DEPARTMENT OF COMMERCE UNITED STATES OF AMERICA

National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material 748

Silver-Vapor Pressure

Vapor Pressure as a Function of Temperature (800-1600 K)

T(K, ITS-90)	P(atm)[a]	(1/T x 10^4) (K^{-1}, ITS-90)	Log P (atm)[a]
800	1.36×10^{-12}	12.500	-11.868
900	1.49×10^{-10}	11.111	-9.828
1000	6.22×10^{-9}	10.000	-8.206
1100	1.32×10^{-7}	9.091	-6.878
1200	1.69×10^{-6}	8.333	-5.772
1235(M.P.)	3.72×10^{-6}	8.097	-5.430
1300	1.36×10^{-5}	7.692	-4.866
1400	7.83×10^{-5}	7.143	-4.106
1500	3.55×10^{-4}	6.667	-3.450
1600	1.32×10^{-3}	6.250	-2.879

1 atmosphere = 101,325 newtons per meter^2

This Standard Reference Material (SRM) is intended primarily for use as a vapor pressure standard. This SRM 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 standard was supplied by Cominco American, Inc., Spokane, Washington. A specially selected lot of high grade silver was further purified by electrolysis, homogenized into a single lot, degassified, and processed into the final rod size.

The above vapor pressure-temperature values for solid and liquid silver are a composite resulting from a weighted averaging of over 250 vapor pressure-temperature measurements made by seven laboratories[*], including NIST. The data and the associated uncertainties from two additional laboratories[*] were also examined, but were found to deviate significantly from the consensus and were not included in the final calculations. The composite temperature-pressure results were obtained by using a pooled third law heat of sublimation[2] at 298 K (68 010 cal/mol) and back-calculating through the third law equation:

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

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).

Gaithersburg, MD 20899
February 1, 1991
(Revision of Certificate dated 8-7-70)

William P. Reed, Acting Chief
Standard Reference Materials Program

(over)

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-68[4] and ITS-90[5] scales are quite small, and the associated changes in the certified vapor pressures are also very small.

The results from the seven 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 748 was performed by R.C. Paule and J. Mandel.

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 use of equation (1). Each laboratory's data has been recalculated at NIST using a single set of free energy functions[3] and identical calculation procedures. For the original certificate, dated August 10, 1970, all temperatures were for the 1968 International Practical Temperature Scale (IPTS-68).[4]

Twenty 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:

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

The slope, B, is a second law heat of sublimation at 298 K. The use of equation (2) is similar to the sigma method, and does not require the specification of a mean effective temperature.[7,8] The procedure is very convenient when the calculations, including the interpolation of free energy functions, are made by computer.

The results from the seven 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 seven laboratories represent a broad cross-section of measurement techniques and include Knudsen (weight loss and condensation methods), torque Knudsen, and mass spectrometric methods. Temperatures were measured by either thermocouples or by optical pyrometer. The average range of the curves was 240 K and the average number of points was 15.

A laboratory wishing to evaluate its apparatus and techniques may use SRM 748 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: tantalum, impervious alumina, dense graphite, and quartz. 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 <u>single</u> temperature-pressure curve using equation (2) should give a B value ($\Delta H^{\circ}_{sub298}$) which agrees approximately 95 percent of the time with the value 68 010 cal/mol (284 550 J/mol(9))within the following limits:

$$\text{Test:}\quad \left|\,68\,010-\Delta H^{\circ}_{sub298}\,\right| \le 1\,700\ \text{cal/mol}$$

If a laboratory prefers to least squares fit the equation

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

to obtain $\Delta \overset{\circ}{H}_{T}$, and then adjust to $\Delta \overset{\circ}{H}_{298}$ using literature $\Delta\left(\overset{\circ}{H}_{T} - \overset{\circ}{H}_{298}\right)$ values, the above slope limits should still be approximately correct.

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

The average third law $\Delta \overset{\circ}{H}_{sub298}$ for a single curve, calculated as an average of individual point $\Delta \overset{\circ}{H}_{sub298}$ values using equation (1) should agree approximately 95 percent of the time with 68 010 cal/mol (284 550 J/mol(9)) within the limits described below:

$$\text{Test:} \quad \left| 68\,010 - \Delta \overset{\circ}{H}_{sub298} \right| \leq 870 \text{ cal/mol}$$

A further description of the evaluation of the variances for SRM 748, and their use in applications involving two or more temperature-pressure curves is given in NBS Spec. Publ. 260-21.

***List of Participating Laboratories**

Aerospace Corporation, P.C. Marx, E.T. Chang and N.A. Gokcen
Air Force Materials Laboratory, G.L. Haury
Douglas Advanced Research Laboratories, D.L. Hildenbrand
Institut für Physikalische Chemie de Universität Wien, (Austria) A. Neckel
Los Alamos Scientific Laboratory, C.C. Herrick and R.C. Feber
Marquette University, T.C. Ehlert
National Institute of Standards and Technology, E.R. Plant and A.B. Sessoms
National Chemical Laboratory, (India), V.V. Dadape
Sandia Corporation, D.A. Northrop
Universita Delgi Studi di Roma, (Italy), V. Piancente and G. DeMaria

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)
Optical Emission Spectroscopy (Engelhard Industries, Newark, New Jersey - A.J. Lincoln)
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 $\Delta \overset{\circ}{H}_{sub298} = 68\,010 \pm 300$ cal/mol ($284\,550 \pm 1\,250$ 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.

3

Temperature K, (IPTS-68)	Condensed Phase[b] $-\frac{G^\circ_T - H^\circ_{298}}{T}$ $\mathrm{cal \bullet mol^{-1} \bullet deg^{-1}}$	Gas Phase $-\frac{G^\circ_T - H^\circ_{298}}{T}$ $\mathrm{cal \bullet mol^{-1} \bullet deg^{-1}}$
298.15	10.169	41.320
600	11.378	42.295
700	11.899	42.708
800	12.408	43.107
900	12.898	43.487
1000	13.366	43.845
1100	13.815	44.184
1200	14.244	44.504
1235 (M.P.)	14.390	44.609
1300	14.767	44.807
1400	15.312	45.094
1500	15.822	45.366
1600	16.303	45.625
1700	16.755	45.871

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[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 (April 1968), and using data of Furukawa, G.T., Saba, W.G., and Reilly, M.L., NSRDS-NBS 18, (April 1968). 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 $\Delta H^\circ_{\mathrm{sub}298}$ = 68 970 ± 570 cal/mol (288 570 ± 2 400 J/mol). The ± uncertainty represents two standard error limits of the pooled value. The pooled second and third law[2] heats are not in particularly good agreement. This problem has been examined in detail and is discussed in NBS Spec. Publ. 260-21. For a number of reasons discussed in NBS Spec. Publ. 260-21, the pooled third law heat is believed to be 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 calorie = 4.1840 joules.