

U. S. Department of Commerce  
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National Bureau of Standards  
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# National Bureau of Standards Certificate

## Standard Reference Material 724a

### Tris(hydroxymethyl)aminomethane, $(\text{HOCH}_2)_3\text{CNH}_2$ for Solution Calorimetry

This Standard Reference Material is provided for the purpose of verifying or comparing results obtained by calorimeters measuring enthalpies of solution. The material is *not* intended as a standard for calibrating calorimeters nor as a replacement for electrical energy calibrations normally performed in solution calorimetry. Deviation of measured values from the certified value for the enthalpy of reaction may serve as an indication of systematic errors in the calorimetry.

This material is certified with respect to exothermic and endothermic enthalpies of reaction. The recommended conditions and procedures must be followed in the use of this material to obtain the certified values of the enthalpy changes.

The quantity of heat evolved during the reaction of Standard Reference Material 724a with 0.100 N hydrochloric acid solution at a concentration of 5 grams per  $\text{dm}^3$  of solution at 298.15 K is

$$245.76 \pm 0.26 \text{ J}\cdot\text{g}^{-1} \quad [1].$$

The uncertainty (0.11 percent) is the square root of the sum of the squares of the following uncertainties: the experimental imprecision at the 95 percent confidence level, 0.03 percent; inhomogeneity in the sample, 0.01 percent; and other possible systematic errors, 0.10 percent.

The quantity of heat absorbed during the reaction of Standard Reference Material 724a with 0.0500 N sodium hydroxide solution at a concentration of 5 grams per  $\text{dm}^3$  solution at 298.15 K is

$$141.80 \pm 0.19 \text{ J}\cdot\text{g}^{-1}.$$

The uncertainty (0.13 percent) is the square root of the sum of the squares of the following uncertainties: the experimental imprecision at the 95 percent confidence level, 0.10 percent; analysis of sodium hydroxide solutions, 0.07 percent; and other possible systematic errors, 0.05 percent.

The above values are based on a comparison of the reaction heat with electrical energy measured in terms of the national standards of resistance, voltage, and time. The adiabatic solution calorimeter and procedures used for the measurements have been described [2,3].

The overall direction and coordination leading to the certification of the enthalpy changes were performed by G. T. Armstrong. The technical measurements were made by M. V. Kilday and E. J. Prosen in the Thermochemistry Section. The assay was performed by G. Marinenko of the Microchemical Analysis Section.

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by T. W. Mears.

Washington, D. C. 20234  
September 24, 1973

J. Paul Cali, Chief  
Office of Standard Reference Materials

Standard Reference Material 724a is tris(hydroxymethyl)aminomethane, TRIS, of high-purity material obtained from a commercial source. The material was found to be homogeneous on the basis of coulometric titrations of 15 randomly selected samples. The mean basimetric assay is  $99.9690 \pm 0.0030$  weight percent (the uncertainty represents the 95 percent confidence interval for the mean). The results of the coulometric analyses, the titration procedures, and the method of selecting the random samples have been described [4].

A comparison of the certified values of enthalpy changes with other measurements reported for the TRIS reactions is given by Prosen and Kilday [3].

General Procedures Recommended by the Standards Committee,  
U. S. Calorimetry Conference, October 1966:

1. The material should be used without further heating or crushing.
2. The TRIS should be spread in thin layers in dishes and stored in a desiccator containing a saturated solution of magnesium nitrate (50% relative humidity [5]).
3. The sample should be weighed in air. For reduction to mass or weight in vacuum the density for TRIS of  $1.35 \text{ g}\cdot\text{cm}^{-3}$  [6] is used. The correction factor,  $f$ , to be applied to the weight in air is:

$$f = 1 + \frac{d(\text{air})}{d(\text{TRIS})} - \frac{d(\text{air})}{d(\text{brass})}$$

4. The samples for calorimetric measurements should be sealed in air at atmospheric pressure (not vacuum). They should not be exposed to heat as in the sealing of glass bulbs with a torch. Care should be taken to avoid the entrapment of particles or of unstirred solution after the sample container is opened in the calorimeter.
5. Air at atmospheric pressure should be above the solution in the calorimeter reaction vessel.

Calorimetric Procedures and Corrections:

General procedures for solution calorimetry are described by J. P. Coughlin in Vol. 2 of Experimental Thermochemistry [7] and by Prosen and Kilday [2,3]. In addition, during the endothermic reactions, if necessary for the proper operation of the calorimeter, precisely measured electrical energy should be added to prevent a decline in the calorimeter temperature. This prevents heat effects during the reactions that are different from those during the electrical calibrations.

In the temperature range, 293 to 303 K, the following values may be used for correcting to 298.15 K:

(1) for the exothermic reaction,  $\Delta C_p = 1.435 \pm 0.023 \text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$

(2) for the endothermic reaction,  $\Delta C_p = 1.025 \pm 0.025 \text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$ .

The uncertainties are the standard errors. The following equation may be used to correct the enthalpy changes measured for the endothermic reaction to the NaOH concentration of the certified value, 0.0500 N:

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

where the enthalpy change is in  $\text{J}\cdot\text{g}^{-1}$  and  $N$  is the normality of the NaOH solution. The standard error of the estimate is  $\pm 0.19 \text{ J}\cdot\text{g}^{-1}$ .

Although most solution calorimeters are of the constant pressure type, some solution calorimetry is done in constant-volume bomb calorimeters. Vaporization and condensation corrections must be considered for both types, although the corrections are usually negligible. The values certified here were obtained with a constant pressure calorimeter.

The condensation correction is assumed to be zero for the exothermic reaction since there is no change in ionic strength during the reaction. However, in the endothermic reaction the vapor pressure of the solution is reduced by the solute added. An approximation for this correction,  $q_c$  (in J), to be subtracted from the observed heat of reaction is obtained from the following equations:

$$(1) \text{ at constant pressure, } q_c = 0.00015 C \cdot H_{\text{vap}} \cdot V_v$$

$$(2) \text{ at constant volume, } q_c = 0.00015 C \cdot E_{\text{vap}} \cdot V_v$$

$H_{\text{vap}}$  is the heat in joules required to saturate 1 cm<sup>3</sup> of space with water, and  $E_{\text{vap}}$  is the corresponding internal energy [8];  $V_v$  is the volume of vapor space above the solution; and  $C$  is the concentration of TRIS, in grams per dm<sup>3</sup> of solution.

A small correction may be made for the heat of vaporization of water in the saturation of the air space in the sample container. An approximate value for this correction,  $q_{\text{vap}}$  (in J), to be added to the observed heat of reaction is obtained from the following equations:

$$(1) \text{ at constant pressure, } q_{\text{vap}} = H_{\text{vap}} \cdot V_a \cdot (1 - \text{RH})$$

$$(2) \text{ at constant volume, } q_{\text{vap}} = E_{\text{vap}} \cdot V_a \cdot (1 - \text{RH})$$

$H_{\text{vap}}$  and  $E_{\text{vap}}$  are defined above; RH is the relative humidity of air in the sample container; and  $V_a$  is the volume of air in the sample container [ $V_a = V_c - (m_s/d_s)$  where  $V_c$  is the internal volume of the sample container in cm<sup>3</sup>,  $m_s$  is the mass of sample in g, and  $d_s$  is 1.35 g·cm<sup>-3</sup>].

Since the air in the reaction vessel and that in the sample container are at approximately atmospheric pressure, no correction need be made for a change in pressure upon opening the sample container.

The enthalpy change,  $\Delta H$ , is measured in constant-pressure calorimeters, and the internal energy change,  $\Delta E$ , is measured in constant-volume calorimeters. However, the two are considered equal since for the present  $\Delta V$  is assumed to be zero.

#### Sources of Error:

The following possible sources of error (discussed in [3]) should be considered for measurements of the TRIS reactions:

- (a) Seemingly insignificant confinement of the atmosphere above the solution in some calorimeters has resulted in unusually large enthalpy changes for the reaction in HCl; this effect was not detected in the reaction in NaOH. It is sometimes not sufficient to rely on ventilation through stirrer bearings, for example. An independent vent to the atmosphere is most effective.
- (b) Inadequate mixing or stirring in the calorimeter may result in enthalpy changes that are too small.
- (c) It has been shown [3] that unless the sample and solution for the exothermic reaction are in equilibrium with air, the enthalpy change may be expected to differ from the certified value.
- (d) For the exothermic reaction, larger enthalpy changes are obtained with more concentrated HCl solutions or with higher TRIS concentrations. The endothermic reaction is sensitive to the NaOH concentration, and departures from the specified concentrations for the certified value will result in different enthalpy changes unless appropriate corrections are made.
- (e) Electrical energy measurements and various features in calorimeter design may also be the source of error in the measured values of enthalpy change. Coughlin [7] and Brunetti, et al. [9] discuss some of these problems. The numerous references describing calorimeters given by Prosen and Kilday [3] may also be useful in locating sources of errors.

Notes and References:

- [1] The joule (J) is one newton-meter and the gram (g), the gram mass or weight in vacuum, is  $10^{-3}$  kilogram as defined in the International System of Units (SI).
- [2] Prosen, E. J., and Kilday, M. V., J. Res. Nat. Bur. Stand. (U.S.), 77A, 179 (1973).
- [3] Prosen, E. J., and Kilday, M. V., J. Res. Nat. Bur. Stand. (U.S.), 77A, 581 (1973).
- [4] Marinenko, G., "Coulometry", pp. 56-58, NBS Technical Note 543 (November 1970).
- [5] Stokes, R. H., and Robinson, R. A., Ind. and Eng. Chem. 41, 2013 (1949).
- [6] Rose, H. A., and van Camp, A., Anal. Chem. 27, 1356 (1955).
- [7] Coughlin, J. P., Chapter 14, Experimental Thermochemistry, Vol. 2, edited by H. A. Skinner, Interscience Publishers, New York, (1962).
- [8] Values recommended by the Standards Committee, U. S. Calorimetry Conference, October 1966:

<u>Temperature</u>	<u>H<sub>vap</sub></u>	<u>E<sub>vap</sub></u>
K	J·cm <sup>-3</sup>	J·cm <sup>-3</sup>
293.15	0.0423	0.0400
298.15	.0561	.0529
303.15	.0735	.0693

- [9] Brunetti, A. P., Prosen, E. J., and Goldberg, R. N., J. Res. Nat. Bur. Stand. (U.S.), 77A, 599 (1973).