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THE EXOTHERMIC ENTHALPY OF TRIS

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ABSTRACT

An LKB reaction calorimeter was used to measure the heat of reaction of TRIS (SRM 724) with 0.1 N HCl under conditions recommended by the National Bureau of Standards. The calorimeter was equipped with a separate electrical energy measurement unit for comparison with the LKB system. The results are within the error limits of the certified value of 7115 ± 8 cal/mol.

Enthalpy data obtained using an unvented reaction vessel and HCl containing dissolved CO_2 will be presented. The Regnault-Pfaundler and modified Dickinson calculation methods for the corrected temperature rise will also be compared for the experiments.

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The standard reaction of TRIS with 0.1 N HCl was used to check out the LKB reaction calorimeter shown on the first slide. Plans for this calorimeter include measuring heats of solution of nuclear materials. A reaction vessel and bath identical to this one will be installed in a glove box for these measurements.

Dry air is passed through the dry-ice bath (left side of calorimeter) to cool the reaction vessel between runs.

Several modifications to the calorimeter were made. It was equipped with a Hewlett-Packard DVM for comparison with the LKB electrical energy measurement unit.

A simplified wiring schematic is shown on the second slide.

The DVM is connected to a relay which switches about every five seconds between the heater and standard resistor to give the voltage and current measurements. The EMF measurements are then recorded with a Hewlett-Packard print-out.

The auxiliary energy measurements were conducted because the LKB is designed to measure the heater resistance at low currents (0.02 amp) in which the resistance of the heater is assumed to remain constant. However, when the run is made at higher currents (0.1 amp) to conform to certain reactions, the resistance of the heater changes. Also a check on the stability of the current of the LKB power supply was desired.

These changes were accomplished with two 12-volt batteries as a power source. The current regulator board was removed and battery leads connected (as shown in diagram) for these runs.

The third slide shows a resistance-time curve for a typical reaction run. The initial period (a-b) of the reaction was started after allowing the calorimetric system to come to thermal equilibrium (~ 15 min.). About 10 points were taken over a period of five minutes before the reaction was initiated at Point b.

Resistance and time measurements were taken as close together as possible during the reaction and until thermal equilibrium was reached at Point c. Finally, about ten points were taken in the final period (c-d).

Calibration runs were made before and/or after the experiment and over the same temperature range. The maximum power output of the LKB unit was 500 mW, thus the calibration time was about 250 seconds and had this shape (point to slide). In some runs, increased power from batteries was used to match the curves of the calibrations and experiment more closely.

The corrected temperature rise of all the experiments was calculated by two computerized methods - Regnault-Pfaundler and a modified version of Dickinson's method. The former

is an exact method and is comparable to the unmodified Dickinson method while the latter method is inexact and commonly used. Results obtained from the two methods were compared.

The Regnault-Pfaundler correction, $\Delta\theta$, for the heat of stirring, heat leakage, etc. was calculated using the equation shown in Slide 4.

The mean resistance value, θ_m , was calculated using the trapezoid rule. The heat leakage constant, K , was calculated from the equation shown. B_1 and B_3 are the slopes; i.e., resistance change divided by the change in time, of the initial and final periods, respectively. All the θ and t values in the initial and final periods were fitted to a straight line by a linear-least squares sub-routine to obtain the slope values. θ_F and θ_I are the mean resistance values of the final and initial periods, respectively; t_c and t_b are the times at the end and beginning of the main period.

The counter-part of equation (1) is based on values of B_3 and θ_F instead of B_1 and θ_I .

The corrected temperature rise using a modification of the Dickinson method is given by Equation (4). The t_x values correspond to θ_x taken as 63 and 50% of the total resistance change in the experiment and calibration, respectively.

Since it was not always possible to make the calibration curve follow the experimental plot exactly, and since the resistance of the thermistor does not change linearly with temperature, the ΔT value was utilized in the calculations and is defined by Equation (5). T_m and R_m are the mean temperature and resistance values, respectively, of the run, and c is a constant characteristic of the thermistor.

Slide 5 shows the enthalpy data of the TRIS-HCl reaction taken when the calorimeter was first operated. The large error limits are probably due to the large enthalpy corrections to 25.0°, weights to only four places, and condensation of liquid on the neck of the reaction vessel since the bath was not maintained above the final reaction temperature.

There is excellent agreement of the results between the two calculation methods and also with reported enthalpy values.

The results of using the modified Dickinson method are less precise as shown by the standard deviation from the mean.

The various stirring speeds, low, medium, and high, did not have any noticable effect on the results.

Slide 6 shows the comparison of results using the two energy measurement stations. The LKB measurements are significantly higher than the results using the DVM measurements. This discrepancy will be discussed later. The second group of experiments represents the vented vessel. The results are not

significantly different indicating that our calorimeter is not sensitive to pressures as reported by some workers.

The final two experiments were made using a battery power source which gave calibration times comparable to reaction times. No significant difference is seen here, either.

The final group of experiments, shown in Slide 7, were done using a new reaction vessel. The calibration of the thermistor, DVM, and standard cell were re-checked prior to this group of experiments. Also the cooling tube was altered to direct the stream of cool air at the base of the vessel to prevent condensation of liquid on the neck. The outer can surrounding the vessel was evacuated during these experiments to eliminate significant heat transfer by convection and conduction. Thus it was felt that this group of experiments should be the most reliable.

In this group of experiments, the two electrical energy measurement stations are in excellent agreement. Thus the difference shown in the last slide was probably due to calibration error in the standard cell.

The use of HCl saturated with CO_2 was reported as affecting the TRIS results. NBS workers reported very high results ($7500 \text{ cal/mol}^{-1}$) while Argonne workers reported slightly low results ($7082 \text{ cal/mol}^{-1}$). To resolve this effect, we ran several experiments with HCl saturated with dry CO_2 (purged

15 minutes). Our values are in agreement with the Argonne workers.

Slide 8 compares our average results with reported values.

We are in excellent agreement with reported values and favor the results of the Lund workers (Irving and Wadsö).

SIMPLIFIED WIRING SCHEMATIC OF CALORIMETER HEATER

2065 RESISTANCE - TIME CURVE FOR TRIS - 0.1 N HCl REACTION

MADE IN U.S.A.
KEUFFEL & ESSER CO.

CORRECTED TEMPERATURE RISE EQUATIONS

$$1. \Delta\theta = [B_1 - K (\theta_M - \theta_I)] (t_c - t_\beta)$$

$$2. \frac{K = B_1 - B_3}{\theta_F - \theta_I}$$

$$3. \theta = \theta_c - \theta_B - \Delta\theta$$

$$4. \theta_1 = \theta_c - \theta_B - B_1 (t_x - t_B) - B_3 (t_c - t_x)$$

$$5. \Delta T = \frac{\theta}{\theta_m} \frac{T_m^2}{C}$$

Slide 5.

EFFECT OF THE CALCULATION METHODS ON THE
TRIS-HCl ENTHALPY RESULTS

<u>Exp. No. and Stirring</u>	<u>Mass of TRIS(g)</u>	<u>-ΔH 298.15K (cal/mol⁻¹)</u>	
		<u>RP</u>	<u>MD</u>
2L	0.5124	7110.6	7094.7
3L	0.5753	7112.0	7111.3
4M	0.5492	7102.7	7109.0
6H	0.4868	7116.1	7117.2
7H	0.4954	7119.2	7113.8
8H	0.4760	7117.7	7118.0
9H	0.4465	7110.6	7109.5
10M	0.4371	7116.0	7120.0
12M	0.585456	7118.9	7121.0
Mean		7113.8	7112.7
Std. Dev.		±5.3	±8.1

Slide 6.

TRIS-HCl ENTHALPY DATA USING TWO ENERGY
MEASUREMENT STATIONS, VENTED REACTION VESSEL, AND
BATTERY POWERS SOURCES

<u>Exp. No. and Stirring</u>	<u>Mass of TRIS(g)</u>	<u>-ΔH 298.15K (cal/mol⁻¹)</u>	
		<u>LKB</u>	<u>DVM</u>
13M	0.50167	7117.6	7111.4
14M	0.55161	7116.3	7111.6
15M	0.56031	7115.7	7111.2
	Mean	7116.5	7111.4
	Std. Dev.	±1.0	±0.2
17M	0.50460	7117.0	7113.6
18M	0.49796	7122.3	7120.0
19M	0.49615	7121.0	7116.3
	Mean	7120.1	7116.6
	Std. Dev.	±2.8	±3.2
21M	0.50001	-	7116.2
22M	0.50279	-	7113.6

Slide 7.

COMPARISON OF ENTHALPY RESULTS USING
HCl SATURATED WITH CO₂ vs. AIR

<u>Exp. No. and Stirring</u>	<u>Mass of TRIS(g)</u>	<u>-ΔH 298.15K (cal/mol⁻¹)</u>	
		<u>LKB</u>	<u>DVM</u>
25H	0.50149	7109.6	7111.5
26H	0.50008	7101.8	7102.9
29H	0.47340	7103.3	7105.7
		Mean	7106.7
27H	0.50174	7129.1	7130.9
28H	0.49828	7073.0	7073.0
31H	0.49663	-	7071.4
		Mean	7091.8

Slide 8.

COMPARISON OF OUR AVERAGE ENTHALPY VALUES WITH
REPORTED RESULTS

<u>INVESTIGATION</u>	<u>$-\Delta H_{298.15K} \text{ cal/mol}^{-1}$</u>
Irving and Wadsö (1964)	7108 ± 4
Gunn (1965)	7107 ± 1
Sunner and Wadsö (1966)	7111 ± 2
Gunn (1970)	7107 ± 1
Hubbard, et al. (1971)	7109 ± 2
Kilday and Prosen (1971)	7116 ± 7
Our work	7114 ± 5