



National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material 746

Cadmium-Vapor Pressure

Vapor Pressure as a Function of Temperature (350-594 K)

T(K, ITS-90)	P(atm) ^a	(1/T x 10 ³) (K ⁻¹ , ITS-90)	Log P(atm) ^a
350	2.50 x 10 ⁻¹¹	2.857	-10.602
400	2.97 x 10 ⁻⁹	2.500	-8.527
450	1.20 x 10 ⁻⁷	2.222	-6.921
500	2.31 x 10 ⁻⁶	2.000	-5.636
550	2.56 x 10 ⁻⁵	1.818	-4.591
594 (M.P.)	1.52 x 10 ⁻⁴	1.684	-3.819

^a1 atmosphere = 101,325 newtons per meter².

This Standard Reference Material (SRM) is intended primarily for use as a vapor pressure standard. It is available in the form of a rod 6.4 mm (0.25 in) in diameter and 64 mm (2.5 in) long. The material has been determined to be homogeneous and of 99.999+ percent purity.¹ The material for this SRM was supplied by Cominco American, Inc., Spokane, Washington. A specially selected lot of cadmium was further purified by distillation and zone refining, homogenized into a single lot, and processed into the final rod size.

The above vapor pressure-temperature values for solid cadmium are a composite resulting from a weighted averaging of over 200 vapor pressure-temperature measurements made by six laboratories*, including NIST, experienced in such measurements. The composite temperature-pressure results were obtained by using a pooled third law heat of sublimation² at 298 K (26 660 cal/mol) and back-calculating through the third law equation:

$$\Delta H_{\text{sub}298}^{\circ} = T \left[\Delta \left(- \frac{G_T^{\circ} - H_{298}^{\circ}}{T} \right) - R \ln P(\text{atm}) \right] \quad (1)$$

Our original measurements and data analyses were made using temperatures in the IPTS-68 scale. The associated IPTS-68 based free energy functions used with the above equation are listed in footnote 3.

The above certification table gives the recalculated vapor pressures for the ITS-90 temperatures. For the convenience of the user, the table also gives the reciprocal temperatures and log pressures. The differences between the IPTS-68⁴ and ITS-90⁵ scales are quite small, and the associated changes in the certified vapor pressures are also very small.

The results from the six experienced laboratories have also been used to statistically estimate the uncertainties of vapor pressure measurement. The thermodynamic aspects considered in the data analysis, as well as a description of two statistical tests for use by a laboratory wishing to evaluate its results, are presented on the following pages.

The overall coordination and evaluation of data leading to certification of SRM 746 was performed by R.C. Paule and J. Mandel of the NIST National Measurement Laboratory.

Gaithersburg, MD 20899
January 15, 1991
(Revision of certificate dated 8-11-70)

William P. Reed, Acting Chief
Standard Reference Materials Program

The technical and support aspects involved in the revision, update, and issuance of this Standard Reference Material were coordinated through the Standard Reference Materials Program by J.C. Colbert. The original coordination of certification efforts was performed by R.E. Michaelis.

Thermodynamics and Statistics

The individual third law heat for each data point was calculated by using equation (1). Each laboratory's data has been recalculated at NIST using a single set of free energy functions³ and identical calculation procedures. For the original certificate, dated August 11, 1970, all temperatures were converted to the 1968 International Practical Temperature Scale (IPTS-68).⁴

Eighteen curves from the above mentioned laboratories were also used to obtain a pooled second law heat of sublimation.⁶ The second law heat for each vapor pressure-temperature curve was obtained by least-squares fitting of the A and B constants in the following equation:

$$\Delta \left(-\frac{G_T^\circ - H_{298}^\circ}{T} \right) - R \ln P \text{ (atm)} = A + \frac{B}{T} \quad (2)$$

The slope, B, is the second law heat of sublimation at 298 K. The above calculational procedure is similar to the sigma method,^{7,8} and does not require the specification of a mean effective temperature. The procedure is very convenient when the calculations, including the interpolation of free energy functions, are made by computer.

The results from the six laboratories were used to obtain a statistical estimate of the within and between-laboratory uncertainties exhibited by a typical in-control laboratory. It should be realized that the following uncertainty limits are not absolute or fixed with respect to time (and progress), but rather represent current average levels of uncertainty of measurement. The data from the six laboratories represent a broad cross-section of measurement techniques and include Knudsen (weight loss), torque Knudsen, and mass spectrometric methods. Temperatures were measured using several types of thermocouples. The average temperature range of the curves was 120 K and the average number of points was 13.

A laboratory wishing to evaluate its apparatus and techniques may use SRM 746 to measure a $\ln P$ vs. $1/T$ curve using about the same temperature range and number of data points as given above, and may then use the two statistical tests listed below. The monomer vapor species should be used in the calculations. The following Knudsen cell materials have been used satisfactorily: impervious alumina, beryllia, dense graphite, iron, and iridium. Experience has shown that the orifice area should be kept smaller than $1 \times 10^{-2} \text{ cm}^2$ to avoid problems of a possible non-unit evaporation coefficient. Should SRM 746 develop a slight oxide coating after extensive exposure to air, the coating may be removed by briefly rinsing the sample in 1-2 N HNO_3 , followed by several distilled water rinses. After making the vapor pressure-temperature measurements, the following statistical tests should be performed:

Test I. Evaluation of the Value of the Slope

The least-squares fit of data for a single temperature-pressure curve using equation (2) should give a B value ($\Delta H_{\text{sub}298}^\circ$) which agrees approximately 95% of the time with the value 26 660 cal/mol (111 550 J/mol⁹) within the limits described below.

$$\text{Test: } |26\,660 - \Delta H_{\text{sub}298}^\circ| \leq 1\,140 \text{ cal/mol}$$

If a laboratory prefers to least-squares fit the equation

$$R \ln P = A' + \frac{B'}{T}$$

to obtain ΔH_T° , and then adjust to $\Delta H_{\text{sub}298}^\circ$ using literature $\Delta (H_T^\circ - H_{\text{sub}298}^\circ)$ values, the above slope limits should still be approximately correct.

Test II. Evaluation of the Absolute Values of the Vapor Pressures

The average third law $\Delta H_{\text{sub}298}^{\circ}$ for a single curve, calculated as an average of individual point ΔH_{298}° values using equation (1) should agree approximately 95% of the time with 26 660 cal/mol (111 550 J/mol⁹) within the limits described below.

$$\text{Test: } |26\,660 - \Delta H_{\text{sub}298}^{\circ}| \leq 420 \text{ cal/mol}$$

A further description of the evaluation of the variances for SRM 746, and their use in applications involving two or more temperature-pressure curves is given in NBS Spec. Publ. 260-21.

*List of Participating Laboratories

Bureau of Mines, A. Landsberg
 Douglas Advances Research Laboratories, D.L. Hildenbrand
 Gulf General Aromic, Inc., H.G. Staley
 Los Alamos Scientific Laboratory, C.C. Herrick and R.C. Feber
 Marquette University, T.C. Ehlert
 National Institute of Standards and Technology, E.R. Plante and A.B. Sessoms
 Sandia Corporation, D.A. Northrop

Footnotes

¹ The following methods were used in the homogeneity testing and purity evaluations:

Linear Electron Accelerator (G.J. Lutz)

Optical Emission Spectroscopy Cominco American, Inc., Spokane, Wash., J.G. Frettingham

Residual Resistivity Ratio, R_{273K}/R_{4K} (V.A. Deason and R.L. Powell)

Spark-Source Mass Spectrometry (C.W. Mueller and P.J. Paulsen)

² The third law $\Delta H_{\text{sub}298}^{\circ} = 26\,660 \pm 150$ cal/mol (111 550 \pm 630 J/mol). The \pm uncertainty value represents two standard error limits of the pooled value. These limits tacitly assume the error in the free energy functions is negligible relative to the error in the heat of sublimation. This is believed to be the case.

³

	Condensed phase ^b	Gas phase
Temperature	$-\frac{G_T^{\circ} - H_{298}^{\circ}}{T}$	$-\frac{G_T^{\circ} - H_{298}^{\circ}}{T}$
K, (IPTS-68)	cal•mol ⁻¹ deg ⁻¹	cal•mol ⁻¹ deg ⁻¹
298.15	12.38	40.065
350	12.51	40.164
400	12.63	40.260
450	12.87	40.444
500	13.10	40.628
550	13.36	40.820
594 (M.P.)	13.61	41.011

^b Converted to IPTS-68⁴ using data of Hultgren, R., Orr, R.L., and Kelley, K.K., loose-leaf supplement to Selected Values of Thermodynamic Properties of Metals and Alloys (Sept. 1966). Conversions were made to IPTS-68 using equations given by Douglas, T.B., J. Res. NBS, 73A, 451-69 (1969).

⁴ The International Practical Temperature Scale of 1968. Metrologia 5, 35-49 (1969).

⁵ The International Temperature Scale of 1990. Metrologia 27, 3-9 (1990).

⁶ The second law $\Delta H_{\text{sub}298}^{\circ} = 26\,610 \pm 380$ cal/mol ($111\,340 \pm 1600$ J/mol). The \pm uncertainty represents two standard error limits of the pooled value. The pooled second law and third law heats⁷ are in excellent agreement. The pooled third law heat, however, is believed to be more accurate and has therefore been used in the calculation of vapor pressures and as the "best value" in the statistical tests.

⁷ Horton, W.S., J. Res. NBS, 70A, 533-9 (1966).

⁸ Cubicciotti, D., J. Phys. Chem., 70, 2410-3 (1966).

⁹ 1 caloric = 4.1840 joules.