NATIONAL BUREAU OF STANDARDS REPORT

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THE ENTHALPIES OF NEUTRALIZATION AND OF HYDROLYSIS OF NBS STANDARD REFERENCE MATERIAL NO. 724a [TRIS(HYDROXYMETHYL)AMINOMETHANE]

Technical Report
to
Office of Standard Reference Materials
National Bureau of Standards
Washington, D. C.

NBS

U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

NATIONAL BUREAU OF STANDARDS

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THE ENTHALPIES OF NEUTRALIZATION AND OF HYDROLYSIS OF NBS STANDARD REFERENCE MATERIAL NO. 724a [TRIS(HYDROXYMETHYL)AMINOMETHANE]

Marthada V. Kilday and Edward J. Prosen

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The Enthalpies of Neutralization and of Hydrolysis of NBS Standard Reference Material No. 724a [tris(hydroxymethyl)aminomethane]

by Marthada V. Kilday and Edward J. Prosen

Abstract

An adiabatic solution calorimeter was used to measure the enthalpies of neutralization of crystalline tris(hydroxymethyl)aminomethane, TRIS, in aqueous HCl solution and of hydrolysis in aqueous NaOH solution. These measurements resulted in the following certified values for the enthalpies of solution of NBS Standard Reference Material No. 724a at constant pressure and at a concentration of 5 grams per 1000 cm^3 of solution and other conditions specified in the certificate:

(1) in 0.100 N hydrochloric acid solution

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

(2) in 0.0500 N sodium hydroxide solution

$\Delta H(298.15\ K) = 141.70 \pm 0.19\ J \cdot g^{-1}$

The results of other experiments are given comparing the reactions of SRM 724 and SRM 724a, and showing some conditions under which high values were obtained for reaction (1).

Key words: tris(hydroxymethyl)aminomethane, 2-amino-2-(hydroxymethyl)-1-3-propanediol, $(HOCH_2)_3CHN_2$, heat of soln. of TRIS in HCl, and heat of soln. of TRIS in NaOH, TRIS.

1. Introduction

In 1964, the U.S. Calorimetry Conference requested that the National Bureau of Standards issue a standard sample of tris (hydroxymethyl) aminomethane, or TRIS, for solution calorimetry. It was assumed that certification of the enthalpy of solution of the material would involve only a series of simple calorimetric experiments to confirm the early results reported by Irving and Wadsö [1] in Sweden. At that time, a new 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 certification work. However, the first results obtained late in 1967 with the new Standard Reference Material No. 724 were greater than 0.1% more exothermic than those reported by two other groups who made extensive studies of the TRIS reaction and achieved results of high precision. The experimental precision of the results obtained with the new calorimeter and SRM 724 was about 0.04%.

An intensive effort began to locate the cause of the descrepancy in the results. No difference was found in the values obtained with samples from different sources, nor in samples which were stored for years in darkness as opposed 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% 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 temperature before leaving the vessel) was compared with a permanent calibrating heater in a Pt well -- the difference between the results obtained with the two heaters was less than 0.004%; temperature differences at various points between the adiabatic shield and the vessel were measured and the currents in the shield heaters were readjusted to produce minimal departures from the vessel temperatures; and the platinum resistance thermometer was replaced by a quartz oscillator thermometer -- none of these produced any detectable change in the results.

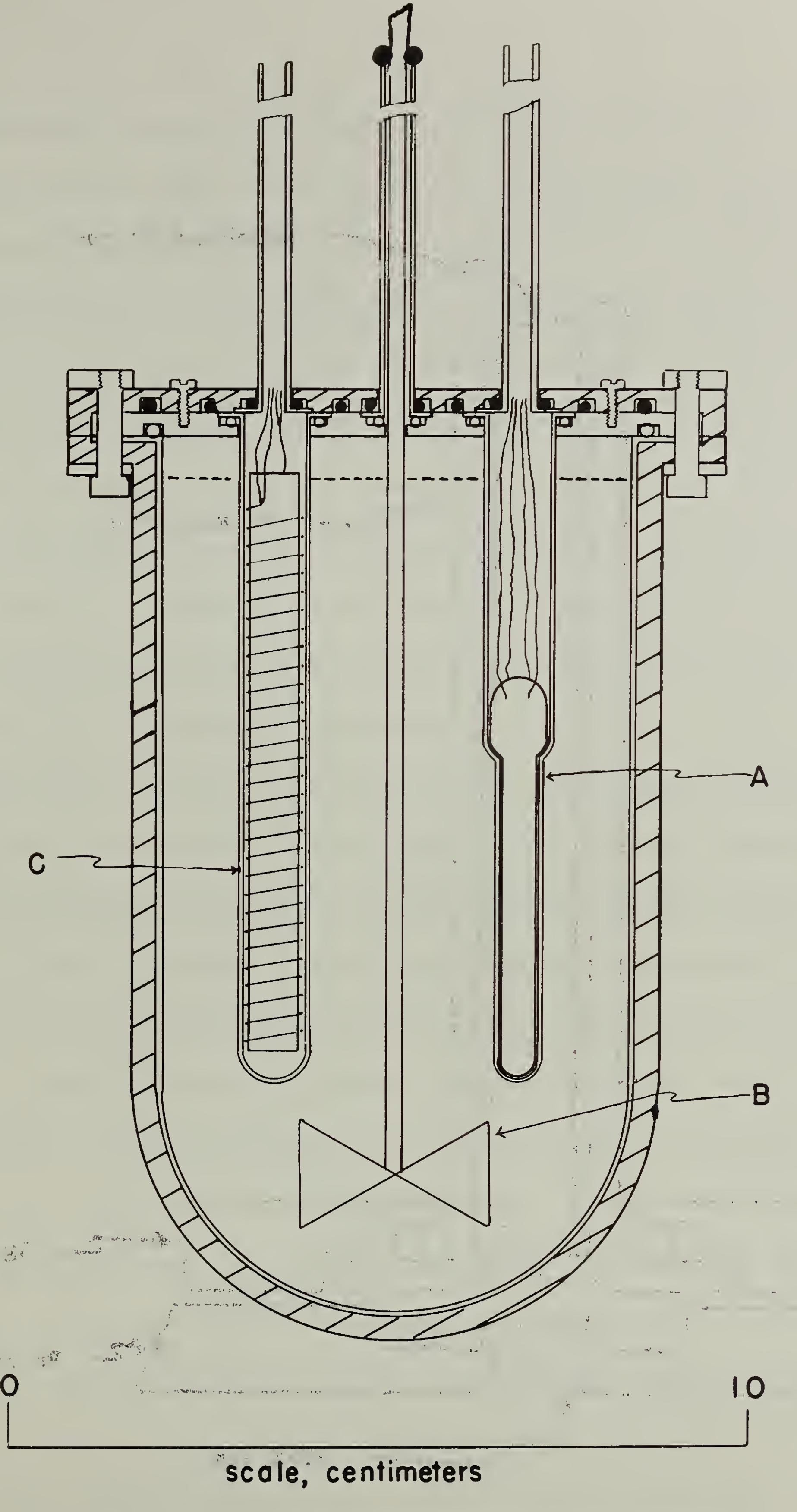
Having eliminated the sample composition and treatment, and the measuring equipment as likely sources of error, we decided to measure for comparison another reaction on which published results were available. The heat of reaction of Gunn's sample of H_2SO_4 was measured in 0.02N and in 0.08N·NaOH; seven experiments in each group agreed with Gunn's values [2] to within a few hundredths of a percent for both reactions, and the standard deviation of the mean of our experiments was 0.01%. Thus, our efforts were directed to investigating conditions of the TRIS reaction in HCl solutions which might explain the existing disagreement.

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 the certified values are based.

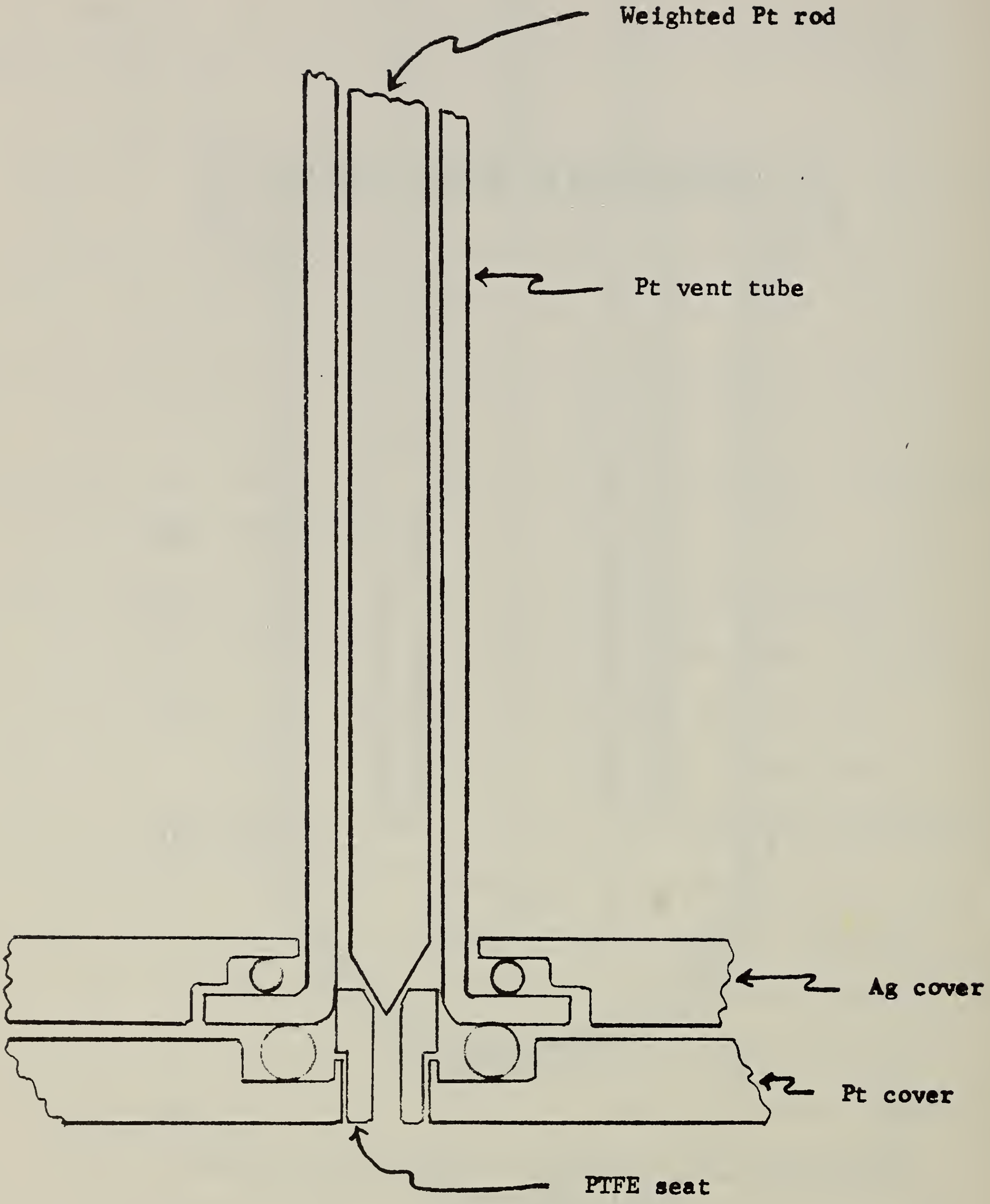
2. The Calorimeter

The adiabatic solution calorimeter employed in the measurements reported in this paper has been previously described in NBS Technical Reports [3] which are available on request to the authors.

Figure 1 is a drawing of the calorimeter vessel showing the well for the platinum resistance thermometer (A), the platinum stirrer (B), and the well for the calibrating heater (C). The vessel is lined with platinum which is surrounded by approximately 3 mm in depth of pure silver. The solution level is 0.5 cm below the cover of the vessel. Five platinum tubes leading from the cover of the vessel carry leads, etc., from the calorimeter. Three of these tubes are shown in figure 1, and in a vertical plane at a 90° angle at the stirrer, are two additional tubes: one carries the push-rod for opening the sample holder, and the other (on the opposite side of the stirrer) is the vent tube. An enlarged view of the vent tube arrangement originally used is shown in figure 2. The weighted platinum rod seats on a polytetrafluroethylene (Teflon) ring with a hole 1.6 mm in diameter. When the rod is in place, this forms a seal for the space above the calorimeter solution; when the rod is withdrawn there is a positive vent to the atmosphere. In some measurements the Pt rod was withdrawn and the upper end of the vent tube was connected by rubber tubing to an open-end manometer containing either marcol (mineral oil) or mercury--thus changes in pressure in the vapor space above the calorimeter solutions could be observed during the experiments. In other measurements, the Pt rod was removed and a Teflon capillary



SOLUTION CALORIMETER VESSEL



Original vent arrangement

FIGURE 2

tube was passed through the rubber tubing and the vent tube. The PTFE seat was removed. The lower end of the capillary tube terminated a little above the stirrer and the upper end could be connected to a gas introduction line. This permitted flushing a gas through the calorimeter solution, and the exit gases passed through the annular space in the vent tube and the rubber tubing to the atmosphere. When the flushing was completed, the Teflon tube was disconnected from the gas inlet line and placed inside the top of the open-end manometer where the rubber tubing was again connected. Thus, the calorimeter solution was essentially saturated with the gas under study, and the space above the solution was filled with the gas at atmospheric pressure.

The venting of the calorimeter was also effected by the type of o-ring used at the top of the Pt tube containing the stirrer shaft (shown at top in figure 1). Normally a PTFE (Teflon) o-ring is used here and is held in place by a brass fitting (not shown). The o-ring is not compressed and functions as a bearing for the stirrer shaft, not as a seal; thus, the calorimeter vapors may diffuse slowly through the tube to the atmosphere, and the pressure above the solution is always near atmospheric pressure. For a special project it was desirable to make the calorimeter "gas-tight," and the PTFE o-ring was replaced by a lubticated Buna N rubber o-ring which was compressed by the fitting to form a seal around the stirrer shaft. Under these conditions when the vessel was filled with helium gas to a pressure of 15 cm of Hg, the leakage rate with the stirrer running was about 3 mm of Hg per minute.

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

(1) In the "unvented" system, the Buna N rubber o-ring was used to seal the stirrer shaft, and the vent tube was sealed as shown in figure 2.

(2) In the "vented" system, the Pt rod (fig. 2) was removed, and the top of the vent tube was connected to the open-end manometer by rubber tubing; a Teflon o-ring was used as a bearing at the top of the stirrer tube.

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

(4) In the systems where the effects of various atmospheric gases on the TRIS reaction were observed, the Buna N rubber o-rings sealed the stirrer shaft, and the Teflon capillary tubing was placed in the vent tube and used as described above.

The Pt sample holder has been described [3]. In this work, the largest sample holder, 2.8 cm^3, was used, and the samples (approximately 1.5 grams) nearly filled the cylinder but were not tightly packed.

3. Calibrations, Units, and Corrections

The experiments reported were performed between February, 1970, and May, 1971, except some preliminary work on the endothermic reaction in January to March, 1969.

Certified NBS calibrations were made as follows: Capsule-type platinum resistance thermometer No. 769892, October, 1961; saturated standard cell No. 2625-2293, July, 1969; and standard resistors No. 117443 (0.1 ohm), No. 119222 (10 ohms), and No. 119184 (10,000 ohms), June, 1969. The records of numerous calibrations over several years for the standard cell and standard resistors provide additional confidence in the values used. An unofficial measurement of the ice point with the Pt resistance thermometer early in 1970 agreed with the correct value within 0.01K, indicating no significant change in the absolute values since the original calibration.

Calibrations were made in this laboratory of the G-3 resistance thermometer bridge dials in January, 1969, and November, 1970, and of the 6-dial potentiometer in January, 1969. The electronic counter used in timing the electrical heating periods was checked against the standard seconds signals available at the National Bureau of Standards.

In some experiments a quartz oscillator thermometer replaced the platinum resistance thermometer for measuring the calorimeter temperature changes The calibration of the quartz thermometer was based on direct comparisons with the platinum resistance thermometer.

The 1961 atomic weights [4] were used in the calculations.

The unit of energy is the joule (J), and 4.1840 joules = 1 thermochemical calorie.

For reduction to weights in vacuum, the following densities were used: 1.35 $g \cdot cm^{-3}$ for TRIS and 0.00118 $g \cdot cm^{-3}$ for air.

4. Experimental Procedures

The general calorimetric procedures followed were described previously [3]. The procedures and conditions used for the TRIS sample and its reactions were those recommended by the Standards Committee, U. S. Calorimetry Conference, October, 1966, which may be obtained upon request to the authors of this technical report.

In the endothermic reactions of TRIS with sodium hydroxide solutions, precisely measured electrical energy was added during the chemical reaction to prevent a drop in the calorimeter temperature which could not be followed by the adiabatic shield. (During rating periods the stirring energy is sufficient to maintain a temperature rise in the calorimeter and assure operation of the controls for the adiabatic shield.) The electrical heating was started at least 1 minute before opening the sample holder and the calorimeter temperature was rising rapidly when the reaction began. Thus, the departures of the shield temperature from the calorimeter temperature were negligible. In earlier experiments, when the chemical reaction and electrical heating were initiated simultaneously large differences between the shield and calorimeter temperatures occurred and corrections were made which were as much as 0.1% of the total heat absorbed. The addition of electrical energy during endothermic reactions is generally desirable to prevent possible vaporization errors during a drop in calorimeter temperature.

The stock solutions of 0.1N HCl were prepared from reagent-grade concentrated HCl diluted with distilled water which was in equilibrium with air, except as noted in special solutions where the distilled water was boiled to remove CO_2 and then dispensed from containers guarded by Ascarite tubes. The solutions were analysed by titration with standard 0.1N sodium hydroxide solutions using a recording pH meter.

The stock solutions of 0.05N NaOH were prepared by dilution of 10N sodium hydroxide with CO_2-free distilled water, and analysed by titration with potassium acid phthalate (SRM 39g) using a recording pH meter.

The initial and final system for each reaction was calibrated electrically.

5. Experimental Results

A quartz oscillator thermometer was used for the calorimeter temperature measurements in the experiments given in table 1 which show the effects of vented and unvented systems [see page 6, (1) and (2)] using the two TRIS samples, SRM 724 and SRM 724a. The average enthalpies for the two samples in vented systems agree within the uncertainties, but in unvented systems the enthalpies are about 3% too high and are less reproducible than in the vented systems. The electrical energy equivalents have not been corrected for small variations in the amount of the calorimetric solutions (the spread of the weights was less than 0.04%), however, they all agree within about 0.1% regardless of whether the system was vented or unvented. This indicates that the high reaction enthalpies obtained in unvented systems were characteristic of the TRIS reaction and not a property of the calorimeter since the venting did not effect the electrical energy experiments. In the vented experiments the manometer indicated that the pressures above the solutions never exceded 5 cm of marcol during the entire experiment.

The expt. nos. omitted from table 1 are as follows: nos. 385 and 396 were calibrations of the quartz oscillator thermometer vs. the Pt resistance thermometer, and nos. 403 and 404 were experiments in which an attempt was made to degas the calorimetric solution by pumping with a vacuum prior to beginning temperature measurements. However, the Teflon o-ring seal on the sample holder leaked under the reduced pressure and the calorimetric solution was drawn into the sample holder when atmospheric pressure was restored above the solution.

Table 1. Results of measurements with TRIS (SRM 724 and 724a) in 0.1N HCl solutions in vented and unvented systems.

Expt. No.	Electrical Energy Equivalents		$-\Delta H$(298.15K)			
			SRM 724		SRM 724a	
	Initial	Final	vented	unvented	vented	unvented
	$J\cdot K^{-1}$	$J\cdot K^{-1}$	$cal\cdot mol^{-1}$			
389	1729.02	1731.24	----	----	7114.4	----
390	1727.75	1730.15	7118.6	----	----	----
391	1728.15	1730.38	---	----	7125.6	----
392	1727.89	1730.15	7111.1	----	----	----
393	1727.68	1729.88	7114.0	----	----	----
394	1727.93	1730.82	----	----	7127.4	----
397	1728.03	1730.09	----	7288.7	----	----
398	1728.25	1730.20	----	----	7117.5	----
399	1727.76	1730.37	7130.0	----	----	----
400	1728.86	1730.66	----	----	----	7321.6
401	1728.02	1730.84	----	7393.0	----	----
402	1731.08	1730.88	----	----	----	7362.6
405	1728.54	1730.07	---	----	7117.4	----
406	1728.02	1730.84	7110.9	----	----	----
407	1727.79	1731.01	7112.4	----	----	----
408	1728.23	1730.14	----	----	7116.0	----
409	1729.92	1730.30	7116.0	----	----	----
410	1728.52	1731.52	----	----	7119.6	----
		Means	7116.1	7340.8	7119.7	7341.9

A study was made of the effects of dissolved gases (the major components of air: N_2, O_2, A, and CO_2) on the TRIS reaction in 0.1N HCl solution. In order to introduce the gas under study into the calorimeter, a capillary teflon tube was passed through the vent tube and into the calorimetric solution as described on page 6, (4). The compressed gas from a commercial cylinder was passed through absorbers containing magnesium perchlorate, Ascarite (this was by-passed when CO_2 was used), and then through a bubbler containing 0.1N HCl solution before entering the calorimeter. The gas was bubbled through the calorimeteric solution at approximately 50 cm^3 per minute for about 90 minutes to saturate the solution and displace the air above the solution with the gas under study. The upper end of the teflon tube was disconnected from the gas introduction line and the vent tube was connected to the open end manometer--thus the atmosphere above the solution was initially at atmospheric pressure.

When the gases were bubbled into the solutions small droplets of solution accumulated on the vessel cover as a result of the bubbles bursting at the surface. These droplets probably caused errors due to abnormal evaporation during the calormetric measurements, therefore, the results are not regarded as calorimetrically precise, but are useful in showing gross effects. The enthalpies of reaction for these experiments are given in table 2. We believe results for N_2, A, and O_2 are essentially the same and the spread of the values is the result of the droplet errors. However, in the case of CO_2 the enthalpy values are about 7% higher than those obtained with the other three gases. This appears to be a significant difference. The result of expt. No. 454 (-7160 cal. mol^{-1}) was not included in the table because the conditions were

Table 2. $-\Delta H(298.15K)$, cal·mol^{-1}, for TRIS in 0.1N HCl with various gases above and saturating the solution

Expt. No.	Atmosphere above and saturating the solution			
	N_2	A	O_2	CO_2
447	7146			
448	7129			
449		7194		
450		7121		
451	7113			
452			7160	
453			7122	
455				7555
456				7609

different from the others. This was the first experiment using CO_2 gas. After the normal flushing period, the open-end manometer containing marcol was connected to the vent tube as usual. However, the pressure over the calorimetric solution dropped rapidly due to the absorption of CO_2 in the system, and it was necessary to open the connection to the manometer to prevent the oil from being drawn into the calorimeter. This was repeated several times and finally the vent tube was closed off leaving the solution and the atmosphere above the solution no longer saturated with CO_2. In expt. Nos. 455 and 456, mercury was used in the manometer instead of marcol and it was possible to proceed normally.

Figure 3 is a plot of the pressures above the solutions vs. time observed in four of the experiments given in table 2; the results were similar in the other corresponding experiments. A factor of 15 was used to convert cm of Hg to cm of marcol in the case of the CO_2 atmosphere, and the larger circles indicate the greater uncertainty in the manometer readings. The vertical lines indicate the time of the electrical heating periods for the initial and final calibrations and the time at which the TRIS reaction was initiated. Negative readings indicate reduced pressure above the solutions. The pressure changes during the first 100 minutes were due to the gas solubilities and equilibrations within the system, but during the calibrations and chemical reactions they were caused by the 0.2K temperature change. In the atmospheres of N_2, O_2. and A, the pressure changes were essentially the same for all calibrations and reactions, as would be expected since the

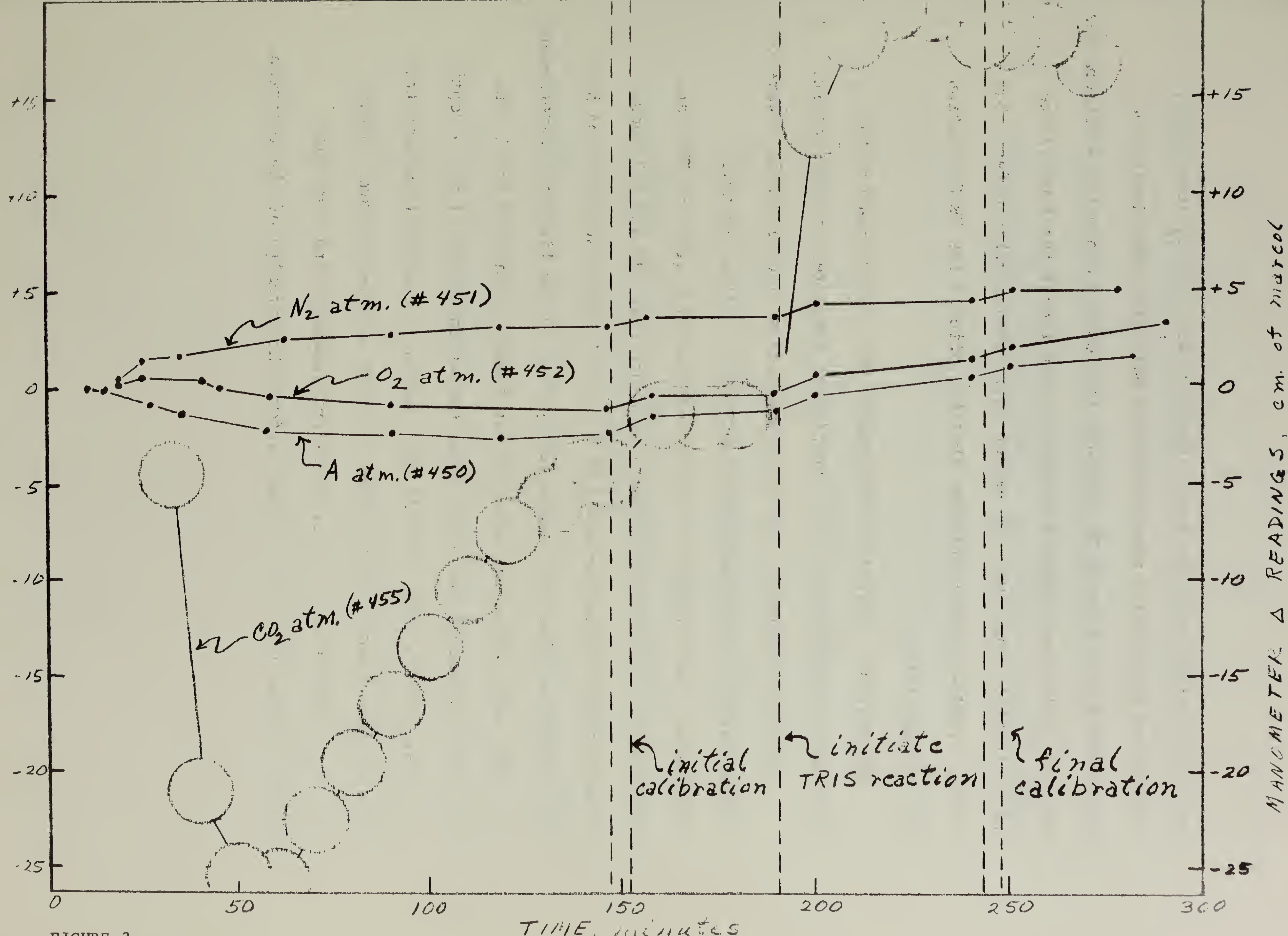

+15
+10
+5
0
-5
-10
-15
-20
-25
0
50
100
150
200
250
300
TIME, minutes
MANOMETER Δ READINGS, cm. of marcol
N_2 atm. (#451)
O_2 atm. (#452)
A atm. (#450)
CO_2 atm. (#455)
initial calibration
initiate TRIS reaction
final calibration

FIGURE 3

temperature rises were the same. However, for the CO_2 atmosphere, although no significant pressure change was detectable during the calibrations, a 0.9 cm of Hg increase in pressure above the solutions was observed during the chemical reactions even though the temperature change remained the same. We cannot fully explain this effect, but it does provide further evidence that CO_2 effects the TRIS reaction in a closed system.

The platinum resistance thermometer was used to measure the calorimeter temperature in all experiments hereafter in this report.

The measurements for the four experiments given in table 3 were on systems vented to the atmosphere [see page 6, (3)]. In this calorimeter, the "standard" systems contained 1.5 grams of TRIS and 302.4 grams of 0.1N HCl solution. In expt. Nos. 530 and 531 these standard weights were increased by 5%, and in expt. Nos. 532 and 533 the standard weights were decreased by 5%. In the first two experiments the vapor space above the solution was almost eliminated and in the last two experiments the vapor space was approximately 1 cm in depth. We assume that in expt. No. 531 the solution accidentally sealed the vent giving a high enthalpy value as in an unvented system, however, the other three values are in excellent agreement and show that changes in the vapor space do not effect the enthalpy of the reaction.

Table 3. Results of measurements with non-standard weights of HCl solution and TRIS

Expt. No.	wt. of HCl soln (in air)	Electrical Energy Equivalents Initial	Electrical Energy Equivalents Final	$-\Delta H$ (298.15K)
	grams	$J \cdot \Omega^{-1}$	$J \cdot \Omega^{-1}$	$cal \cdot mol^{-1}$
(5% more than the standard wt. of HCl and TRIS:				
530	317.36	17,730.6	17,756.4	7115.5
531	317.38	17,731.9	17,764.	7156.
(5% less than the standard wt. of HCl and TRIS:				
532	287.38	16,498.1	16,516.9	7115.1
533	287.47	16,505.7	16,527.4	7115.2

Factors: 40.98 $J \cdot \Omega^{-1} \cdot g^{-1}$ for initial system

41.26 $J \cdot \Omega^{-1} \cdot g^{-1}$ for final system

The experiments in table 3 also provided information for calculating factors (at the bottom of the table) for correcting the electrical energy equivalents of the initial and final systems to the standard weights of HCl in order that the precision of the measurement of electrical energy equivalents could be determined. The weights in air of the HCl solutions are given and the corrections were applied accordingly to obtain the values for the electrical energy equivalents given in table 4; here the standard deviation of the mean was less than 2 $J \cdot \Omega^{-1}$ or ± 0.01 percent. The mean energy equivalents for each experiment before correction to the standard weight of HCl solution was multiplied by ΔR_c reaction to obtain ΔH at the mean temperature of reaction, $\overline{T}$ reaction. The correction to 298.15 K is the product of ΔCp, 1.435 $J \cdot g^{-1} \cdot K^{-1}$, and ($\overline{T}$ reaction -25.°C). The slopes in the initial and final rating periods (which were a least squares fit of 5 points) were extrapolated to the time of initiating the reaction to obtain the corrected temperature rise, ΔR_c. A bridge dial correction was also applied. Since this is an adiabatic calorimeter the slopes in the initial and final rating periods are almost the same, and the time chosen for the time of reaction is not very significant. The "Stirring Energy Correction" given in table 4 is the net result of the extrapolations of the initial and final rating periods, and this correction is uncertain by 1 or 2 percent for fast reactions such as TRIS in HCl solution.

Table 4. Results of measurements leading to the certified values for the exothermic enthalpy of reaction of SRM 724a, TRIS, in 0.1 N HCl.

Expt. No.	Mass of TRIS	Wt. in air of HCl soln.	Electrical Energy Equivalents		Stirring Energy Correction	ΔR_c reaction	$\overline{T}$ reaction	Corr. to 298.15 K	$-\Delta H$(298.15 K)	
			Initial	Final						
	g	g	$J \cdot \Omega^{-1}$	$J \cdot \Omega^{-1}$	Ω	Ω	°C	$J \cdot g^{-1}$	$J \cdot g^{-1}$	$cal \cdot mol^{-1}$
(Vented to marcol manometer):										
521	1.49696	302.445	17,121.5	17,151.1	0.000522	0.021514	24.796	-0.29	245.96	7121.0*
522	1.49214	302.420	17,116.9	17,146.0	.000497	.021454	24.795	-.29	246.01	7122.4
523	1.52225	302.410	17,123.3	17,143.1	.000495	.021882	24.997	.00	246.27	7130.2*
524	1.53278	302.380	17,114.5	17,140.8	.000494	.021993	24.996	.00	245.76	7115.4
527	1.50880	302.380	17,115.1	17,141.0	.000474	.021660	24.994	-.01	245.90	7119.3*
Mean			17,118.3	17,144.4					245.98	7121.7
sdm			±1.8	±1.9					±0.08	±2.4
%			(±0.01)	(±0.01)					(±0.03)	(±0.03)
(Vented to atmosphere):										
528	1.52958	302.425	17,119.6	17,139.9	.000474	.021941	24.993	-.01	245.70	7113.5
529	1.52074	302.410	17,116.9	17,140.4	.000479	.021826	24.993	-.01	245.82	7117.1*
532	1.45790	287.385	17.113.4	17,136.4	.000518	.021677	25.208	+.30	245.75	7115.1
533	1.43550	287.470	17,117.5	17,143.5	.000519	.021333	25.208	+.30	245.75	7115.2*
534	1.52143	302.415	17,117.4	17,145.9	.000554	.021856	24.802	-.28	245.81	7116.6*
Mean			17,117.0	17,141.2					245.76	7115.5
sdm			±1.0	±1.6					±0.02	±0.6
%			(±0.01)	(+0.01)					(±0.01	(±0.01)

*Initially solutions were CO_2-free

The first five experiments given in table 4 were vented to the marcol manometer [see page 6, (2)], and the last five were vented to the atmosphere [page 6, (3)]. The electrical energy equivalents in the two groups are the same within the uncertainties, but a lower mean enthalpy of reaction was obtained in the second group and the precision was significantly improved. It appears that even the small confinement of the atmosphere above the solution imposed by the open-end marcol manometer produced somewhat high enthalpy values for the reaction. The last five experiments in table 4 are the basis for the certified enthalpy of reaction of SRM 724a (TRIS) in 0.1N HCl under the specified conditions.

In an effort to detect an effect on the enthalpy of reaction by the presence of small amounts of CO_2 in the HCl solutions, the experiments marked by an asterisk in table 4 employed HCl solutions prepared from boiled distilled water which was guarded by Ascarite absorbers. However, the solutions were weighed and transferred to the calorimeter in the presence of air, and approximately 3 hours elapsed before the TRIS reaction occurred, consequently the solution was probably almost in equilibrium with the CO_2 in air by the time the reaction occurred. No difference was apparent in the results obtained with these "CO_2-free" HCl solutions and those originally in equilibrium with air.

Four additional measurements of the TRIS reaction in 0.1N HCl solution were made to obtain the temperature coefficient of the reaction. These were also vented to the atmosphere; the results are as follows:

Expt. No.	$\overline{T}$ reaction °C	$-\Delta H$ ($\overline{T}$) $J \cdot g^{-1}$
535	29.938	239.15
536	20.478	252.25
537	20.556	252.32
538	29.948	238.36

A least squares fit of these data plus the last 5 experiments in table 4 resulted in the following equation for the relationship of temperature and enthalpy of solution (in °C and $J \cdot g^{-1}$):

$$\Delta H(\overline{T}) = -245.76 + 1.435\ (\overline{T}-25),$$

except that the value of the constant enthalpy term at 25°C was reduced by 0.04 $J \cdot g^{-1}$ to correspond to the certified value.

The standard errors of the two constants were ± 0.07 and ± 0.023, respectively, and the standard error of the estimate was ± 0.22 $J \cdot g^{-1}$. Thus ΔCp for the reaction is 1.435 ± .023 $J \cdot g^{-1} \cdot K^{-1}$ or 41.54 ± 0.67 $cal \cdot mol^{-1} \cdot K^{-1}$.

In the endothermic reactions of TRIS with 0.0500 N NaOH solutions, the reaction occurred while electrical energy was added to the calorimeter (see section 4). Table 5 gives the results of 9 experiments which are the basis for the certified value for the enthalpy of reaction of SRM 724a with 0.0500 N NaOH solution at a concentration of 5 grams of sample in 1000 cm^3 of solution. All of the measurements were on systems vented to the atmosphere except the three which are marked with an asterisk and were vented to the marcol manometer [see page 6, (2) and (3)]. For this reaction there appears to be no difference in the enthalpy values obtained with the two venting conditions.

The electrical energy equivalents given in table 5 have not been corrected as in table 4 for small differences in the weights of the calorimetric solutions from the standard system and are the energy equivalents of the actual systems. In Expt. No. 541, there was a malfunction of the electronic counter during the final calibration and an estimated value of 17,380 $J \cdot \Omega^{-1}$ was used for the calculations. Experiment No. 546 was lost because the counter malfunction necessitated leaving the calorimeter assembled overnight and the sample holder obviously leaked as a result of a drop in temperature.

Table 5. Results of measurements leading to the certification of the endothermic enthalpy of reaction of SRM 724a with 0.0500N NaOH

Expt. No.	Electrical Energy Equivalents		Stirring Energy Correction	ΔRc of Reaction + Elect. energy	$\overline{T}$ reaction	Corr. to 298.15 K	NaOH conc.	Corr. to 0.0500N NaOH	ΔH(298.15K)	
	Initial	Final								
	$J\cdot\Omega^{-1}$	$J\cdot\Omega^{-1}$	Ω	Ω	°C	$J\cdot g^{-1}$	Normality	$J\cdot g^{-1}$	$J\cdot g^{-1}$	$cal\cdot mol^{-1}$
539	17,360.4	17,382.2	0.000731	0.068443	25.024	-0.02	0.0487	-0.22	141.82	4,106.2
540	17,361.4	17,379.1	.000805	.068278	25.021	-0.02	.0487	-0.22	142.02	4,111.8*
541	17,360.3	--	.000766	.055982	24.985	+0.02	.0487	-0.22	141.37	4,093.1
542	17,364.0	17,382.6	.000664	.056105	24.963	+0.04	.0487	-0.22	141.64	4,100.7*
543	17,364.2	17,379.3	.000801	.055751	25.162	-0.17	.0487	-0.22	141.77	4,104.5
544	17,360.0	17,376.8	.000843	.055720	25.168	-0.17	.0487	-0.22	141.65	4,101.1*
545	17,356.4	17,380.6	.000779	.055804	25.164	-0.17	.0489	-0.18	141.62	4,100.2
547	17,364.0	17,383.2	.000715	.056145	24.970	+0.03	.0489	-0.18	141.53	4,097.7
548	17,361.4	17,377.6	.000576	.060575	25.148	-0.15	.0489	-0.18	141.84	4,106.5
						Mean			141.70	4,102.5
						Standard deviation of the mean			±0.06 (0.04%)	±1.8
						Mean of 6 similar expts. with SRM 724			141.63	4,100.6
						Standard deviation of the mean			±0.03 (0.02%)	±0.7

*Vented to marcol manometer

The procedure for calculating $\Delta H(298.15\ K)$ in table 5 was similar to that used for the exothermic reaction and described above, except that the "Electrical Energy added During Reaction," given in table 6 was subtracted from the net heat evolved during the reaction period which was the product of ΔR_c and the mean electrical energy equivalent.

For the correction to 298.15 K, $\Delta Cp = 1.033\ J \cdot g^{-1} \cdot K^{-1}$ was used; this value was determined by the use of 4 additional experiments:

Expt. No.	$\bar{T}$ reaction °C	$-\Delta H(\bar{T})$ in 0.0500N NaOH $J \cdot g^{-1}$
549	29.980	146.64
550	22.293	139.17
551	22.409	139.58
552	29.919	147.52

A least squares fit of the data for the mean temperature of reaction and the enthalpy values in 0.0500N NaOH resulted in the following equation for the relationship of temperature and the enthalpy of reaction (in °C and $J \cdot g^{-1}$):

$$\Delta H(\bar{T}) = 141.70 + 1.033\ (\bar{T} - 25),$$

except that the value of the constant enthalpy at 25°C was reduced by $0.10\ J \cdot g^{-1}$ to correspond to the certified value. The standard errors of the constants were ± 0.09 and ± 0.041, respectively, and the standard error of the estimate was $\pm\ 0.32\ J \cdot g^{-1}$.

Table 6. Electrical energy added to the calorimeter during the endothermic reactions of SRM 724a (TRIS) in 0.0500N NaOH solutions.

Expt. No.	Time of Elect. Heating before react.	E	I	t	E/I = R	Electrical Energy added During Reaction
	minutes	volts	amp.	sec	Ω	J
539	$1\frac{1}{4}$	18.65942	0.1926715	390.2940	96.8458	1403.16
540	$1\frac{1}{4}$	18.65945	.1926707	390.1824	96.8463	1402.76
541	$1\frac{1}{4}$	18.65707	.1926458	330.2647	96.8465	1187.04
542	$1\frac{1}{4}$	18.65649	.1926397	330.2258	96.8465	1186.82
543	$1\frac{1}{4}$	18.63263	.1923931	329.7832	96.8467	1182.20
544	$2\frac{1}{4}$	18.62740	.1923397	330.2887	96.8464	1183.35
545	$2\frac{1}{4}$	18.62060	.1922698	330.3186	96.8462	1182.60
547	$1\frac{1}{4}$	18.68088	.1928915	330.4768	96.8466	1190.83
548	$\frac{3}{4}$	28.57851	.2951283	150.2719	96.8342	1267.44

The enthalpy of reaction is dependent on the concentration of the NaOH solution, and the corrections to 0.0500 N NaOH in table 5 were obtained from the following equation (in normality and $kJ\cdot mol^{-1}$):

$$\Delta H(298.15\ K) = 17.680 - 10.59(N) + 5.19(N)^2$$

The standard errors of the constants were ±0.013, ±0.18, and ±0.19 respectively; and the standard error of the estimate was ±0.022 $kJ\cdot mol^{-1}$. The equation was obtained from a least squares fit of 11 preliminary experiments using SRM 724, the first NBS standard sample of TRIS, in which the concentration of NaOH was varied:

Expt. No.	Normality of NaOH	ΔH(298.15 K)
		$kJ\cdot mol^{-1}$
264	0.005	17.643
265	.005	17.632
274	.049	17.170
275	.049	17.148
276	.051	17.155
273	.051	17.151
272	.051	17.148
270	.144	16.231
271	.144	16.305
268	.944	12.320
269	.944	12.300

The heats agree within the uncertainties of the NaOH analyses with those reported by Hill, et al [5].

At the bottom of table 5 are the results of 6 preliminary experiments using SRM 724. A difference in procedure was that the TRIS reaction was started only a few seconds after beginning the electrical heating. This resulted in a drop of the calorimeter temperature because of the heater lag; consequently, there was a relatively large difference between the calorimeter and shield temperatures, and a correction was made which was about 0.1% of the heat absorbed by the TRIS reaction. Although the experimental precision appears better in the older experiments, the corrections for departure from adiabatic conditions are quite uncertain, and we believe the experimental precision in the more recent experiments is more realistic. However, the agreement of the mean values for the two samples is excellent. In table 6 are given the time intervals between the beginning of electrical heating and the initiation of the TRIS reaction for the corresponding experiments in table 5.

In table 6 are the values used in determining the quantity of electrical energy added to the calorimeter during the endothermic TRIS reactions (see table 5). The voltage drop across the heater, E, was calculated from the voltage drop across a 10-ohm standard resistor in series with a 10-K ohm standard resistor, and the combination is in parallel with the calorimeter heater. The current through the heater, I, was calculated from the potential drop across a 0.1-ohm standard resistor in series with the calorimeter heater. The time of heating, t, was measured on an electric counter (actuated through a mercury switch) which counted a 10 K HZ standard frequency available at the National Bureau of Standards. The product, E·I·t, is the amount of electrical energy added to the calorimeter during the TRIS reaction.

The ratio, E/I, is equivalent to the average heater resistance and is an indicator of the precision of the current and potential measurements. It is also interesting to note that in the last experiment in table 6 where the voltage was increased by 10 volts, the heater resistance decreased by 0.01% as a result of the higher temperature even though the heater is in very close contact with a platinum well immersed directly in the calorimetric solution. For this reason, both E and I should be measured if results of highest accuracy are to be achieved.

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) Condensation correction in vapor space above solution, about -0.001 J or < 0.0005 percent;

(4) Vaporization correction for air in sample holder, < 0.05J or < 0.02 percent.

The first three corrections are opposite in sign to the fourth resulting in a net correction of about 0.01% in the worst case.

6. Discussion and Conclusions

The effects of various venting conditions reported in this paper for the exothermic TRIS reaction in HCL solutions have not been observed in any other reactions studied in this laboratory and appear to be characteristic of this reaction. The presence of traces of CO_2 in the calorimetric solutions apparently has no significant effect on the enthalpy of the exothermic reaction under normal conditions; however, we have observed some significant effects in a closed system. Until these effects can be thoroughly investigated, understood, and explained, a certified value of higher accuracy than that chosen in this paper for the exothermic TRIS reaction in HCl solution cannot reasonably be expected. Therefore, we have assigned a larger uncertainty (0.10 percent for other possible systematic errors, see below) to the certified value than would be normal if based only on our experimental results.

Two other groups have made extensive studies of the TRIS reaction and report results of high precision. For the ΔH(298.15 K) of SRM 724 in 0.1 N HCl at a concentration of 5 grams per 1000 cm^3 of solution, Hill, et al, report -245.54 ± 0.03 $J \cdot g^{-1}$[5] and Gunn reports -245.47 ± 0.01 $J \cdot g^{-1}$[2]. The uncertainties given here were the standard deviations of the means of the experimental values, and both measurements were made in isoperibol calorimeters, the first at constant pressure and the second at constant volume.

We have been unable to detect a difference in the values obtained with SRM 724 and with SRM 724a. Our certified value for ΔH(298.15 K) of SRM 724a in 0.1 N HCl solution at a concentration of 5 grams per 1000 cm^3 of solution is -245.76 ± 0.26 $J \cdot g^{-1}$ under the specified conditions. The uncertainty (0.11%) is the square root of the sum of the squares of the following uncertainties: the experimental precision at the 95% confidence level, 0.03%; inhomogeniety of the sample, 0.01% [6]; and other possible systematic errors, 0.10%. These measurements were made in an adiabatic calorimeter at constant pressure.

The endothermic reaction of TRIS in NaOH solutions has been studied by Hill, et al, who report a value of 141.90 ± 0.04 $J \cdot g^{-1}$ for ΔH(298.15K) for the reaction of SRM 724 in 0.0500N NaOH at a concentration of 5 grams per 1000 cm^3 of solution. The uncertainty is the standard deviation of the mean of the experimental values.

Our certified value for the reaction of SRM 724a in 0.0500N NaOH under the specified conditions is ΔH(298.15K) = 141.70 ± 0.19 $J \cdot g^{-1}$. The uncertainty (0.13%) is the square root of the sum of the squares of the following uncertainties: the experimental precision at the 95% confidence level, 0.10%; analysis of sodium hydroxide solutions, 0.07%; and other possible systematic errors, 0.05%. Higher accuracy in the enthalpy value is not expected for this reaction because of its sensitivity to the concentration of the NaOH solution and the possible effects of atmospheric CO_2.

7. References

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