Certificate of Analysis
Standard Reference Material 746
Cadmium-Vapor Pressure

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

T(K, IPTS-68)	P(atm)[a]	$(1/T \times 10^3)$ $(K^{-1}$, IPTS-68)	Log P(atm)[a]
350	2.49×10^{-11}	2.857	-10.603
400	2.97×10^{-9}	2.500	- 8.528
450	1.20×10^{-7}	2.222	- 6.922
500	2.31×10^{-6}	2.000	- 5.637
550	2.56×10^{-5}	1.818	- 4.592
594 (M. P.)	1.51×10^{-4}	1.684	- 3.820

[a] 1 atmosphere = 101,325 newtons·meter^{-2}

This SRM is available in the form of 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 standard 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 measurments made by six laboratories* experienced in such measurements. The composite temperature-pressure results were obtained by using a pooled third law heat of sublimation[2] at 298 K (26660 cal/mol) and back-calculating through the third law equation:

$$\Delta H^\circ_{sub\,298} = T \left[\Delta \left(-\frac{G^\circ_T - H^\circ_{298}}{T} \right) - R \ln P\,(\mathrm{atm}) \right] \qquad (1)$$

For the convenience of the user, the above table also includes calculated reciprocal temperatures and log pressures. The free energy functions for use in the equation are listed.[3]

The results from the six experienced laboratories have also been used to estimate statistically 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.

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 R. E. Michaelis.

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J. Paul Cali, Acting Chief
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The individual third law heat for each data point was calculated by use of equation (1). Each laboratory's data have been recalculated at NBS using a single set of free energy functions[3] and identical calculation procedures. All temperatures have been 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.[5] 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:

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

The slope, B, is a second law heat of sublimation at 298 K. The above calculational procedure is similar to the sigma method, and does not require the specification of a mean effective temperature.[6,7] 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 the 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, berylia, dense graphite, iron, and iridium. Experience has shown that the orifice area should be kept smaller than 1×10^{-2} 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 ($\Delta H^\circ_{sub\,298}$) which agrees approximately 95 percent of the time with the value 26,660 cal/mol (111,550 J/mol[8]) within the following limits:

$$\text{Test:} \qquad \left|26{,}660 - \Delta H^\circ_{sub\,298}\right| \leqslant 1140 \text{ cal/mol}$$

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 ΔH_{298}° using literature $\Delta(H_T^\circ - H_{298}^\circ)$ 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 $\Delta H^\circ_{sub\,298}$ for a single curve, calculated as an average of individual point ΔH°_{298} values using equation (1) should agree approximately 95 percent of the time with 26,660 cal/mol (111,550 J/mol[8]) within the limits described below:

$$\text{Test:} \quad \left|26{,}660 - \Delta H^\circ_{sub\,298}\right| \leqslant 420 \text{ cal/mol}$$

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 Atomic, Inc., H. G. Staley
Los Alamos Scientific Laboratory, C. C. Herrick and R. C. Feber
Marquette University, T. C. Ehlert
National Bureau of Standards, 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, Washington - 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 $\Delta H^\circ_{sub\,298} = 26.660 \pm 150$ cal/mol (111,550 ± 630 J/mol). The ± 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.

Temperature K.(IPTS-68)	Condensed phase[b] $-\frac{G^\circ_T - H^\circ_{298}}{T}$ cal·mol⁻¹·deg⁻¹	Gas phase $-\frac{G^\circ_T - H^\circ_{298}}{T}$ 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-68[4] 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 second law $\Delta H^{\circ}_{sub\,298}$ = 26,610 ± 380 cal/mol (111,340 ± 1600 J/mol). The ± uncertainty represents two standard error limits of the pooled value. The pooled second law and third law heats[2] 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.

[6] Horton, W. S., J. Res. NBS, **70A**, 533-9 (1966).

[7] Cubicciotti, D., J. Phys. Chem., **70**, 2410-3 (1966).

[8] 1 calorie = 4.1840 joules.