



# National Institute of Standards & Technology

## Certificate of Analysis

### Standard Reference Material 745

#### Gold-Vapor Pressure

#### Vapor Pressure as a Function of Temperature (1300-2100 K)

<u>T(K, ITS-90)</u>	<u>P(atm)<sup>a</sup></u>	<u>(1/T) x 10<sup>4</sup> (K<sup>-1</sup>, ITS-90)</u>	<u>Log P(atm)<sup>a</sup></u>
1300	9.99 x 10 <sup>-9</sup>	7.692	-8.001
1337 (M.P.)	2.51 x 10 <sup>-8</sup>	7.474	-7.600
1400	1.02 x 10 <sup>-7</sup>	7.143	-6.991
1500	7.40 x 10 <sup>-7</sup>	6.667	-6.131
1600	4.16 x 10 <sup>-6</sup>	6.250	-5.380
1700	1.91 x 10 <sup>-5</sup>	5.882	-4.719
1800	7.29 x 10 <sup>-5</sup>	5.556	-4.137
1900	2.44 x 10 <sup>-4</sup>	5.263	-3.614
2000	7.10 x 10 <sup>-4</sup>	5.000	-3.149
2100	1.89 x 10 <sup>-3</sup>	4.762	-2.725

<sup>a</sup>1 atmosphere = 101,325 newtons per meter<sup>2</sup>.

This Standard Reference Material is intended primarily for use as a vapor pressure standard. It is available as a 1.4 mm (0.055 inch) diameter wire, 152 mm (6 inches) long. Extensive homogeneity testing was performed at the NIST laboratories in Gaithersburg, Maryland, and in Boulder, Colorado, and the material was found to be entirely satisfactory within limits of the analytical methods used. The purity of the gold material has been established to be 99.999 + %.<sup>1</sup>

The above vapor pressure-temperature values for solid and liquid gold are a composite resulting from a weighted averaging of 256 vapor pressure-temperature measurements made by eight laboratories\*, including NIST. Data from three additional laboratories\* and their uncertainties 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<sup>2</sup> at 298 K (87,720 cal/mol) and back-calculating through the third law equation:

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

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-68<sup>4</sup> and ITS-90<sup>5</sup> scales are quite small, and the associated changes in the certified vapor pressures are also very small.

Gaithersburg, MD 20899  
August 27, 1990  
(Revision of certificate dated 5-14-69)

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The results from the eight 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 three statistical tests for use by a laboratory wishing to evaluate its precision and accuracy, are presented on the following pages.

The overall coordination and evaluation of data leading to certification of SRM 745 was performed by R.C. Paule and J. Mandel of the NIST National Measurement Laboratory.

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 have been recalculated at NIST using a single set of free energy functions and identical calculation procedures. For the original certificate, dated May 14, 1969, all temperatures were converted to the 1968 International Practical Temperature Scale (IPTS-68).<sup>4</sup>

Data from the above mentioned eight laboratories were also used to obtain a pooled second law heat of sublimation.<sup>6</sup> 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:

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

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

The results from the eight 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 eight 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 both thermocouples and optical pyrometers.

A laboratory wishing to determine the precision and accuracy of its apparatus and techniques may use SRM 745 to measure a  $\ln P$  vs.  $1/T$  curve over as wide a temperature interval as practical. The monomer vapor species should be used in the calculations. Regarding Knudsen cell materials, the use of dense or pyrolytic graphite has been satisfactory. Metallic cells such as tungsten are satisfactory if a graphite or  $Al_2O_3$  cup liner is used to avoid creeping of the molten gold. After making the measurements, the following three statistical tests should be performed.

#### Test I. Evaluation of the Scatter of Points about a Line

The data should be least-squares fitted to equation (2) using the free energy functions given in footnote (3) to obtain the standard deviation of the fit ( $S_{fit}$ ) for the left hand side of equation (2). Using a chi square table<sup>8</sup> and  $\nu$  degrees of freedom (number of points-2), a laboratory's  $S_{fit}$  value should be less than the following limit, approximately 95% of the time:

$$\text{Upper Limit} = 0.141 \frac{\sqrt{\chi_{95\%, \nu}^2}}{\nu}$$

If the laboratory prefers to least-squares fit the equation:

$$R \ln P (\text{atm}) = A' + \frac{B'}{T} \quad (3)$$

then the upper limit constant, 0.141, should be changed to 0.142.

### Test II. 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 87,720 cal/mol (367,040 J/mol<sup>10</sup>) within the limits described below.

$$\text{Variance of B} = V(B) = 8.30 \times 10^5 + \left[ \frac{0.0200}{\sum_i \left[ \frac{1}{T_i} - \left( \frac{1}{\bar{T}} \right) \right]^2} \right]$$

$$\text{Test: } \left| 87,720 - \Delta H_{\text{sub}298}^{\circ} \right| \leq 2.0 \sqrt{V(B)}$$

If the laboratory prefers to least-squares fit equation (3) to obtain  $\Delta H_T^{\circ}$ , and then adjust to  $\Delta H_{\text{sub}298}^{\circ}$  using literature  $\Delta (H_T^{\circ} - H_{\text{sub}298}^{\circ})$  values<sup>3</sup>, the above slope limits should still be approximately correct.

### Test III. 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  $\Delta H_{\text{vap}298}^{\circ}$  values [using equation (1)] should agree approximately 95% of the time with 87,720 cal/mol (367,040) J/mol<sup>10</sup> within the limits described below.

$$\text{Variance of 3rd Law } \overline{\Delta H_{\text{sub}298}^{\circ}} = V(3L) = 4.56 \times 10^5$$

$$\text{Test: } \left| 87,720 - \overline{\Delta H_{\text{sub}298}^{\circ}} \right| \leq 2.0 \sqrt{V(3L)}$$

This test assumes that a laboratory has made at least five temperature-pressure measurements.

A further description of the evaluation of the variances for SRM 745, and their use in applications involving two or more temperature-pressure curves are given in NBS Spec. Publ. 260-19.

#### \*List of Participating Laboratories

Aerospace Corporation, P.C. Marx, E.T. Chang and N.A. Gokcen  
 Air Force Materials Laboratory (MAMS), H.L. Gegel  
 Air Force Materials Laboratory (MAYT), G.L. Haury  
 Douglas Advanced Research Laboratories, D.L. Hildenbrand  
 Gulf General Atomic, Inc., H.G. Staley, P. Winchell, J.H. Norman and D.A. Bafus  
 Michigan State University, J.M. Haschke and H.A. Eick  
 National Institute of Standards & Technology, E.R. Plante and A.B. Sessoms  
 Philco-Ford Corporation, N.D. Potter  
 Space Sciences, Inc., M. Farber, M.A. Frisch and H.C. Ko  
 Universita Degli Studi di Roma, V. Piacenta and G. DeMaria  
 University of Pennsylvania, W.W. Worrell and A. Kulkarni

## Footnotes

<sup>1</sup> The following methods of analysis were used in the homogeneity testing and purity evaluations.

- a. Neutron Activation Analysis (W.D. Kinard, D.A. Becker, P.D. LaFleur)
- b. Polarography (E.J. Maienthal)
- c. Spectrophotometry (T.A. Rush, D.H. Christopher, R.W. Burke)
- d. Spark-Source Mass Spectrometry - Isotopic Dilution (P.J. Paulsen, D.E. Kelleher and R. Alvarez)
- e. Vacuum Fusion (J.T. Sterling)
- f. Optical Emission Spectroscopy (R. Alvarez)
- g. Residual Resistivity Ratios,  $R_{273K}/R_{4K}$  (J.C. Moulder, V.A. Deason and R.L. Powell)

<sup>2</sup> The third law  $\Delta H_{sub298}^{\circ} = 87,720 \pm 210$  cal/mol ( $367,040 \pm 900$  J/mol). The  $\pm$  uncertainty value represents one standard error 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.

<sup>3</sup>

Temperature K, (IPTS-68)	Condensed phase <sup>a</sup>	Gas phase <sup>b</sup>
	$\frac{G_T^{\circ} - H_{298}^{\circ}}{T}$	$\frac{G_T^{\circ} - H_{298}^{\circ}}{T}$
	cal•mol <sup>-1</sup> deg <sup>-1</sup>	cal•mol <sup>-1</sup> deg <sup>-1</sup>
298.15	11.319	43.120
1200	15.352	46.304
1300	15.751	46.607
1338(M.P.)	15.896	46.718
1400	16.236	46.894
1500	16.749	47.165
1600	17.233	47.426
1700	17.674	47.673
1800	18.117	47.910
1900	18.515	48.138
2000	18.913	48.356
2100	19.275	48.567
2200	19.636	48.768

<sup>a</sup> Converted to IPTS-68 from data of J.W. Tester, R.C. Feber and C.C. Herrick, J. Chem. Eng. Data 13, 419-21, (July, 1968).

<sup>b</sup> From data of R. Hultgren, R.L. Orr, P.D. Anderson and K.K. Kelley, "Selected Values of Thermodynamic Properties of Metals and Alloys," pp. 38-42, (June, 1960), John Wiley & Sons, Inc., N.Y. (1963).

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

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

<sup>6</sup> The second law  $\Delta H_{sub298}^{\circ} = 88,140 + 500$  cal/mol ( $368,800 + 2100$  J/mol). The  $\pm$  uncertainty represents one standard error of the pooled value.

<sup>7</sup> a. W.S. Horton, J. Res. NBS, (Phys. and Chem.), 533-9 (1966).

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

<sup>8</sup> Handbook of Chemistry and Physics, p. A-162, 48th Ed. (1967-8), Chemical Rubber Publishing Co., Cleveland, Ohio.

<sup>9</sup> The value of the pooled third law heat of sublimation is used in this application as the center point, rather than the pooled second law heat of sublimation. The difference between the second and third law heats is small (420 cal/mol) and is well within the stated limits of uncertainty (see footnotes 2 and 6).

<sup>10</sup> 1 calorie = 4.1840 joules.