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Enthalpies of Reaction of Tris(hydroxymethyl)aminomethane in HCl(aq) and in NaOH(aq)

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The enthalpy of reaction of tris(hydroxymethyl)aminomethane, NBS Standard Reference Material 724a, measured in an adiabatic solution calorimeter at 298.15 K in 0.1 *N* HCl solution is -245.76 ± 0.26 J · g^{-1}, and in 0.0500 *N* NaOH solution is 141.80 ± 0.19 J · g^{-1}. The conditions applicable and the factors included in the overall uncertainties are discussed in detail. For the reaction in 0.1 *N* HCl in the range, 293 to 303 K, $\Delta Cp = 1.435 \pm 0.023$ J · g^{-1} · K^{-1}, and in 0.0500 *N* NaOH in the range, 295 to 303 K, $\Delta Cp = 1.025 \pm 0.025$ J · g^{-1} · K^{-1}.

Possible sources of error in measurements of the reactions are discussed. A summary of other enthalpy measurements of the reaction in 0.1 *N* HCl is given.

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

1. Introduction

Tris(hydroxymethyl)aminomethane or 2-amino-2-(hydroxymethyl)-1,3-propanediol, $(HOCH_2)_3CNH_2$, is popularly known as TRIS or by the trade name, THAM.[1] For some years it has been used in medicine and as a buffer in analytical chemistry. Recently it was issued by the National Bureau of Standards as a standard reference material for solution calorimetry, SRM 724 and 724a.[2] The experimental work which is the basis for the certified enthalpy values for this standard reference material is discussed in sections 3.3 and 3.4.

The neutralization reaction with excess aqueous hydrochloric acid may be written

$$n[(HOCH_2)_3CNH_2]\ (c) + (n+x)H^+(aq) \rightarrow$$
$$n[(HOCH_2)_3CNH_3]^+(aq) + xH^+(aq).$$

Under some conditions (described in secs. 3.1a and 3.1b) side reactions may occur which produce high enthalpy values. For the dissolution reaction in water, slightly alkaline solutions are preferred for calorimetric measurements to eliminate possible reaction with CO_2 dissolved in the water.

The use of the reaction of tris(hydroxymethyl)-aminomethane with 0.1 *N* hydrochloric acid solution "as a test reaction for rapid moderately exothermic reactions" was proposed by Irving and Wadsö [1][3] in 1964. The same year, the U.S. Calorimetry Conference requested that the National Bureau of Standards (U.S.) issue a sample to be used as a standard reference material for solution calorimetry. At that time, a new vacuum-jacketed adiabatic solution calorimeter had been constructed (in the Thermochemistry Section at NBS) which was still untested, but was believed to be capable of high precision and accuracy, and well-qualified to do the enthalpy certification work. It was assumed that the certification would involve only a series of simple calorimetric experiments to confirm the work of Irving and Wadsö. However, the first results obtained late in 1967 with the new Standard Reference Material No. 724 were approximately 0.1 percent more exothermic than the values reported by Irving and Wadsö, and the experimental imprecision of the measurements was about twice that expected of the calorimeter.

An intensive effort began to locate the cause of the discrepancy in the results. No difference was found in the enthalpy value obtained with samples from different sources, nor in samples which were stored for years in darkness when compared to those stored in the presence of fluorescent lighting, nor in samples stored in the room atmosphere as compared to those stored in a hygrostat of 50 percent relative humidity. The calibrations of our bridge, potentiometer, standard resistors, standard cell, and electronic counter were checked; a dummy heater with its leads directly in the calorimeter solution (thus at calorimeter tem-

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[1] Fisher Scientific Co. Trademark. Commercial materials are identified in this paper in order to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Bureau of Standards.

[2] Available at Office of Standard Reference Materials, National Bureau of Standards, Washington, D.C. 20234.

[3] Figures in brackets indicate literature references at the end of this paper.

perature before leaving the vessel) was compared with the permanent calibrating heater in the platinum well—the difference between the results obtained with the two heaters was less than 0.004 percent; temperature differences at various points between the adiabatic shield and the vessel were measured and the currents in the shield were readjusted to produce minimal departures from the vessel temperatures; and the platinum resistence thermometer was replaced by a quartz-oscillator thermometer—none of these produced any detectable change in the results.

Having eliminated the sample composition and treatment, and the measuring equipment as likely sources of error, we decided to measure for comparison the enthalpy of another reaction on which published results were available [3], the reaction of $H_2SO_4 \cdot 8H_2O$ in 0.02 *N* and in 0.08 *N* sodium hydroxide solutions. The results we obtained [2] agree with Gunn's values [3] within a few hundredths of a percent. The standard deviation of the mean for our experiments was 0.01 percent, which was a definite improvement over the imprecision in the experiments with TRIS.

Our efforts were then directed to investigating conditions of the TRIS reaction in aqueous HCl which might explain the existing discrepancy in the enthalpy values obtained by various laboratories. Much is still not understood about this reaction, but we report here the results of some of our measurements which have led to our confidence in the experiments on which are based the certified enthalpy values for Standard Reference Materials 724 and 724a under certain specified conditions. We have also summarized values obtained by other laboratories (published and unpublished) for the TRIS reaction in aqueous HCl.

2. Materials, Apparatus, and Procedures

2.1. Tris(hydroxymethyl)aminomethane

Our measurements reported in this paper were made using two samples of TRIS, SRM 724 and SRM 724a. The latter sample is to be issued upon depletion of the first sample, SRM 724.

SRM 724 was prepared from tris(hydroxymethyl)-aminomethane obtained from several commercial sources, and the purifications[4] and assay[5] were performed in the Analytical Chemistry Division. In the purification, each 1-kg lot was washed twice by stirring with methanol and filtering. The material recovered from the second washing was dissolved in hot water and filtered. The TRIS was crystallized by slowly dripping the filtrate into vigorously agitated methanol. The crystalline TRIS was filtered, washed with cold methanol, and then the entire crystallization procedure was repeated. The crystals from the second crystallization were air-dried for a day or more, and then dried at about 338 K in a rotating vacuum drier until the product was free-flowing and showed no tendency to stick to the walls. The assay of this material is 99.94 ± 0.01 percent $(HOCH_2)_3CNH_2$. An indirect coulometric procedure was used for the assay (see [4] for details of the procedure).

The material for SRM 724a was 10 kg of TRIS obtained from a commercial source and was not further purified. (This material was part of a total of 60 kg, and 50 kg was used for acidimetric standard, SRM 723). The assay is 99.9690 ± 0.0030 weight percent.[5] The results of the coulometric analyses, the titration procedures, and the method of selecting the random samples have been described [5].

The general procedures recommended by the Standards Committee, U.S. Calorimetry Conference, October 1966, were followed (except as noted in this work) in the storage and use of the TRIS samples, i.e., the material was stored in a hygrostat containing a saturated solution of magnesium nitrate (50 percent relative humidity), it was used without further heating or crushing and the calorimetric samples were weighed in air, sealed with air in the sample holder at atmospheric pressure, and not exposed to heat.

2.2. Solutions

The calorimetric solutions (approximately 300 cm^3 in volume) were taken from stock solutions, 2 dm^3 in volume, which were stored in polyethylene bottles. The solutions for the reaction with HCl were prepared by dilution of ACS reagent grade hydrochloric acid (37.0–38.0%) with distilled water. The solutions were analysed by titration with (1) 0.1 *N* standardized sodium hydroxide solutions using a recording pH meter, or (2) ACS analytical reagent grade sodium carbonate which had been dried for 1 h at 545 K, using bromphenol blue as an end point indicator. The 0.1 *N* HCl solutions were within 2 percent of the nominal value and the estimated uncertainty in the analyses is 0.5 percent or less.

The distilled water used in the preparation of the 0.1 *N* HCl was in equilibrium with air (which contains 0.03% CO_2). The decision not to use CO_2-free solutions was based on the following considerations. The Standards Committee of the Calorimetry Conference made no recommendations regarding the treatment of the aqueous calorimetric solutions except that there should be "approximately one atmosphere air pressure in the vapor space over the solution; the solution may then be assumed to be essentially saturated with air." Furthermore, many solution calorimeters are constant pressure systems which are not sealed from the atmosphere and may be affected to some extent by the atmosphere. An important factor influencing the choice of the reaction of TRIS in aqueous HCl as a standard was that a reproducible enthalpy value could be obtained without the need for special procedures and analyses. It is not necessary that the reaction be accurately defined as long as the enthalpy values are reproducible and the defined conditions can be obtained in various calorimeters. We concluded that the most reproducible condition for the preparation of the HCl solutions (without using elaborate analyses and precautions in preparation and handling) was to use solutions which were in equilibrium with air; this

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[4] D. Enagonio, Separation and Purification Section.
[5] G. Marinenko, Microchemical Analysis Section.

is one of the conditions for the certified enthalpy value for the reaction with HCl.

In preparing the aqueous NaOH solutions for the endothermic reactions, the distilled water was boiled at least 15 min and as it cooled it was guarded by a CO_2-absorption tube. Stock solutions, stored in closed polyethylene bottles, were prepared by dilution of 10 N NaOH and analyzed by titration using potassium acid phthalate (SRM 84g) and a pH meter or phenolphthalein as an end-point indicator. During the titrations, CO_2-free air was passed through the solution in the flask to reduce reaction with CO_2 in the atmosphere. The uncertainty in the analyses is estimated to be as much as 1 percent in some cases because of the possibility of some reaction with atmospheric CO_2. In the use of the solutions, the only precautions taken to avoid reaction with CO_2 were to use solutions prepared and analysed not more than 2 weeks prior to the calorimetric experiments, to transfer the solutions as quickly as possible from one container to another, and to avoid breathing directly on the solutions. In this way, carbonate formation in the solutions was minimized.

2.3. Apparatus

The vacuum-jacketed adiabatic solution calorimeter used for all of these measurements has been described in detail [2]. The sample holder and all parts in contact with the calorimetric solutions were of platinum-iridium alloys. The volume of the sample holder used in this work was 2.7 cm^3, the mass of the TRIS samples was 1.5 g, and the volume of the calorimetric solutions was approximately 300 cm^3. The volume of the vapor space above the solution was normally about 15 cm^3, but in certain special experiments (such as those using different masses of solutions described in sec. 3.2) the vapor space volume was from near 0 to 40 cm^3. The stirring rate was 350 rpm in these experiments (except as noted) and 3 to 5 $\mu K \cdot min^{-1}$. The uncertainty in the stirring energy in an experiment is estimated to be 5 percent of the total stirring energy or less, based on results obtained over a period of 8 years.

The experiments reported here were performed between February 1970 and May 1971, except some preliminary work on the endothermic reaction in January to March 1969 and some very recent work on the effects of CO_2 and on the effect of the presence of gold which was done between July and October 1972.

In various groups of experiments three different systems (described previously [2]) were used as noted to measure the calorimeter temperature. In each system the temperature-sensing unit was placed in the platinum well which projected from the vessel cover and extended into the solution to about 1 cm above the stirrer propeller. The well was centered on the same radius as were the vent and sample holder shown in figure 1. Between January and August 1970, an experimental system was used which employed a modified quartz-oscillator thermometer with digital read-out. A 25-Ω platinum resistance thermometer with a G–3 Mueller resistance bridge and an electronic null detector were used to measure the calorimeter temperature prior to January 1970, and between September 1970 and June 1972. Since June 1972, the temperature has been measured with a quartz-oscillator combined with direct frequency counting and digital print-out. Both of the quartz-oscillator systems were calibrated by comparison with the platinum resistance thermometer system.

2.4 Apparatus Modifications for This Work

This calorimeter was designed primarily to measure enthalpies of reaction or heats of reaction at constant pressure [2]. During the search for the cause of the small disagreement in enthalpy values measured by various laboratories for the reaction of TRIS in 0.1 N HCl, temporary modifications of the calorimeter were made in order to magnify certain effects and are explained in this section.

Figure 1 is a diagram of the calorimeter vessel and some of its associated parts. Five platinum tubes (two are not shown) lead up from the cover of the vessel; at left, the vent tube (B); in the center, the tube which surrounds the stirrer shaft; and at right, the tube containing the push-rod which opens the sample holder. In the upper right of figure 1 is an enlarged view of the original vent seal at the vessel cover. It consisted of a weighted platinum rod (D) which seated in a polytetrafluoroethylene (PTFE) ring (diameter of hole = 1.6 mm) located between the two parts of the vessel cover. In some experiments the rod was in place and it formed a seal; in other experiments the rod was withdrawn and there was a direct vent between the vapor space above the solution and the atmosphere. In some experiments the rod was withdrawn and the upper end of the vent tube was connected by rubber tubing to an open-end manometer (A) containing either mineral oil or mercury. This limited the diffusion of vapor from the calorimeter, and made possible observations of changes in pressure in the vapor space above the solutions during the experiment when there was a seal at the stirrer. The capillary tube, C, shown in figure 1 was used only in a special group of experiments and will be discussed later in this section.

The o-rings at the top of the platinum tubes for the stirrer and push-rod (fig. 1) also limit the extent to which the calorimeter is sealed from the atmosphere. Normally, since this is essentially a constant pressure system, PTFE o-rings are used. They are intended to function more as bearings than as seals; they wear with use and flow when heated; they form poor and unreliable seals under these conditions; however, they provide a good bearing surface for reproducible stirring energy. We have found that these bearings may hold pressures up to 10 cm of mineral oil. In experiments where good seals around the stirrer shaft and push-rod are needed, the PTFE o-rings are replaced by heavily lubricated rubber o-rings which are compressed by brass fittings (not shown in fig. 1).

In the measurements reported in this paper, four venting arrangements were used:

(1) In the "unvented" or sealed system, the vessel was sealed by nitrile rubber o-rings around the stirrer

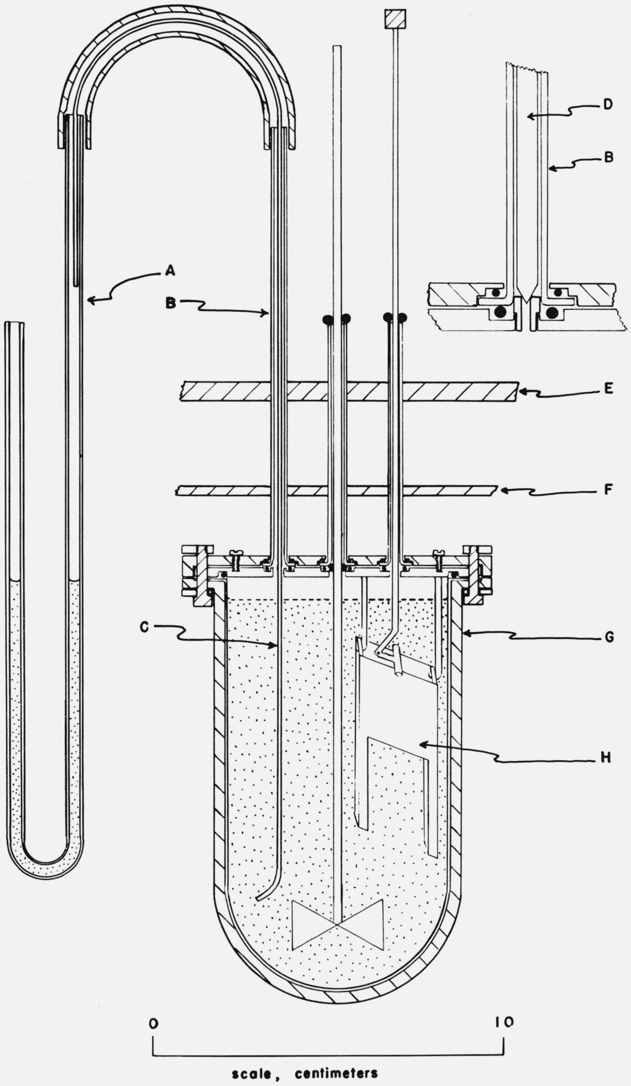

FIGURE 1. *Diagram of the calorimeter with modifications for some of this work.*

(A) Glass, open-end manometer filled with mineral oil or Hg; (B) Vent tube; (C) PTFE capillary tube; (D) Weighted platinum rod for sealing vent; (E) Cover of calorimeter jacket; (F) Cover of adiabatic shield; (G) The silver calorimeter vessel, platinum-lined; (H) Platinum sample holder.

shaft and the push-rod, and the vent was sealed at the vessel cover by the weighted platinum rod (see fig. 1, upper right).

(2) In the "vented" system which was partially closed to the atmosphere, the platinum rod was removed and the top of the vent tube was connected through rubber tubing to an open-end manometer. PTFE o-rings were used as bearings at the top of the stirrer and push-rod tubes.

(3) In the vented system open to the atmosphere, the arrangement was similar to (2) except that the rubber-tubing was disconnected from the manometer.

(4) In the system where the effects of various atmospheric gases on the TRIS reaction were studied, nitrile rubber o-rings formed seals at the top of the stirrer and push-rod tubes. The platinum rod and the PTFE ring were removed from the vent tube, and a PTFE capillary tube (C) was passed through the rubber tubing and vent tube as shown in figure 1. The lower end of the capillary tube was located a little above the stirrer and the upper end could be connected to a gas introduction line. The gas was passed through the capillary tube and bubbled through the solution; the exit gases passed through the space between the capillary and the vent tube and the rubber tubing to the atmosphere. When the gas flushing was completed, the capillary tube was disconnected from the gas introduction line and placed inside the top of the open-end manometer where the rubber tubing was connected as shown in figure 1. The calorimeter solution was thus essentially saturated with the gas under study and the space above the solution was filled with the gas at atmospheric pressure.

2.5. Calibrations and Physical Constants

The platinum resistance thermometer was calibrated in October 1961 and checked at the ice point in 1968 (see [2] for the calibration data), and 1 K equals 0.10104 Ω at 298.15 K. For converting the quartz-oscillator readings, Q, to the equivalent temperature, T (in °C) on the platinum resistance thermometer we use the linear equation, $T=A+B(Q)$. The constants, A and B, are 0.10030 and 1.01080, respectively, for the experimental quartz-oscillator system, and -8.41001 and 1.01273, respectively, based on a calibration in June 1972 for the system currently in use.

The last certified NBS calibrations of the three standard resistors (0.1 Ω, 10 Ω, and 10 kΩ used in the electrical energy measurement circuit) were made in June 1969, and of the standard cells in terms of the NBS absolute volt of 1968, in July 1969. The records of these calibrations at 1- or 2-year intervals provides additional confidence in the values used because of the consistent trends in the calibrated values. Dial calibrations of the G–3 Mueller resistance bridge were made in this laboratory in January 1969 and November 1970, and of the six-dial potentiometer, in January 1969.

The heat attributed to the chemical reaction is obtained from comparison of the calorimeter temperature rise with that resulting from the addition of precisely, measured electrical energy. The time of electrical heating is based on the standard frequency signals available at NBS.

The 1969 atomic weights [6] were used to obtain the molar mass for TRIS ($C_4H_{11}O_3N$), 121.1369. For energy conversions, 4.184 joules = 1 thermochemical calorie. The following densities were used in computing buoyancy factors: 1.35 $g \cdot cm^{-3}$ for TRIS [7], and 0.00118 $g \cdot cm^{-3}$ for air under the average conditions in this laboratory.

3. Experimental Results

The objective in this work was to provide certified enthalpy values for the reaction of Standard Reference

Material 724a (TRIS) with 0.100 *N* HCl, an exothermic reaction, and with 0.0500 *N* NaOH, an endothermic reaction, under the conditions recommended by the Standards Committee of the U.S. Calorimetry Conference in October 1966. We observed large variations in the enthalpy of the reaction in aqueous HCl under extreme conditions, and we conclude that under less extreme conditions small variations in the enthalpies of reaction occur when there are small departures from the standard conditions. The results of our measurements under the extreme conditions, some supplemental measurements, and the work which is the basis for the certified enthalpies of reaction are discussed in the following subsections.

3.1. Anomalous Effects in the Closed Calorimeter

The experiments described in sections 3.1a and 3.1b are not of high precision. It is unlikely that the conditions of these experiments would be used in precision calorimetry, however, the results under the extreme conditions may serve to explain small variations in the enthalpy of reaction when there are small departures from the conditions of the certified values. The possibility of the occurrence of these variations to an undetermined extent has prompted the assignment of a larger uncertainty to the certified value for the reaction in aqueous HCl than would otherwise have been necessary.

The calorimeter was designed primarily as a constant pressure calorimeter. The modifications made to seal the calorimeter did not result in a constant volume system in the usual sense because slow leakage sometimes occurred at the seal around the stirrer. However, the leakage rate was usually slow enough to allow observations of pressure changes above the solution during an experiment.

a. The Venting Effect

In an earlier investigation where the enthalpy of reaction of gaseous ketene in aqueous NaOH was measured [8], it was necessary to make the calorimeter sufficiently gas-tight so that the gaseous products could be collected and analysed. Following that investigation the reaction of TRIS in 0.1 *N* HCl was measured as a check on the performance of the calorimeter. The enthalpy values were about 3 percent higher than those previously measured under what were believed to be identical conditions; the only difference was that the PTFE o-ring bearing was replaced with a lubricated nitrile o-ring at the top of the tube surrounding the stirrer shaft. The calorimeter was an unvented system, arrangement (1) as described in section 2.4. When the nitrile o-ring seal around the stirrer was replaced by a PTFE o-ring bearing which was not a seal, the enthalpies measured for the TRIS reaction were again the lower values obtained before sealing the calorimeter.

In table 1 are the results of measurements of the reaction of SRM 724 or SRM 724a with 0.1 *N* HCl in the vented and in the unvented calorimeter, arrangements (2) and (1), respectively, as described in section 2.4. The pressure changes observed in the vented system appear to be insignificant and will be discussed in section 3.1b. The initial systems were always at

TABLE 1. *Results of measurements of the reaction of SRM 724 and 724a with* 0.1 N HCl *solutions in vented and unvented systems*

Expt. No.	Electrical energy equivalents		$-\Delta H$(298.15 K)			
			SRM 724		SRM 724a	
	Initial	Final	Vented	Unvented	Vented	Unvented
	$J \cdot K^{-1}$	$J \cdot K^{-1}$	$J \cdot g^{-1}$			
389	1729.06	1731.24			245.73	
390	1727.79	1730.15	245.87			
391	1728.19	1730.38			246.11	
392	1727.93	1730.15	245.61			
393	1727.72	1729.88	245.71			
394	1727.97	1730.82			246.18	
397	1728.07	1730.09		251.75		
398	1728.29	1730.20			245.83	
399	1727.80	1730.37	246.11			
400	1728.90	1730.66				252.88
401	1728.06	1730.84		255.35		
402	1731.12	1730.88				254.28
405	1728.58	1730.07			245.83	
406	1729.26	1729.45	245.61			
407	1727.83	1731.01	245.66			
408	1728.27	1730.14			245.78	
409	1729.96	1730.30	246.17			
410	1728.56	1731.52			245.91	
		Mean Sdm	245.82 ±0.09	253.55	245.91 ±0.06	253.58

atmospheric pressure and the increase in the pressure above the solutions during an experiment amounted to only about 5 cm of mineral oil (approx. density = 0.9 g · cm^{-3}).

The Expt. No. in table 1 is the serial number of experiments with this calorimeter. The temporary quartz-oscillator thermometer system (see sec. 2.3) was used in this group of experiments. The mean values of the enthalpies using SRM 724 and SRM 724a agree with each other within the experimental imprecision for both the vented and unvented systems. The mean enthalpies in the unvented system are more than 3 percent larger and less reproducible than those in the vented system. However, there is no significant difference in the electrical energy equivalents measured for the initial and final systems in these experiments. The energy equivalents may differ by as much as 0.1 percent between experiments because of small variations in the mass of the calorimetric solutions. The agreement between the electrical energy equivalents in the vented and unvented systems indicates that the calorimeter was performing properly in both systems. The disagreement between the enthalpy values for the reaction in the vented and unvented systems indicates the possibility of a side reaction causing a larger exothermic enthalpy value in the closed system. The observations of pressure above the solutions in the vented system indicated that the increase in pressure during the reaction was similar to that which occurred during the electrical calibrations; the temperature rise was essentially the same in the reaction and in the calibrations.

The vapor space volume above the solutions in these experiments was approximately 20 cm^3. Condensation within this vapor space would produce an exothermic heat which might be different in a vented system than in an unvented system. However, since there is no change in ionic strength for the hypothetical reaction, the condensation correction is assumed to be zero.

It was also possible that the venting effect was the result of a side reaction catalysed by the platinum which lines this calorimeter. However, this effect has been observed by Duer [9] in an isoperibol calorimeter with no platinum parts; the vessel was glass with a stainless steel lid. His enthalpy measurements with SRM 724 in 0.1 N HCl averaged −249.24 ± 0.96 J · g^{-1} in four experiments before providing a definite vent to the atmosphere; after venting the calorimeter, the average of five experiments was −246.19 ± 0.25 J · g^{-1}. The uncertainties are 2 sdm, the difference between the two enthalpy values is 1.2 percent, and the experimental imprecision was definitely improved by venting the calorimeter.

P. J. Gardner [10] has given us permission to publish his results of measurements of the TRIS reaction with a new calorimeter constructed during his tenure of a Visiting Fellowship to the Chemistry Department at the University of Otago during 1971–72. The isoperibol calorimeter was glass with reentrant wells for the thermistor and heater. The stirrer was steel with PTFE bearings which presumably formed good seals initially, but after wearing did not seal the calorimeter. The following enthalpy values were first measured for the reaction of TRIS in 0.1 *N* HCl: −7520, −7150, −7300, −7150, −7130, and −7330 cal · mol^{-1}; the average was 7263 ± 62(sdm) cal · mol^{-1} or 250.86 ± 2.14 J · g^{-1}. These results were very erratic and high. He measured another test reaction which gave satisfactory agreement with published values. He then returned to the TRIS reaction. By this time he was using longer fore periods to insure thermal equilibrium before the reaction, and the PTFE stirrer bearings had worn and the calorimeter was probably vented to the atmosphere. This time the mean of seven experiments was 7118 ± 5(sdm) cal · mol^{-1} or 245.85 ± 0.17 J · g^{-1}. These two sets of results are similar to ours in the vented and unvented systems.

Robie and Hemingway [11] found a venting effect, but in the opposite direction. Their isoperibol calorimeter is lined with gold. The average of their ten enthalpy measurements with SRM 724 in a sealed calorimeter was −245.16 ± 0.38 J · g^{-1} [12] and after venting the calorimeter, the average of five experiments was −245.64 ± 0.24 J · g^{-1} [11]; these two values are within the experimental imprecisions (2 sdm) given and may not be significantly different, however, there does appear to be an improvement in the precision of the measurements upon venting the calorimeter. In September 1972, we made four measurements of the TRIS reaction using 0.6 g of gold turnings with TRIS in the sample holder. The average enthalpy in these experiments was −245.78 ± 0.32 J · g^{-1} which agrees well with the certified value, −245.76 J · g^{-1} (discussed in sec. 3.3); the experimental imprecision, 2 sdm, is larger than normal because of stirring problems at that time. However, it appears that the presence of gold did not affect the enthalpy of reaction significantly.

We have looked for the venting effect in other reactions such as that of H_2SO_4 (aq) in NaOH(aq) [2] and in KCl(c) in H_2O [13]. These enthalpies of reaction were the same in the unvented calorimeter or in the calorimeter open to the atmosphere.

b. The CO_2 Effect

In June 1970, a preliminary investigation was made of the effects of dissolved gases (the major components of air: N_2, O_2, Ar, and CO_2) on the TRIS reaction in 0.1 *N* HCl. The results of this investigation were reported informally at the U.S. Calorimetry Conference in October 1970.

The gas under study was introduced into the calorimeter through a PTFE tube, (C), in figure 1. The compressed gas from a commercial cylinder was passed through a tube containing magnesium perchlorate and a CO_2 absorber (this was by-passed when CO_2 was used), and then through a bubbler containing 0.1 *N* HCl before entering the PTFE tube and the calorimeter as described in section 2.4. The gas was bubbled through the calorimetric solution at approximately 50 cm^3 · min^{-1} for about 90 min while stirring to saturate the solution and displace air above the solution with the gas under study. Small droplets of solution accumulated on the vessel cover as a result of gas bubbles bursting at the surface of the solutions. These droplets probably caused errors due to evaporation to the main solution during the experiment, therefore, the results are not of high precision but are useful in showing gross effects.

The temporary quartz-oscillator thermometer system was used for measurement of the calorimeter temperature. The vent tube was connected to an open-end manometer and the pressures above the solutions were recorded during the experiment. Arrangement (4), section 2.4, was used for these measurements. In the nine preliminary experiments the enthalpies of reaction (in $J \cdot g^{-1}$) were: N_2 atmosphere, −246.8, −246.2, and −245.7; O_2 atmosphere, −247.3 and −246.0; Ar atmosphere, −248.5 and −246.0; and CO_2 atmosphere, −260.9 and −262.8. The last two values are obviously about 7 percent higher than the others which we regard as normal values within the experimental uncertainties of these rough experiments.

In all of these experiments, except the two using CO_2, the manometer contained mineral oil. With CO_2 the pressure changes were larger and it was necessary to use mercury in the manometer. One end of the manometer was open to the atmosphere and the readings indicated the difference between the pressure above the calorimetric solution and the atmospheric pressure. Figure 2 is a plot of the manometer readings, $P_{cal} - P_{\text{atm}}$, versus time for four of the experiments using different gaseous atmospheres. The pairs of vertical lines mark the electrical heating periods for the calibrations and the single vertical line marks the time when the TRIS reactions were started. At the left of figure 2, the set of points at the top are for the N_2 atmosphere; the second set, for the O_2 atmosphere; the third set, for the Ar atmosphere; and the fourth set at the bottom, for the CO_2 atmosphere. The larger circles marking the pressure readings for the CO_2 atmosphere indicate that the readings were actually made as cm of Hg and were converted to cm of mineral oil using a factor of 15; thus, the uncertainty in these readings is greater than for the other three gases and roughly proportional to the diameter of the circles. When the connection between the manometer and the vent tube was made initially, the readings were all zero (or at atmospheric pressure). With N_2 atmosphere, the pressure above the solution continuously increased during the experiment. The changes in pressure for the O_2 and Ar atmospheres were similar; there was initially a small reduction in pressure as the system continued to absorb the gas, a leveling off, and then increasing pressure above the solution during the remainder of the experiment. In the atmospheres of N_2, O_2, and Ar, the increase in pressure during the TRIS reaction was essentially equal to that during the electrical calibrations. This is to be expected since the temperature rise was the same for the reaction and for the calibrations.

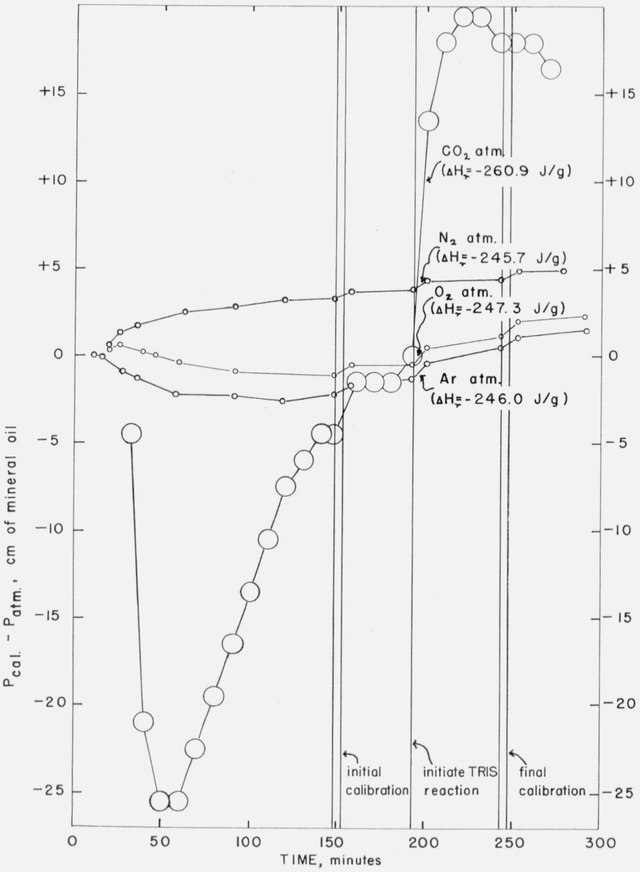

FIGURE 2. *Plots of observed pressures in the vapor space above the solutions during preliminary* TRIS *experiments in a sealed calorimeter where the* HCl *solutions were saturated with various gases: Curves at left (top to bottom)* N_2, O_2, Ar, *and* CO_2 *atmospheres.*

Negative pressure reading indicates reduced pressure above the solution.

The pressure changes in the CO_2 atmosphere were quite different. Initially there was a large and rapid reduction in pressure as the system continued to absorb CO_2. After reaching a minimum the pressure steadily increased and began to level off near atmospheric pressure. (It was learned that this was due to air leakage through the stirrer seal and will be discussed later in this section.) The pressure changes during the calibrations are negligible, but during the TRIS reaction there was a pressure increase of approximately 20 cm of mineral oil or more than 1 cm of Hg. This unmistakable increase in pressure above the solution was a result of the TRIS reaction in the presence of CO_2. This was accompanied by an additional exothermic heat effect when air was also present as shown by the high $-\Delta H_r$ values. When the calorimeter is not sealed, the additional exothermic effect in solutions saturated with CO_2 is not found.

To confirm our earlier results with the CO_2 atmospheres, we measured enthalpies of the TRIS reaction with and without CO_2 in July 1972, where the calorimeter temperatures were measured with the new quartz-oscillator system (see sec. 2.3). The precision of the calorimetry was improved in these experiments by preventing the accumulation of droplets of solution on the vessel cover during the preliminary gas flushing. This was accomplished by flushing the CO_2 through the solution before the cup of the vessel was attached to the cover, with a space of about 2 cm between the solution

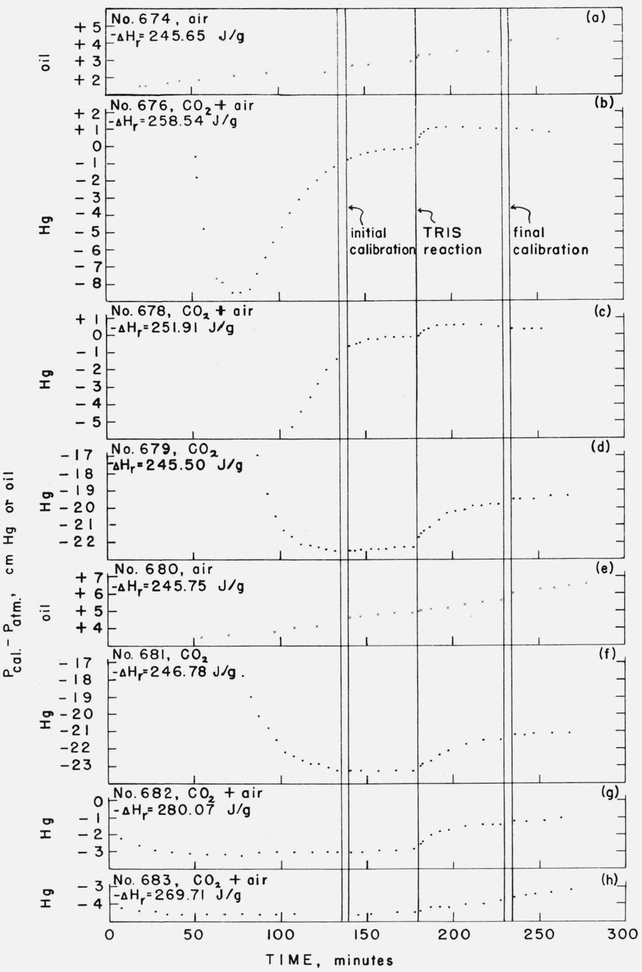

FIGURE 3. *Plots of observed pressures in the vapor space above the solutions during later* TRIS *experiments in a sealed calorimeter in atmospheres of air, air + CO_2, and CO_2.*

The scale for (a) and (e) is cm of oil, and cm of Hg for all others.

and the cover. Then the PTFE tube was withdrawn so that the lower end of the tube was about 2 mm below the cover of the vessel. The flushing with CO_2 above the solution level was continued during the assembly of the calorimeter.

In figure 3 are the plots of manometer readings, $P_{\mathrm{cal}} - P_{\mathrm{atm}}$, versus time for the eight later experiments. Plots (a) and (e) are for Expt. Nos. 674 and 680 with air above the solution where the pressures are given as cm of mineral oil and the shapes of the curves are similar to those in figure 2 for N_2, O_2, and Ar atmospheres. No gas was bubbled through the solutions and the systems were in equilibrium with air. The measured enthalpies of reaction were close to the certified value. Plots (b) and (c) in figure 3 were for CO_2 atmospheres and are similar to the corresponding curve in figure 2 except that the pressures are in cm of Hg. There was the characteristic increase in pressure above the solution during the TRIS reaction and the high enthalpy of reaction, $-258.54 \mathrm{~J} \cdot \mathrm{g}^{-1}$ and $-251.91 \mathrm{~J} \cdot \mathrm{g}^{-1}$. After Expt. No. 678, (c) in figure 3, it was suspected that air leakage through the seal at the stirrer was the cause of the curve leveling off near atmospheric pressure. A better seal at the stirrer was formed by the use of more lubricant on the nitrile o-ring. Evidence of the improvement in the seal may be seen in figure 3, plots (d) and (f) where, with CO_2 atmospheres, the reduced pressures above the solutions remained at more than 20 cm of Hg until starting the TRIS reaction. The pressure increase in Expt. No. 681 was slower than in Expt. No. 679 because of the slower stirring rate, 200 rpm, instead of the usual 450 rpm used for other experiments in this group. It was unexpected that in these two experiments where the atmosphere was relatively pure CO_2, the enthalpies of the TRIS reactions were very close to those from the reactions in the presence of air alone. With the suspicion that both air and CO_2 are required to obtain the strongly exothermic side reaction, in two experiments, (g) and (h) in figure 3, some air was admitted to the CO_2- saturated system after the minimum pressure was reached. Again in the presence of CO_2 + air the enthalpies of reaction, $-280.07 \mathrm{~J} \cdot \mathrm{g}^{-1}$ (g) and $-269.71 \mathrm{~J} \cdot \mathrm{g}^{-1}$ (h), were significantly larger than in the presence of air or CO_2 alone.

It was also observed in the systems saturated with CO_2, that upon initiating the reaction the increase in pressure above the solution was relatively slow. It can be seen in figure 3 that the increase in pressure extended over a period of about 15 min. However, in atmospheres of air, N_2, O_2, and Ar, the increase in pressure was almost instantaneous. The gas which was in the sample holder obviously expanded rapidly because it was at the source of the heat of reaction.

Although these results cannot be regarded as quantitatively precise, they do indicate two effects in the TRIS reaction with 0.1 *N* HCl in a closed system: (1) an increase in the pressure above the solution during the reaction in the presence of CO_2, and (2) a side reaction in the presence of CO_2 + air which is more exothermic than the reaction in the presence of only air or CO_2. If only the hypothetical reaction occurred in the system saturated with CO_2, a slightly smaller value for $-\Delta H_r$ would be expected because of the reduction in solubility of CO_2 at the higher temperature. However, the effect of the change in composition of the solution on the CO_2 solubility is not known. Quantitative and qualitative analyses of the solutions and gases, and more accurate pressure measurements would be necessary if the side reaction is to be fully described.

Variations in the enthalpy of reaction may be expected, especially in constant volume systems, unless care is taken to exclude CO_2 from the system. If CO_2 is absent from the system, the enthalpy value may be slightly lower than the certified value, where the solutions are in equilibrium with air which contains 0.03 percent CO_2.

3.2 Supplemental Measurements

Our enthalpy calculations are based on the assumption that the energy equivalents at the mean tempera-

TABLE 2. *Measurements of electrical energy equivalents at various temperatures for initial and final systems in the* TRIS *reaction with* 0.1 N HCl

Expt.	Initial system			Final system		
No.	ΔT	$\bar{T}$	*EEE*	ΔT	$\bar{T}$	*EEE*
	K	*K*	$J \cdot K^{-1}$	*K*	*K*	$J \cdot K^{-1}$
*477	1.28279	295.72	1730.35	1.28096	301.09	1733.07
	1.28262	297.01	1730.33	1.28064	302.37	1733.40
	1.28347	298.57	1729.50	1.28080	303.66	1733.29
	1.28242	299.58	1730.81	1.28050	304.95	1733.57
		(Mean)	1730.25		(Mean)	1733.33
693	0.22025	297.46	1727.35	0.22008	298.38	1730.15
	.22010	297.69	1727.26	.22021	298.61	1729.73
	.22028	297.93	1727.32	.22009	298.85	1729.90
		(Mean)	1727.31		(Mean)	1729.93
695	0.57543	296.53	1727.87	0.57436	298.53	1729.15
	.57471	297.12	1727.80	.57390	299.12	1728.78
	.57385	297.71	1726.97	.57423	299.71	1728.54
		(Mean)	1727.55		(Mean)	1728.82

*The temporary quartz thermometer used in this experiment had a different heat capacity than the new quartz-oscillator used in the other two experiments; this accounts for the difference in the *EEE*.

ture of the chemical reaction are the same as those at the mean temperatures of the electrical calibrations. Therefore, multiple electrical calibrations of the initial and final systems for the TRIS reaction in 0.1 *N* HCl were measured to determine whether the energy equivalents changed significantly with temperature. The results of these measurements in three experiments are given in table 2. The earlier quartz thermometer system (discussed in sec. 2.3) was used in Expt. No. 477 and the corrected temperature rise, ΔT, was 1.28 K for each of the four electrical calibrations of the initial and final systems. There was no consistent change in the electrical energy equivalents, EEE, with temperature and the maximum departure from the mean of the group was 0.04 percent. Although EEE of the initial systems would change by about 0.02 percent per deg (from known heat capacity data), this trend was considered negligible in relation to our measurements of the TRIS reaction because the difference between the mean temperature of the calibration and that of the reaction was less than 0.3 K. In Expt. Nos. 693 and 695 the temperatures were measured with the later quartz-oscillator system (discussed in sec. 2.3) and the temperature rises during the calibrations were 0.22 K and 0.57 K, respectively. There was no evidence of a change in the energy equivalents with temperature in this range and the stated assumption was justified.

There are small differences in the electrical energy equivalents for different experiments because of small variations in the mass of solutions used. The energy equivalents actually measured for each system are used in the calculations of heat evolved or absorbed. However, the differences in the energy equivalents do not reflect the precision of the measurement of the electrical energy equivalents. In order to obtain a factor for correcting the energy equivalents to a standard mass of solution, measurements were made on systems containing 5 percent more and 5 percent less than the standard mass of HCl solution (302.7 g) and of TRIS (1.50 g); these results are given in table 3. In these four experiments the temperature was measured with the platinum resistance thermometer and the system was vented to the atmosphere, arrangement (3) described in section 2.4. The vapor space above the solution in the vessel was nearly eliminated in Expt. Nos. 530 and 531, and was less than 40 cm³ in volume in Expt. Nos. 532 and 533. Arvidsson and Westrum measured the heat capacity of TRIS as $Cp(298.15 \text{ K}) = 39.96$ cal · mol^{-1} · K^{-1} or 0.1394 J · g^{-1} · Ω^{-1} [14]. The corrections to the energy equivalents here were less than 0.02 J · Ω^{-1} for the differences from the standard mass of TRIS: these corrections were neglected. The factors for correcting to the standard mass of HCl solution

TABLE 3. *Electrical energy equivalents of initial and final systems for the* TRIS *reaction in* 0.1 N HCl *using more and less than the standard mass of* HCl *solution and of* TRIS

Expt. No.	Mass of HCl soln.	Electrical energy equivalents	
		Initial	Final
	g	$J \cdot \Omega^{-1}$	$J \cdot \Omega^{-1}$
5% more than the standard mass of HCl and TRIS:			
530	317.68	17,730.6	17,756.4
531	317.71	17,731.9	17,764.0
(Mean)	317.70	17,731.2	17,760.2
5% less than the standard mass of HCl and TRIS:			
532	287.68	16,498.1	16,516.9
533	287.77	16.505.7	16,527.4
(Mean)	287.72	16,501.9	16,522.2

Factors: 41.00 J · Ω^{-1} · g^{-1} for initial system
41.29 J · Ω^{-1} · g^{-1} for final system

TABLE 4. *Corrections to the measured electrical energy equivalents (table 5) and the energy equivalents corrected to a standard mass of* HCl *solution for initial and final systems of the* TRIS *reaction in* 0.1 N NCl

Expt. No.	Mass of TRIS	Mass of HCl soln.	Correction to 302.70g HCl		Energy equivalent corrected	
			Initial	Final	Initial	Final
	g	*g*	$J \cdot \Omega^{-1}$	$J \cdot \Omega^{-1}$	$J \cdot \Omega^{-1}$	$J \cdot \Omega^{-1}$
521	1.49696	302.76	−2.5	−2.5	17,117.6	17,146.7
522	1.49214	302.73	−1.2	−1.2	17,115.3	17,149.3
523	1.52248	302.72	−0.8	−0.8	17,122.5	17,141.8
524	1.53278	302.69	+0.4	+0.4	17,116.1	17,142.1
527	1.50880	302.69	+0.4	+0.4	17,116.7	17,142.3
(Mean)					17,117.6	17,144.4
(sdm)					±1.3	±1.5
					(0.008%)	(0.009%)
528	1.52958	302.74	−1.6	−1.6	17,117.4	17,137.3
529	1.52074	302.72	−0.8	−0.8	17,116.1	17,139.2
532	1.45790	287.68	+615.8	+620.2	17,113.9	17,137.1
533	1.43550	287.77	+612.1	+616.4	17,117.8	17,143.8
534	1.52143	302.73	−1.2	−1.2	17,115.6	17,144.0
(Mean)					17,116.2	17,140.3
(sdm)					±0.7	±1.5
					(0.004%)	(0.009%)

given at the bottom of table 3 were obtained from the two means for mass of HCl solution and for the energy equivalents for the initial and final systems. These factors were used to obtain corrections to the energy equivalents for TRIS experiments to be described in the next section, 3.3, and the pertinent data are given in table 4. In each group the standard deviation from the mean of the corrected energy equivalent was less than ± 0.01 percent which is an indication of the precision of the calorimetry.

3.3 ΔHr of SRM 724a in HCl (aq)

Some of our measurements of the enthalpy of reaction of SRM 724a in 0.1 *N* HCl using the platinum resistance thermometer system previously described [2] are given in table 5. The masses of TRIS and of the HCl solution for these experiments were listed in table 4. The electrical energy equivalents given in table 5 are the values actually measured (not corrected to a standard mass of HCl solution). The "Stirring energy correction" is the net result of the extrapolations from the mid-points of the initial and final rating periods to the time of starting the reaction; it was subtracted from the difference between the temperatures at the mid-points of the rating periods to obtain the corrected temperature rise, ΔRc reaction. The enthalpy of solution at the temperature of reaction is $\Delta H(T) = -[\overline{\mathrm{EEE}}\ (\Delta Rc)]/(\text{mass of TRIS})$, where $\overline{\mathrm{EEE}}$ is the mean of the initial and final electrical energy equivalents. The enthalpy of reaction, $\Delta H(298.15\ \mathrm{K})$, is the sum of $\Delta H(T)$ and the correction obtained from $\Delta Cp = 1.435$ $\mathrm{J \cdot g^{-1} \cdot K^{-1}}$ which will be discussed later in this section.

The first five experiments given in table 5 were vented to the manometer containing mineral oil, arrangement (2) described in section 2.4, and are in good agreement with the vented experiments given in table 1 where the quartz-oscillator thermometer was used. The last five experiments listed in table 5 were vented to the atmosphere, arrangement (3) in section 2.4. Here the mean enthalpy of reaction was slightly smaller and the precision of the measurements was significantly improved as compared to the first five experiments. Thus, it appears that even the seemingly insignificant confinement by the open-end manometer of the vapor space above the solution may have affected the enthalpy of solution.

In table 5, the values for $-\Delta H(298.15\ \mathrm{K})$ which are marked with an asterisk were measured in a solution which was initially CO_2-free; the unmarked values were in solutions always in equilibrium with air. The CO_2-free solution was prepared in a Pyrex glass Erlenmeyer flask. The distilled water was boiled approximately 30 min to remove CO_2. Immediately after removing the flask from the heat, the concentrated HCl solution was added. Then the flask was sealed by a rubber stopper containing a glass siphon tube with a stopcock on the outer end. The air intake for the flask was guarded by a tube containing $MgClO_4$ and a CO_2 absorber. After cooling, the solution was analysed as 0.0984 *N* by titration with 0.1 *N* standard sodium hydroxide solution using a pH recording electrometer. All portions of the HCl solution were dispensed through the glass stopcock into a polyethylene bottle for weighing the calorimetric solutions. The weight of the solution was adjusted and the solution was poured into the cup of the calorimeter vessel which was quickly attached to the cover. Thus, although the HCl solution was initially CO_2-free, the calorimetric solutions were exposed to the atmosphere during weighing and transfer to the vessel as well as during the experiment since the calorimeter was not gas-tight. It is therefore not surprising that no significant difference was observed between the enthalpy values for experiments using solutions initially CO_2-free and those using solutions always in

TABLE 5. *Calorimetric data for reaction of SRM 724a in* 0.1 N HCl *solution*

The last five experiments are the basis for the certified enthalpy value

Expt. No.	Electrical energy equivalents		Stirring energy correction	ΔRc reaction	$\overline{T}$ reaction	Corr. to 298.15 K	$-\Delta H$(298.15 K)
	Initial	Final					
	$J \cdot \Omega^{-1}$	$J \cdot \Omega^{-1}$	Ω	Ω	K	$J \cdot g^{-1}$	$J \cdot g^{-1}$
Vented to manometer:							
521	17,120.1	17,149.2	0.000522	0.021514	297.946	−0.29	*245.96
522	17,116.5	17,145.2	.000497	.021454	297.945	− .29	246.01
523	17,123.3	17,142.6	.000495	.021882	298.147	.00	*246.24
524	17,115.7	17,141.7	.000494	.021993	298.146	.00	245.77
527	17,116.3	17,141.9	.000474	.021660	298.144	−.01	*245.90
						(Mean)	245.97
						(sdm)	±0.08
							(0.03%)
Vented to atmosphere:							
528	17,119.0	17,138.9	0.000474	0.021941	298.143	−0.01	245.70
529	17,116.9	17,140.0	.000479	.021826	298.143	−.01	*245.82
532	16,498.1	16,516.8	.000518	.021677	298.358	+.30	245.75
533	16,505.7	16,527.4	.000519	.021333	298.358	+.30	*245.75
534	17,116.8	17,145.2	.000554	.021856	297.952	−.28	*245.81
						(Mean)	245.76
						(sdm)	±0.02
							(0.01%)

*Initially solutions were CO_2-free.

equilibrium with air. The analysis of the latter stock solution was 0.1003 *N*.

A value of ΔCp for the reaction of TRIS in 0.1 *N* HCl was obtained from a least squares fit of the data in table 6 to a linear equation. A quadratic equation was also fitted by least squares and this indicated that the data did not justify a quadratic term. ΔCp for the reaction is 1.435 ± 0.023 $J \cdot g^{-1} \cdot K^{-1}$ or 41.54 ± 0.67 $cal \cdot mol^{-1} \cdot K^{-1}$ (the uncertainty is the standard error). This is in excellent agreement with the value of 1.437 $J \cdot g^{-1} \cdot K^{-1}$ reported by Hill et al. [15].

The certified value for the enthalpy of reaction of SRM 724a in 0.1 *N* HCl solution is

$$\Delta H(298.15 \text{ K}) = -245.76 \pm 0.26 \text{ J} \cdot \text{g}^{-1} \qquad (1)$$

and is based on the last 5 experiments in table 5. The conditions which apply to this value are as follows:

(1) The standard reference material should be used without further crushing or heating.
(2) The concentration should be 5 g of the sample per dm^3 of 0.100 *N* HCl solution.
(3) The sample and the calorimetric solution should be in equilibrium with air at atmospheric pressure.
(4) Measurements should be made at constant pressure.

The overall uncertainty (0.11%) assigned to the certified enthalpy value is the square root of the sum of the squares of the following uncertainties: the experimental precision at the 95 percent confidence level, 0.03 percent; inhomogeniety in the sample, 0.01 percent; and other possible systematic errors, 0.10 percent. The latter is larger than would have been assigned if the anomalous effects of venting and CO_2 were unknown. Until these effects can be fully explained and the conditions of the reaction more precisely defined, a smaller uncertainty can not be assigned.

TABLE 6. *Data used in obtaining the relationship of temperature and the enthalpy of reaction of* TRIS *in 0.1 N* HCl

Expt. No.	$\bar{T}$ reaction	$-\Delta H(T)$
	K	$J \cdot g^{-1}$
536	293.628	252.25
537	293.706	252.32
534	297.952	246.09
528	298.143	245.71
529	298.143	245.83
532	298.358	245.45
533	298.358	245.45
535	303.088	239.15
538	303.098	238.36

The following possible errors and corrections to the ΔH_{soln} were considered for the worst conditions and found to be negligible:

(1) Heater lead corrections, −0.004 percent;
(2) Factor switch on potentiometer,−0.004 percent;
(3) Vaporization correction for air in sample holder, <0.05 *J* or <0.02 percent.

The first two corrections are opposite in sign to the third resulting in a net correction of about 0.01 percent in the worst case.

3.4. ΔHr of SRM 724a in NaOH(aq)

The platinum resistance thermometer was used to measure the calorimeter temperature in all experiments in this section. The NaOH solutions were prepared and analysed as described in section 2.2.

The enthalpy of reaction of TRIS in aqueous NaOH is dependent on the NaOH concentration. In 11 preliminary experiments we measured the enthalpy of reaction of SRM 724 at various concentrations of NaOH as given in table 7. The mass of the samples was between 1.7 and 2.1 g and the mass of the solutions was 307 to 308 g. The correction to 298.15 K was obtained from $\Delta Cp = 1.03\ \mathrm{J \cdot g^{-1} \cdot K^{-1}}$ (eq (3) discussed later in this section). A least squares fit of the NaOH concentration and enthalpy of reaction data in tables 7 and 8 resulted in the following equation (in $\mathrm{J \cdot g^{-1}}$):

$$\Delta H(298.15\ \mathrm{K}) = 146.03 - 87.8(N) + 43.2(N)^2, \quad N < 1.0 \tag{2}$$

where N is the normality of the NaOH solution. The standard error of the estimate is $0.19\ \mathrm{J \cdot g^{-1}}$. This equation agrees with the values reported by Hill et al. [15], within the uncertainties of the NaOH analyses.

In tables 8 and 9 are the data for 9 more recent experiments with SRM 724a which are the basis for the certified value for the enthalpy of reaction in 0.0500 N NaOH. The electrical energy equivalents for the initial and final systems are given and the stirring energy correction was described in section 3.3. (In Expt. 541 there was a malfunction of the electronic counter and an estimated value was used for the electrical energy equivalent of the final system.) The observed temperature rise, ΔRc net, is the result of the endothermic chemical reaction plus the electrical energy added to prevent a drop in the calorimeter temperature. (Without the addition of electrical energy, adiabatic conditions could not be maintained because the adiabatic shield would be warmer than the vessel.) Details of these electrical energy measurements are given in table 9.

After initiating the electrical heating, a time lag of 10 to 20 s occurs before there is a noticeable rise in the calorimeter temperature, however, the endothermic TRIS reaction in NaOH rapidly absorbs heat as soon as the sample holder is opened. Therefore it was necessary to delay initiation of the reaction until the calorimeter temperature was rising from electrical heating to prevent a drop in the calorimeter temperature. The time interval between the start of electrical heating

TABLE 7. *Data used in obtaining the relationship of* NaOH *concentration and the enthalpy of reaction of* TRIS *in* NaOH(aq)

Expt. No.	Normality of NaOH	$\bar{T}$ reaction	$\Delta H(T)$	Correction to 298.15 K	ΔH(298.15 K)	
	mol · dm⁻³	*K*	*J · g⁻¹*	*J · g⁻¹*	*J · g⁻¹*	*kJ · mol⁻¹*
264	0.005	297.974	145.47	0.18	145.65	17.644
265	.005	297.933	145.33	.23	145.56	17.632
274	.049	297.741	141.33	.42	141.75	17.171
275	.049	297.792	141.20	.37	141.57	17.149
272	.051	297.740	141.14	.43	141.57	17.149
273	.051	297.744	141.17	.42	141.59	17.152
276	.051	297.735	141.19	.43	141.62	17.156
270	.144	297.923	133.76	.22	133.98	16.230
271	.144	297.936	134.38	.22	134.60	16.306
268	.944	297.978	101.53	.18	101.71	12.321
269	.944	297.932	101.32	.23	101.54	12.300

TABLE 8. *Calorimetric data for experiments which are the basis for the certified enthalpy value for the reaction of SRM 724a in* 0.0500 N NaOH

Expt. No.	Electrical energy equivalents		Stirring energy correction	ΔRc net	Q reaction	Sample mass	NaOH conc.	Corr. to 0.0500 N NaOH	$\bar{T}$ reaction	Corr. to 298.15 K	ΔH(298.15 K)
	Initial	Final									
	J · Ω⁻¹	*J · Ω⁻¹*	*Ω*	*Ω*	*J*	*g*	*mol · dm⁻³*	*J · g⁻¹*	*K*	*J · g⁻¹*	*J · g⁻¹*
539	17,360.8	17,382.2	0.000731	0.068443	−214.20	1.50772	0.0487	−0.11	298.174	−0.02	141.93
540	17,361.8	17,379.1	.000805	.068278	−216.74	1.52355	.0487	− .11	298.171	−0.02	*142.13
541	17,360.7	(17,380)	.000766	.055982	−214.61	1.51584	.0487	− .11	298.135	+0.02	141.48
542	17,364.4	17,382.6	.000664	.056105	−212.09	1.49550	.0487	− .11	298.113	+0.04	*141.75
543	17,364.6	17,379.3	.000801	.055751	−213.70	1.50330	.0487	− .11	298.312	−0.17	141.88
544	17,360.4	17,376.8	.000843	.055720	−215.58	1.51776	.0487	− .11	298.318	−0.17	*141.76
545	17,356.8	17,380.6	.000779	.055804	−213.35	1.50277	.0489	− .09	298.314	−0.17	141.71
547	17,364.4	17,383.2	.000715	.056145	−215.37	1.52006	.0489	− .09	298.120	+0.03	141.62
548	17,361.8	17,377.6	.000576	.060575	−215.27	1.51439	.0489	− .09	298.298	−0.15	141.91
										Mean =	141.80
										sdm =	±0.06

*Vented to manometer.

TABLE 9. *Data for electrical energy added during the reaction of SRM 724a in* 0.0500 N NaOH

Expt. No.	Reaction delay	E	I	t	$\frac{E}{I}=R$	EIt
	s	V	A	s	Ω	J
539	75	18.65942	0.1926715	390.2940	96.8458	1403.16
540	75	18.65945	.1926707	390.1824	96.8463	1402.76
541	75	18.65707	.1926458	330.2647	96.8465	1187.04
542	75	18.65649	.1926397	330.2258	96.8465	1186.82
543	75	18.63263	.1923931	329.7832	96.8467	1182.20
544	135	18.62740	.1923397	330.2887	96.8464	1183.35
545	135	18.62060	.1922698	330.3186	96.8462	1182.60
547	75	18.68088	.1928915	330.4768	96.8466	1190.83
548	45	28.57851	.2951283	150.2719	96.8342	1267.44

and the opening of the sample holder is the "Reaction delay" given in table 9; the variations shown here did not affect the enthalpy of reaction.

The voltage drop across the calorimeter heater, E, the current through the heater, I, and the time of heating, t, are also given in table 9. The resistance of the calorimeter heater, E/I, indicates the precision of the electrical energy measurements. In Expt. No. 548 the voltage was increased by 10 V; the heater resistance decreased by 0.01 percent. The total electrical energy added during the chemical reaction period, EIt, is subtracted from the product of ΔRc net and the mean electrical energy equivalent to obtain Q reaction (table 8). The enthalpy of reaction at the reaction temperature, $\Delta H(T)$, is $-Q$ reaction/(sample mass). A correction for condensation in the vapor space above the solution was estimated to be about 0.001 J in the worst case and was neglected.

Equation (2) was used for the corrections to 0.0500 N NaOH (table 8). Similar corrections were made to $\Delta H(T)$ in four additional experiments used in obtaining ΔCp for the reaction. The results of these experiments are as follows:

Expt. No.	$\bar{T}$ reaction	$\Delta H(T)$
	K	$\mathrm{J \cdot g^{-1}}$
549	303.130	146.74
550	295.443	139.17
551	295.559	139.17
552	303.069	147.12

A least squares fit of the data for the mean temperature of reaction, $\bar{T}$ reaction, and for $\Delta H(T)$ in 0.0500 N NaOH from these experiments and those in table 8 gave the following equation for the range, 295 to 303 K (in $\mathrm{J \cdot g^{-1}}$):

$$\Delta H(T) = 141.80 + 1.025(T - 298.15\ \mathrm{K}) \qquad (3)$$

The standard errors of the constants are 0.05 and 0.025, respectively, and the standard error of the estimate is 0.19 $\mathrm{J \cdot g^{-1}}$. Thus, $\Delta Cp = 1.025 \pm 0.025$ $\mathrm{J \cdot g^{-1}}$ or 29.7 ± 0.7 $\mathrm{cal \cdot mol^{-1}}$. This value was used for the corrections to 298.15 K in table 8.

The enthalpy values in table 8 which are marked with an asterisk were obtained in systems vented to the manometer containing mineral oil (see sec. 2.4) and all others were vented to the atmosphere; there appears to be no significant difference in the results.

In a group of earlier experiments (Nos. 272–277 made in March 1969) the conditions were similar to those in tables 8 and 9 except that the SRM 724 reaction was started only a few seconds after beginning the electrical heating. Because of the heater lag the calorimeter temperature dropped and there was a relatively large difference between the temperatures of the vessel and the shield; a correction (described in [2]) for the heat transferred to the vessel was about 0.03 percent of the heat absorbed by the reaction. The mean of these six experiments was $\Delta H(298.15\ \mathrm{K}) = 141.63$ $\pm$ 0.03(sdm) $\mathrm{J \cdot g^{-1}}$. Although the mean enthalpy is within the combined experimental imprecision (2 sdm) of that given in table 8, the latter is probably a better value since no corrections were necessary for departures from adiabatic conditions. The standard deviation of the mean for the earlier experiments was smaller than that for the experiments in table 8 because conditions were reproduced in all six experiments. The fact that there were variations in Reaction delay, E, and t (as shown in table 9) suggests that the larger imprecision is more realistic.

Based on the experiments in table 8, the certified value for the enthalpy of solution of NBS Standard Reference Material 724a in 0.0500 N NaOH solution at a concentration of 5 g per $\mathrm{dm^3}$ of solution is

$$\Delta H(298.15\ \mathrm{K}) = 141.80 \pm 0.19\ \mathrm{J \cdot g^{-1}}.$$

The sample should be used without further heating or crushing, and it should be with air at atmospheric pressure in the sample container. Air at atmospheric pressure should be above the calorimetric solution.

The overall uncertainty (0.19 $\mathrm{J \cdot g^{-1}}$ or 0.13%) assigned to the certified value is the square root of the sum of the squares of the following uncertainties: the experimental imprecision at the 95 percent confidence level (2.31 sdm), 0.15 $\mathrm{J \cdot g^{-1}}$; analysis of sodium hydroxide solutions, 0.10 $\mathrm{J \cdot g^{-1}}$; and other possible systematic errors, 0.07 $\mathrm{J \cdot g^{-1}}$.

4. Other Values Reported

Most measurements of the enthalpies of the TRIS reactions have been reported in the literature as an indication of the calorimetric accuracy and precision applicable to some other primary study. Consequently, these TRIS values are not indexed and are essentially lost to the usual literature searching procedures. We have made an effort to collect as many results as possible of TRIS measurements in various calorimeters using different procedures. Some of these are as unpublished data for which more detailed information is available from the authors.

The endothermic reaction of TRIS in 0.05 *N* NaOH has been measured by only one other group, Hill, Öjelund and Wadsö [15]. Their value of $\Delta H(298.15\ \mathrm{K}) = 141.90 \pm 0.04$ (sdm) $\mathrm{J \cdot g^{-1}}$ is in good agreement with our value, 141.80 ± 0.06 (sdm) $\mathrm{J \cdot g^{-1}}$ given in section 3.4.

In table 10 is a summary of measurements of the enthalpy of the TRIS reaction in 0.1 *N* HCl using samples other than the Standard Reference Material, and in table 11 is a similar summary where SRM 724 was used (SRM 724a was used in [39] and this work). These tables are a reasonably complete summary and show the range of values obtained as well as the precision of various measurements.

The first two columns in tables 10 and 11 give the reference, the authors, and the year when the enthalpy values were reported either by publication or by private communication; the order is chronological. The next column describes the calorimeter in code[6] and with a reference which describes the calorimeter used. A majority of the calorimeters are the constant pressure, isoperibol, and glass type; only two are constant volume, six are metal, and one is adiabatic. The last columns list the enthalpy values at 298.15 K, the number of experiments averaged, and the un-

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[6]

Code	*Type of calorimeter*
H	Constant pressure
U	Constant volume
I	Isoperibol
A	Adiabatic
G	Glass
M	Metal
C	A commercial calorimeter which must pass an acceptance test based in part upon the value obtained for the TRIS reaction.

TABLE 10. *Summary of values reported for the enthalpy of reaction of* TRIS *in 0.1* N HCl *using samples other than the standard reference material (SRM 724 or 724a)*

Reference No.	Author(s) and year reported	Calorimeter[a]	$-\Delta H(298.15\ \mathrm{K})$		Number averaged	Uncertainty	
						2 sdm	Other
			cal · mol⁻¹	*J · g⁻¹*		*J · g⁻¹*	*J · g⁻¹*
[1]	Irving and Wadsö (1964)	H,I,G,[43]	7105	245.40	8	0.28	...
			7099	245.19	5	0.41	...
			7106	245.44	5	0.34	...
			7100	245.23	6	0.28	...
			7105	245.40	7	0.28	...
			7106	245.44	5	0.28	...
			[b]7104	245.37	Mean	...	...
[16]	Gunn (1965)	U,I,M,[16]	7107.0	245.47	7	0.03	...
			7107.1	245.47	6	0.03	...
[17]	Held and Criss (1965)	H,I,G,[17]	7113	245.68	5	...	1.00
[18]	Sunner and Wadsö (1966)	H,I,G,[18],C	[c]7112	245.64	...	...	...
			7111	245.61	6	0.07	...
[19]	Becker, Lindenbaum, and Boyd (1966)	H,I,G,[44]	7118	245.85	...	...	0.62
[20]	Finch, Gardner, and Sen Gupta (1966)	H,I,G,[45]	7150	247.0	7	...	1.7
[21]	Vacca and Arenare (1967)	H,I,G,[46]	7109	245.54	5	0.03	...
[22]	Wilson and Worrall (1967)	H,I,G,[47]	7110	245.6	3	...	1.7
[23]	Wood, et al (1967)	H,I,G,[23]	7117	245.8	3	1.2	...
[24]	Kanbour and Joncich (1967)	H,I,G,[24]	7123	246.02	6	0.45	...
[25]	Curnutt (1968)	H,I,G,[25]	7115.8	245.76	7	0.14	...
[26]	Richards and Woolf (1968)	H,I,M,[48]	7120	245.92	...	...	0.52
		H,I,G,[26]	7100	245.23	...	...	0.69
[35]	Hansen (1969)	H,I,G,[49]	7125	246.1	9	1.2	...
[27]	Cunningham, House, and Powell (1970)	H,I,G,[50]	7144	246.7	4	2.5	...
[28]	Beck, Wood, and Greenwood (1970)	H,I,G,[23]	7108	245.5	10	1.4	...
[29]	Cook, Davies, and Staveley (1971)	H,I,G,[18],C	7110.7	245.60	3	0.04	...
[30]	Cassel and Wen (1972)	H,I,G,[30]	7109	245.54	7	0.28	...
[31]	Vanderzee and King (1972)	H,I,G,[51]	7110	245.57	26	0.14	...
[32]	Olofson (1972)	U,I,M,[32]	7120	245.92	10	0.68	...
[33]	Somsen and de Visser (1972)	H,I,G,[18],C	7104	245.37	8	0.10	...
[10]	Gardner (1972)	H,I,G,	7118	245.85	7	0.34	...

[a] See footnote 6 in text for explanation of code.

[b] This value was later changed to 7107 (245.47 $\mathrm{J \cdot g^{-1}}$) to correct a computational error.

[c] This is reported as the "best" value for this commercial calorimeter.

TABLE 11. *Summary of values reported for the enthalpy of reaction of* TRIS *in* 0.1 N HCl *using SRM 724 and 724a*

Reference No.	Author(s) and year reported	Calorimeter[a]	$-\Delta H(298.15\ \mathrm{K})$		Number averaged	Uncertainty	
						2 sdm	Other
			cal · mol⁻¹	*J · g⁻¹*		*J · g⁻¹*	*J · g⁻¹*
[34]	Fitzgibbon and Holley (1968)	H,I,M,[52]	7110.7	245.60	7	0.34	0.5
[15]	Hill, Öjelund, and Wadsö (1969)	H,I,G[18],C	7109.0	245.54	6	0.05	....
[35]	Hansen (1969)	H,I,G,[49]	7125	246.1	9	0.6	....
			7108	245.5	9	0.6	....
[36]	Johnson and Hubbard (1969)	H,I,G,[18],C	7108	245.51	....	....	0.21
[37]	Kreis and Wood (1969)	H,I,G,[23]	7123	246.0	3	....	....
[3]	Gunn (1970)	U,I,M,[16]	7107.0	245.47	5	0.02	....
[38]	O'Hare, Johnson, and Appelman (1970)[b]	H,I,G,[18],C	7109.6	245.56	7	0.04	....
[39]	Brunetti, Prosen, and Goldberg (1971)	H,I,G,[39]	7120.2	245.93	9	0.09	....
[40a]	Tso and Criss (1972)	H,I,G,[17]	7110	245.57	8	0.35	....
[40b]	Tsai and Criss (1972)	H,I,G,[17]	7113	245.68	5	0.35	....
[40c]	Chang and Criss (1972)	H,I,G,[17]	7111	245.61	9	0.35	....
				245.62	[40] Mean	....	....
[9]	Duer (1972)	H,I,G	7128	246.19	5	0.25	....
[41]	Baker, et al (1972)	H,I,G,[41]	7080	244.5	....	....	0.69
[42]	Navratil and Oetting (1972)	H,I,G,[42]	7108	245.50	8	0.17	....
[11]	Robie and Hemingway (1972)	H,I,M,[12]	7111.8	245.64	5	....	0.24
[53]	Christensen, Kimball, and Izatt (1973)	H,I,G,[54]	7104	245.3	8	0.3	....
	This work	H,A,M,[2]	7115.4	245.76	5	0.04	0.26

[a] See footnote 6 in text for explanation of code.

[b] Results reported at Second International Conference on Calorimetry and Thermodynamics at Orono, Main (July 1971) and published in [39].

certainty. The uncertainty is given as 2 sdm where it was specifically defined, and as "other" where it was not defined. In two cases where 2 sdm is also given, "other" refers to the estimated overall uncertainty assigned.

The spread of the data in tables 10 and 11 is essentially the same, there is no significant difference between the maximum and minimum values. There appears to be little difference in the results from a single calorimeter of measurements using samples of different origins [1, 16, 3, 18, 15]; this has also been our experience in measurements not given here.

Gunn [16] found that the enthalpy of reaction in 0.2 N HCl was about 0.4 J · g^{-1} (12 cal · mol^{-1}) higher than in 0.1 N HCl at a concentration of 6 g of TRIS per dm^3 of solution. Doubling the TRIS concentration in 0.2 N HCl increased the enthalpy about 0.07 J · g^{-1} (2 cal · mol^{-1}) and tripling the TRIS concentration increased the enthalpy about 0.21 J · g^{-1} (6 cal · mol^{-1}). Held and Criss [17] found no concentration dependence in the enthalpy using 0.25 to 0.076 mmol samples in 80 cm^3 of 0.1 N HCl (0.38 to 0.12 g · dm^{-3}). Criss et al. [40a, b, c], measured the reaction in dilute solutions (ranging from 0.002 to 0.01 molal or 0.2 to 1.0 g · dm^{-3}) with apparently no significant difference from the values obtained at the recommended concentration of 5 g · dm^{-3} or 0.04 molal.

We have found no difference in the enthalpy values obtained at various stirring speeds. However, Olofson [32] has suspected that the reaction is sensitive to insufficient mixing in the calorimeter, and Gardner [10] measured 7118 ± 5(sdm) cal · mol^{-1} at 700 rpm and 7109 ± 6(sdm) cal · mol^{-1} at 470 rpm. This difference may not be significant, but it is a factor to be investigated if low enthalpy values are obtained in a calorimeter.

Christensen et al. [53], reported low enthalpy values when glass ampoules sealed with a flame were used. This was believed to be the result of partial decomposition of the sample.

The experimental precision of data, such as that given in tables 10 and 11, is sometimes mistakenly used as a gauge of the accuracy of the measurements. To a certain extent this reasoning is justified by the fact that those who strive for high precision are usually simultaneously concerned with achieving high accuracy, but the latter is more difficult to determine absolutely. Some of the values reported in the tables are obviously measured in calorimeters designed for applications where relative enthalpies are of interest rather than absolute enthalpies, and high precision and accuracy are of little concern. Therefore, in order to separate the measurements in calorimeters where an effort was apparently made to achieve high precision and accuracy, we have listed in table 12, in ascending order of the $-\Delta H(298.15\ \mathrm{K})$, only those values in which the standard deviation of the mean was 0.1 percent (2 sdm = 0.5 J · g^{-1}) or less. In cases where more than one value was reported using a single calorimeter, the value of highest precision is given in the table. Also, the calorimeters marked with "C" in tables 10 and 11 are considered as a single value because the measurements were made in a commercial calorimeter and are subject to a bias because of its acceptance test. The overall uncertainty assigned to this work, 0.26 J · g^{-1} (see sec. 3.3), includes all of the values in table 12 within their experimental uncertainties (2 sdm).

5. Discussion and Conclusions

The overall uncertainties assigned to the certified values for the enthalpies of the exothermic and endothermic reactions of the Standard Reference Material 724a should be small enough for greatest significance but large enough to include conceivable future adjustments in the mean enthalpy values as more information is acquired about calorimetry and the chemical behavior of the reactions. The values given in table 12 are measured in calorimeters capable of relatively high precision, and yet the spread of the results is nearly 0.4 percent (or 0.89 $J \cdot g^{-1}$), which indicates the presence of errors beyond the experimental imprecision. Some time will probably elapse before the spread of these values can be explained and the overall uncertainty in the certified value reduced accordingly.

This work provided the only value in table 12 which was measured in an adiabatic calorimeter; this eliminates the heat transfer corrections necessary in isoperibol calorimeters, but may conceivably introduce some errors of which we are not aware in the present state of adiabatic calorimetry. Gunn [3, 16] has measured the reaction in a constant-volume, rocking-bomb system; the fact that his value falls near the lower end of the values in table 12 suggests a possible need for a $P-V-T$ correction which is not presently known. Wadsö and co-workers [1, 15, and 18] have made relatively extensive studies of the TRIS reactions using various samples and highly reproducible calorimetric procedures. The emphasis in our work has been to measure the reaction under various conditions in an effort to find possible explanations for the unexpected, large spread in the enthalpy values reported.

TABLE 12. *Summary of the measurements of highest precision for various calorimeters (from tables 10 and 11)*

Ref. No.	Authors	$-\Delta H$(298.15 K)	2 sdm[a]
		$J \cdot g^{-1}$	$J \cdot g^{-1}$
[53]	Christensen, et al.	245.3	0.3
[1]	Irving and Wadsö	245.47	0.3
[3]	Gunn	245.47	0.02
[42]	Navratil and Oetting	245.50	0.2
[21]	Vacca and Arenare	245.54	0.03
[30]	Cassel and Wen	245.54	0.3
[31]	Vanderzee and King	245.57	0.1
[34]	Fitzgibbon and Holley	245.60	0.3
[40]	Criss, et al.	245.62	0.4
[11]	Robie and Hemingway	245.64	0.2
[18]	Sunner and Wadsö	245.64	0.1
	This work	245.76	0.04
[25]	Curnutt	245.76	0.1
[10]	Gardner	245.85	0.3
[39]	Brunetti, et al.	245.93	0.1
[24]	Kanbour and Joncich	246.02	0.5
[9]	Duer	246.19	0.3

[a] The uncertainties are rounded to the nearest 0.1 $J \cdot g^{-1}$ unless they are less than 0.05 $J \cdot g^{-1}$.

All calorimeters represented in table 12 were lined primarily with glass except two which were lined with gold (Gunn, and Robie and Hemingway), and two which were lined with platinum (Fitzgibbon and Holley, and this work). Thus, the material lining the calorimeters does not account for extreme values.

It is possible that the venting effect described in section 3.1a is responsible for some of the high values, and that inadequate stirring is responsible for some of the low values; however, we are reasonably certain that these are not sources of error in our work. The variations in samples, concentrations, and CO_2 in the HCl solutions (see sec. 3.1b) are not likely to cause errors beyond the experimental imprecision. Electrical energy and calorimeter temperature measurements are always a source of possible error (see [39]); we have thoroughly checked these systems which have been described in detail for this calorimeter [2].

The relatively large overall uncertainty assigned to the certified values for the enthalpy of reaction of SRM 724a in 0.1 N HCl has been a disappointment to some. However, very few calorimetrists are concerned with accuracy and precision of measurements beyond the assigned uncertainty of ±0.11 percent. Measured enthalpy values can be expected to fall within these limits providing the conditions described in section 3.3 are met. Perhaps in the future after further studies have been made of the chemistry of the reaction and the effects of various conditions on the enthalpy of reaction, it will be possible to define more specifically conditions for the reaction in 0.1 N HCl and to provide a certified value to which a smaller overall uncertainty can be assigned.

There is good agreement between the two values reported ([15] and sec. 3.4) for the endothermic reaction of the Standard Reference Material in 0.05 N NaOH, and the uncertainty assigned to the certified value is approximately as expected. Because of the calorimetric problems with endothermic reactions, the CO_2 reaction with dilute NaOH solutions, and the sensitivity of the enthalpy of reaction to NaOH concentrations, it was expected that the uncertainty would be larger than that for the exothermic reaction.

The Standard Reference Material 724a is useful not only for comparing the accuracy of calorimetric measurements, but for checking the relative performance of a calorimeter from time to time. It provides a method for checking quickly and easily whether modifications in a calorimeter have produced changes in the precision or absolute values of measurements. However, it is recommended that the TRIS reactions not be used instead of the usual electrical energy measurements to calibrate calorimeters. Although the search must continue for a reaction which can be certified with less uncertainty, for the present, SRM 724a is the best available.

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