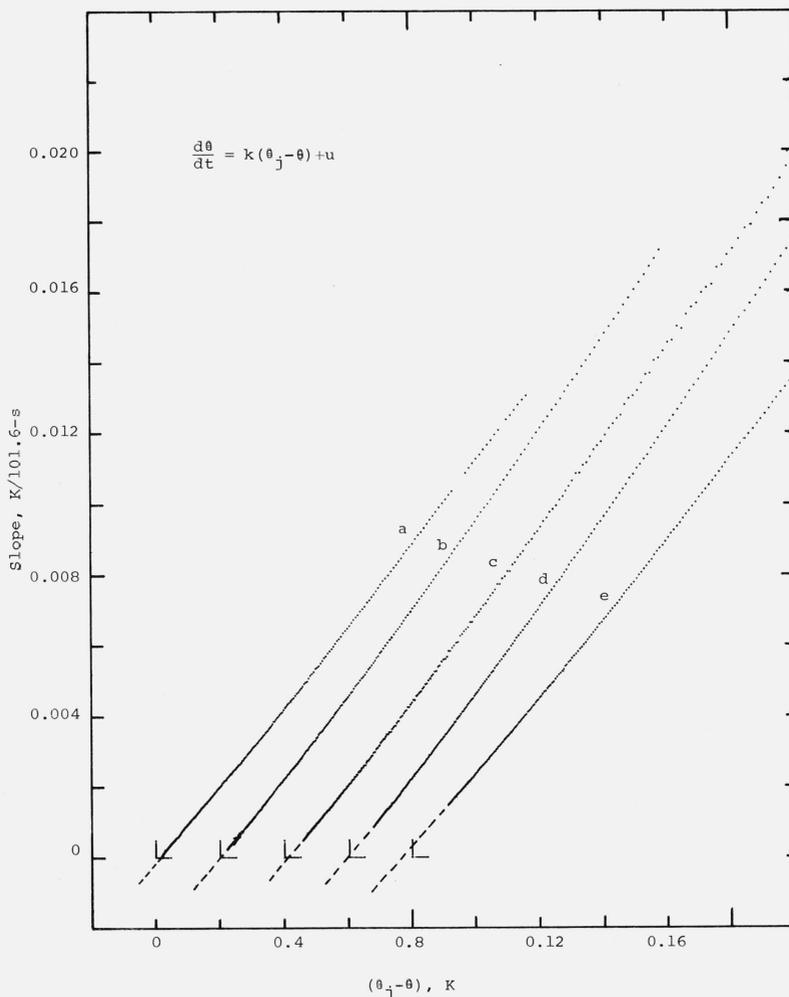


FIGURE 3. Characterization of the calorimeter parameters u and k by plotting s , the average slope between adjacent data points, versus $(\theta_j - \theta)$, as the calorimeter temperature approaches θ_∞ .

θ_j was taken as a constant using the jacket temperature observed at the end of the experiment. X-axis origin displaced 0.2 °C for each successive plot as indicated. For curve a, b, c, d, and e respectively: θ_j (°C) = 28.19, 25.15, 25.15, 25.15, 25.15; RPM = 300, 300, 101, 300, 800; u (°C/101 sec) = -0.00020, 0.00000, -0.00015, 0.00000, 0.00030; oil was on the surface of the calorimetric liquid during d and e.

between adjacent data points) versus $(\theta_j - \theta)$, employing eq (12),

$$d\theta/dt = k(\theta_j - \theta) + u. \quad (12)$$

Temperature and time data were recorded at 101.6-s intervals for periods up to fourteen hours, as the calorimeter temperature approached θ_∞ . This procedure was repeated for various jacket temperatures and stirring speeds. From the intercepts and slopes of the plots (see fig. 3) values of u and k , respectively, were obtained. At stirring speeds and jacket temperatures similar to those used in the TRIS experiments, zero or small, negative intercept values were obtained for u . Higher stirring speeds gave larger, positive values, as did the lower stirring rates after bending the paddle blades of the stirrer-ampoule holder to increase stir-

ring efficiency. These results confirmed the view that low stirring energies were more than compensated by cooling effects, resulting in small, negative values of u , as previously calculated from normal rating period data. The above procedure was found to be very useful in characterizing the various operational parameters of the calorimeter.

As a means of guarding against possible systematic errors in the calculation of the corrected temperature rise, a comparison was made between the results obtained with the computer program we used and a program also written specifically for quartz thermometry by S. R. Gunn.³ For three values of ΔT_{corr} , calcu-

³ Lawrence Radiation Laboratory, University of California, Livermore, Calif. 94550.

TABLE 2. Calorimetric data for the reaction of TRIS with 0.1 N HCl

Expt. No.	Electrical energy equivalent		Mass of TRIS in vacuum	Corrected temperature rise	Q reaction	-Q vaporization	Assigned reaction temperature	-ΔH(298.15 K)
	Initial	Final						
	<i>J · K⁻¹</i>	<i>J · K⁻¹</i>	<i>g</i>	<i>K</i>	<i>J</i>	<i>J</i>	<i>°C</i>	<i>J · g⁻¹</i>
9 a	443.839	444.609	0.500758	0.277398	123.227	0.030	24.789	245.836
10 a	444.373	444.977	.505858	.279860	124.447	.030	24.785	245.758
11 a	446.939	446.793	.505409	.278566	124.482	.028	24.779	246.032
12 b	491.951	492.334	.558259	.279037	137.326	.024	24.951	245.962
13 c	492.932	493.531	.557665	.277890	137.064	.022	24.962	245.767
15 d	491.587	491.693	.537582	.269113	132.307	.023	24.967	246.109
16 d	492.310	492.839	.562404	.280911	138.370	.022	24.971	246.030
17 e	493.010	494.116	.560898	.279550	137.976	.022	24.986	246.009
18 e	493.129	493.693	.543787	.270891	133.661	.023	24.994	245.829
								Mean = 245.926
								Sdm = 0.043

Experiment Nos. 1 to 8 were the first measurements made with the solution calorimeter facility. Difficulties were experienced due to erratic stirring energy and a malfunctioning timer. Expt. No. 14 was not completed. Therefore these experiments were not included in table 2.

- a Original vessel, digital voltmeter employed in calibration circuit.
- b Second vessel, original heater installed.
- c As b, but potentiometer now in calibration circuit.
- d As c, with calorimeter venting increased.
- e As d, with new calibration heater in vessel.

lated from the data of a typical TRIS experiment, two of the values agreed to within 0.002 percent, and the third to within 0.011 percent, clearly minimizing the probability of error from the method of data treatment.

4.2. Enthalpy of Reaction

The enthalpy of the TRIS-HCl reaction at the mean reaction temperature, T_m , was calculated from eq (13)

$$-\Delta H(T_m) = \overline{EE} \times \Delta T_{\text{corr}} \quad (13)$$

where \overline{EE} is the average of the initial and final state electrical energy equivalents. This enthalpy is equivalent to the isothermal enthalpy at the mean reaction temperature [6b], assuming no significant change in heat capacity over the temperature range of the measurement.

The measured enthalpy was corrected for the following effects: (1) the heat of vaporization of a small amount of water into the increased vapor space that resulted from breaking the sample ampoule (0.016 to 0.025%), and (2) the correction of the measured enthalpy to 298.15 K (0.004 to 0.130%). In applying the latter correction, ΔC_p for the TRIS-HCl reaction was taken to be $1.435 \text{ J} \cdot \text{K}^{-1} \cdot \text{g}^{-1}$ [1]. No correction was made for the heat of breaking the ampoule. Several sealed ampoules, both empty and with a drop of water added, were broken in 0.1 N HCl. However, the analysis of drift data in experiments in which sample ampoules were and were not broken showed that the heat effect (0.015J) associated with breaking the ampoules is less than the uncertainty of the temperature rise calculation.

5. Results and Discussion

5.1. Experimental Results

The results of nine TRIS-HCl experiments are listed in table 2. Inspection of the calculated values of the reaction enthalpy indicates no apparent differences due to the various experimental parameters that were changed during the course of the investigation. Namely, the changes made in the calibrating instruments, heaters, solution vessel, and venting did not affect the results. In view of this, the nine results were averaged to give a value of $-245.93 \text{ J} \cdot \text{g}^{-1}$ ($29791 \text{ J} \cdot \text{mol}^{-1}$) with a standard deviation of the mean of $0.043 \text{ J} \cdot \text{g}^{-1}$ ($5.2 \text{ J} \cdot \text{mol}^{-1}$).

5.2. Estimate of Uncertainty

In table 3 we estimate reasonable upper limits for possible sources of systematic errors in our experiments. If all of the listed sources of systematic error were in the same direction, the results would be in error by 0.07 percent.

A reasonable assignment of uncertainty would be twice the standard deviation of the mean ($\pm 0.035\%$), if we were to assume that all of our measurement errors were random errors. However, in view of possible sources of systematic error, we have added our estimate of possible systematic errors to the random error and assigned an overall uncertainty of ± 0.10 percent to the TRIS-HCl reaction enthalpy and obtain a value of $-245.93 \pm 0.26 \text{ J} \cdot \text{g}^{-1}$ at 298.15 K.

5.3. Conclusion

The enthalpy reported in this paper for the TRIS-HCl reaction is one of the higher values that have been

TABLE 3. *Judgement of possible sources of systematic error*

Source of error	Estimate of Error (percent)
Electrical power measurements.....	0.005
Time interval measurements.....	.003
Mass measurements.....	.005
Heater lead correction.....	.010
Assigned reaction temperature.....	.010
Vapor space correction.....	.003
Heat of bulb breaking.....	.010
Non-equivalence of heat sources.....	.020
Total.....	0.066

reported [1], the range of values of high precision being from 245.3 to 246.2 J·g⁻¹. It is uncertain at present whether this spread represents difficulties inherent in the solution calorimetry, or is due to anomalies in the test reaction itself. The value reported in this paper agrees within the assigned uncertainties of the NBS certificate value of 245.76 ± 0.26 J·g⁻¹ [7].

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6. References

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