

National Bureau of Standards Certificate

Standard Reference Material 1654 α -Quartz for Hydrofluoric Acid Solution Calorimetry

This Standard Reference Material is provided for the purpose of verifying or comparing results obtained by calorimeters measuring enthalpies of solution in aqueous hydrofluoric acid. 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 indicator of systematic errors in the calorimetry.

SRM No.	Description	$\Delta H_{\text{soln}}(353.15\text{K})$ in HF(aq, 24.4 wt.%) $\text{J}\cdot\text{g}^{-1}$
1654	α -Quartz for Hydrofluoric Acid Solution Calorimetry	-2362.2 ± 1.1

The α -quartz samples are natural Brazilian quartz and are available in 25-gram units. The particle sizes in the sample are in the range that passes a #200 sieve and is retained on a #400 sieve. Spectroscopic analysis indicated the presence of less than 0.001 wt percent Al and Mg; no other metals were detected. Samples stored in an atmosphere of air at approximately 295 K and 40 percent relative humidity lost 0.015 percent in weight upon drying at 540 K.

The certified value of the enthalpy of solution of the sample in aqueous hydrofluoric acid is the mean of nine experiments in an adiabatic solution calorimeter at constant pressure using a concentration of approximately 5 g of the sample per 1000 cm³ of hydrofluoric acid solution. The value is based on a comparison of the reaction energy with electrical energy measured in terms of the national standards of resistance, voltage, and time. (See reverse of certificate.)

The uncertainty limit reported is the square root of the sum of the squares of the following (in $\text{J}\cdot\text{g}^{-1}$):

1. 0.4, the estimated limit of experimental precision at the 95 percent confidence level;
2. 0.3, the estimated limit of error in the analysis of HF stock solutions;
3. 1.0, the estimated limit of error from inhomogeneity of possible impurities in the sample; and
4. 0.2, the estimated limit of other possible systematic errors.

The joule (J) is one newton-meter and the gram (g), 10⁻³ kilogram as defined in the International System of Units (SI), is the gram mass (weight in vacuum).

The overall direction and coordination leading to the certification was performed by G. T. Armstrong. The technical measurements were made by M. V. Kilday and E. J. Prosen.

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
April 7, 1971

J. Paul Cali, Chief
Office of Standard Reference Materials

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CALORIMETRIC PROCEDURES AND CORRECTIONS:

The standard should be used without further crushing or heating. Samples may be weighed in air, and reduced to weight in vacuum using the value, $2.66 \text{ g}\cdot\text{cm}^{-3}$, for the density of α -quartz.

Air at approximately atmospheric pressure should be above the solution in the calorimeter reaction vessel. Corrections for vaporization and condensation may be necessary in some calorimeters such as those of constant volume.

Under the conditions of the certification a period of approximately two hours is required for complete reaction. The reaction time may be reduced by increasing the temperature of reaction or by increasing the concentration of the hydrofluoric acid solution. For example, the time required for complete reaction at 358 K in 24 percent HF is approximately 1 hour, and at 353 K in 30 percent HF it is approximately 1.5 hours.

The following equation represents the relationship between the enthalpy of solution of α -quartz in 24.4 percent HF (in $\text{J}\cdot\text{g}^{-1}$) and the mean temperature of reaction (in kelvins) between 298 K and 358 K:

$$-\Delta H_{\text{soln}}(T) = 2275.0 + 1.586(T-298.15).$$

The standard error of the estimate is $\pm 2.4 \text{ J}\cdot\text{g}^{-1}$, and ΔC_p for the reaction is $-1.586 \pm 0.025 \text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$.

The relationship between the enthalpy of solution of the α -quartz at 353.15 K (in $\text{J}\cdot\text{g}^{-1}$) and the concentration of the hydrofluoric acid solution (in percent by weight) in the range, 18 to 30 wt. percent, is given by the following equation:

$$-\Delta H_{\text{soln}}(353.15 \text{ K}) = 2362.20 + 1.398(\text{wt. \% HF} - 24.40) + 0.0714(\text{wt. \% HF} - 24.40)^2.$$

The standard error of the estimate is $\pm 1.7 \text{ J}\cdot\text{g}^{-1}$.

Errors due to surface energy effects or to separation of particle sizes in this sample have proven to be insignificant.

General procedures for solution calorimetry are described by J. P. Coughlin in Chapter 14, Vol. 2, of *Experimental Thermochemistry* [2], and a detailed description of the procedures for the certification of this sample is given in reference 1.

The certified value for the enthalpy of solution of SRM 1654 is in very good agreement with values reported from other laboratories for measurements on other α -quartz samples of various origins. Following is a list of the results of other investigators, corrected to the conditions of the certified value for SRM 1654: Roth and Troitzsch, $-2343.1 \text{ J}\cdot\text{g}^{-1}$ [3]; Troitzsch, $-2378.6 \text{ J}\cdot\text{g}^{-1}$ [4]; Torgeson and Sahama, $-2351.4 \text{ J}\cdot\text{g}^{-1}$ [5]; King, -2371.6 and $-2356.9 \text{ J}\cdot\text{g}^{-1}$ [6]; Kracek, et al., -2371.6 and $-2359.8 \text{ J}\cdot\text{g}^{-1}$ [7]; King, $-2367.0 \text{ J}\cdot\text{g}^{-1}$ [8]; Jeffes, et al., $-2376.5 \text{ J}\cdot\text{g}^{-1}$ [9]; Stevens and Turkdogan, $-2350.7 \text{ J}\cdot\text{g}^{-1}$ [10]; Waldbaum and Hovis, $-2367.2 \text{ J}\cdot\text{g}^{-1}$ [11]. All of these measurements employed isoperibol calorimeters.

References:

- [1] M. V. Kilday and E. J. Prosen, NBS Tech. Report No. 10 561 (1971).
- [2] J. P. Coughlin, Chapter 14, Experimental Thermochemistry, Vol. 2, edited by H. A. Skinner, Interscience Publishers, New York (1962).
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- [6] E. G. King, J. Am. Chem. Soc. 73, 656 (1951).
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- [11] D. R. Waldbaum and G. L. Hovis, Abstracts of Geological Soc. Am. Meeting, Milwaukee, Wisc. (1970).