National Bureau of Standards

Certificate

Standard Reference Material 724

Tris(hydroxymethyl)aminomethane, $(HOCH_2)_3CNH_2$

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 solution may serve as an indication of systematic errors in the calorimetry.

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

The quantity of heat evolved during the reaction of Standard Reference Material 724 with 0.100 N hydrochloric acid solution at a concentration of 5 grams per 1000 cm^3 of solution at 298.15 K is

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

The uncertainty (0.11 percent) 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; 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 724 with 0.0500 N sodium hydroxide solution at a concentration of 5 grams per 1000 cm^3 of solution at 298.15 K is

$$141.70 \pm 0.19 \text{ J} \cdot \text{g}^{-1}.$$

The uncertainty (0.13 percent) is the square root of the sum of the squares of the following uncertainties: the experimental precision at the 95 percent confidence level,

(over)

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. Detailed descriptions of the adiabatic solution calorimeter and the measurements are given in NBS Technical Reports [2], which are available on request.

The purifications were performed by Delmo Enagonio of the Separation and Purification Section. The assays of the purified tris(hydroxymethyl)aminomethane were carried out by G. Marinenko of the Microchemical Analysis Section.

The overall direction and coordination leading to the certification of enthalpies were performed by G. T. Armstrong. The technical measurements were made by M. V. Kilday and E. J. Prosen in the Thermochemistry 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   J. Paul Cali, Chief
April 14, 1972   Office of Standard Reference Materials

(Replaces Provisional Certificate of Analysis dated January 30, 1967.)

The certified values are the result of measurements using Standard Reference Material 724a, which is similar to SRM 724, and will be issued upon depletion of SRM 724. The measurements of the exothermic enthalpy on SRM 724 and SRM 724a showed no difference within the precision of the measurement.

This Standard Reference Material was prepared by the treatment of tris(hydroxymethyl)aminomethane obtained from several commercial sources. Purification was performed on 1 kg lots. Each 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(hydroxymethyl)aminomethane was crystallized by slowly dripping the filtrate into vigorously agitated methanol. The crystalline tris(hydroxymethyl)aminomethane was filtered, washed with cold methanol, and then the entire crystallization procedure repeated. The crystals from the second crystallization were air-dried for a day or more, and then dried 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 $(HOCH_2)_3CNH_2$. The crystallized tris(hydroxymethyl)aminomethane was assayed by an indirect coulometric procedure developed by the Microchemical Analysis Section based on a modification of the procedure described by J. K. Taylor and S. W. Smith[3]. The method consists of the coulometric back-titration of excess hydrochloric acid which is added by weight to the tris(hydroxymethyl)aminomethane samples. The differential potentiometric inflection point of $\Delta pH/\Delta coul.$ as a function of charge was taken as the titration end point. The hydrochloric acid was of azeotropic composition and its actual hydrogen-ion concentration was determined coulometrically. The value of the faraday used in this work was 96,487.0 coulombs per gram equivalent[4]. The 1961 values for atomic weights, based on the C-12 nuclide were used[5].

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[6]).
3. The sample should be weighed in air. For reduction to weight in vacuum the density of 1.35 $g \cdot cm^{-3}$ for TRIS is used. The correction factor, f, to be applied to the weight in air is:

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

4. The samples for calorimetric measurements should be sealed under approximately 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 broken or opened in the calorimeter.
5. Air at approximately atmospheric pressure should be above the solution in the calorimeter reaction vessel.
Item 5 is important. Seemingly insignificant confinement of the atmosphere above the solution in some calorimeters has resulted in high values for the exothermic reaction; this effect was not detected in the endothermic reaction. It is sometimes not sufficient to rely on ventilation through stirrer bearings. An independent vent to the atmosphere is most effective.

Calorimetric Procedures and Corrections:

General procedures for solution calorimetry are described by J. P. Coughlin in Chapter 14, Vol. 2, of Experimental Thermochemistry[7] and by Prosen, et al.[2]. In addition, if

possible during the endothermic reactions, precisely measured electrical energy should be added to prevent a decline in the calorimeter temperature. This prevents abnormal heat exchange between the calorimeter and its environment during the reaction.

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, $\Delta Cp = 1.435 \pm 0.023$ $J \cdot g^{-1} \cdot K^{-1}$
(2) for the endothermic reaction, $\Delta Cp = 1.033 \pm 0.041$ $J \cdot g^{-1} \cdot K^{-1}$.
The uncertainties are the standard errors for the slopes.

Although most solution calorimeters are of the constant pressure type, some solution calorimetry is done in the constant-volume bomb calorimeters. Therefore, vaporization and condensation corrections must be considered for both types, although the corrections are usually negligible. The values certified here apply to the constant pressure type.

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, is obtained from the following equations:

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

H_{vap} is the heat in joules required to saturate 1 cm^3 of space with water, and E_{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 1000 cm^3 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_{vap}, is obtained from the following equations:

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

H_{vap} and E_{vap} are defined above; RH is the relative humidity of air in the sample container; and V_a = internal volume of sample container, in cm^3 $- \dfrac{\text{mass of sample, in grams}}{1.35}$.

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, ΔH, is measured in constant-pressure calorimeters, and the internal energy change, ΔE, is measured in constant-volume calorimeters. However, the two are considered equal since for the present ΔV is assumed to be zero.

Comparison with other published work:

An adiabatic solution calorimeter was used for the measurements of the certified values for the enthalpies of solution; the value for the exothermic reaction is the mean of 5 experiments and the value for the endothermic reaction is the mean of 9 experiments. The certified values are in only fair agreement with the results reported by Gunn[9], and Hill, Öjelund, and Wadsö[10]. Both of these studies were performed in isoperibol calorimeters and achieved results of high precision. Therefore, an abnormally high uncertainty has been assigned to the certified values until the discrepancies between results can be resolved. The measurements by others were made on Standard Reference Material 724, however, no difference between the enthalpy values for SRM 724 and SRM 724a has been detected.

The value reported by Gunn, for the exothermic reaction is $\Delta H(298.15 \text{ K}) = -245.47 \pm 0.01(\text{sdm}) \text{ J} \cdot \text{g}^{-1}$, which is $0.29 \text{ J} \cdot \text{g}^{-1}$ less than the certified value. His work was done in a rocking bomb calorimeter and he has shown that heater lead errors in his system are unlikely. However, his measurements were made at constant volume, and the certified value is at constant pressure.

Hill, et al., used a glass calorimeter for their measurements. Their value for the exothermic reaction, $\Delta H(298.15 \text{ K}) = -245.54 \pm 0.03(\text{sdm}) \text{ J} \cdot \text{g}^{-1}$, is $0.22 \text{ J} \cdot \text{g}^{-1}$ less than the certified value, and their value for the endothermic reaction, $\Delta H(298.15 \text{ K}) = +141.90 \pm 0.04(\text{sdm}) \text{ J} \cdot \text{g}^{-1}$, is $0.20 \text{ J} \cdot \text{g}^{-1}$ more than the certified value.

The uncertainties applied to the certificate values are large enough to approximately overlap these values. The three investigations have agreed within the experimental uncertainties on the value for ΔCp for the exothermic reaction; no other value of ΔCp for the endothermic reaction was reported.

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] Kilday, M. V., and Prosen, E. J., The Enthalpy of Solution of NBS Standard Reference Material No. 1654 (α-quartz) in Aqueous Hydrofluoric Acid, NBS Report No. 10561 (April, 1971); and Kilday, M. V., and Prosen,

E. J., The Enthalpies of Neutralization and of Hydrolysis of NBS Standard Reference Material No. 724a [tris(hydroxymethyl)aminomethane], NBS Report No. 10621 (October, 1971).

[3] Taylor, J. K., and Smith, S. W., J. Res. Nat. Bur. Stand. (U.S.), 63A, 153 (1959).

[4] New Values of Physical Constants Recommended by NAS-NRC, Nat. Bur. Stand. (U.S.), Tech. News Bull. 47, 175 (1963).

[5] Cameron, A. E., and Wichers, E., J. Am. Chem. Soc. 84, 4175 (1962).

[6] Stokes, R. H., and Robinson, P. A., Ind. and Eng. Chem. 41, 2013 (1949).

[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:

Temperature, K	H_{vap}, J	E_{vap}, J
293.15	0.0423	0.0400
298.15	.0561	.0529
303.15	.0735	.0693

[9] Gunn, S. R., J. Chem. Thermodynamics 2, 535-547 (1970).

[10] Hill, J. O., Öjelund, G., and Wadsö, I., J. Chem. Thermodynamics 1, 111 (1969).