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DIVISION OF INORGANIC CHEMISTRY
COMMISSION ON HIGH TEMPERATURES
AND REFRACTORY MATERIALS

ANALYSIS OF INTERLABORATORY MEASUREMENTS ON THE VAPOR PRESSURE OF CADMIUM AND SILVER

Prepared for publication by
ROBERT C. PAULE and JOHN MANDEL

LONDON
BUTTERWORTHS

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ABSTRACT

Detailed statistical analyses have been made of results obtained from a series of interlaboratory measurements on the vapor pressures of cadmium and silver. Standard Reference Materials 746 (cadmium) and 748 (silver) which were used for the measurements have been certified over the respective pressure ranges 10^{-11}–10^{-4} atm and 10^{-12}–10^{-3} atm. The temperature ranges corresponding to these pressures are 350–594 K for cadmium and 800–1 600 K for silver. The heats of sublimation at 298 K and the associated two standard error limits for cadmium and silver are 26660 ± 150 cal/mol and 68010 ± 300 cal/mol, respectively. Estimates of uncertainty have been calculated for the certified temperature/pressure values as well as for the uncertainties expected from a typical single laboratory's measurements. The statistical analysis has also been made for both the second and third law methods, and for the within- and between-laboratory components of error. The uncertainty limits are observed as functions of both the heat of sublimation and the temperature.

At the XXVIth Council Meeting of IUPAC in Washington, DC, on 21 and 23 July 1971, the use of metallic cadmium and silver as standards for testing apparatus and procedures for vapor pressure measurement, proposed by the Commission on High Temperatures and Refractory Materials, was approved.

1. INTRODUCTION

This report is part of a continuing program to establish five new vapor pressure standard reference materials, and constitutes the second report

† W. S. Horton, Chairman (USA); G. D. Rieck, Secretary (Netherlands); Members: C. B. Alcock (Canada), R. Collongues (France), E. Fitzer (Germany), A. E. Sheindlin (USSR). Associate Members: F. Cabannes (France), J. Hlaváč (Czechoslovakia), G. De Maria (Italy), H. Mii (Japan), K. Motzfeldt (Norway), H. Nowotny (Austria). National Representatives: E. R. McCartney (Australia), J. Drowart (Belgium), N. F. Bright (Canada), Atma Ram (India), U. Colombo (Italy), S. T. Mrowec (Poland), A. Magnéli (Sweden), B. C. H. Steele (UK), D. D. Cubicciotti (USA).

of the Task Force on Vapor Pressure of the Commission on High Temperatures and Refractory Materials. The materials cadmium, silver, gold, platinum and tungsten are being certified by the US National Bureau of Standards for vapor pressures as a function of temperature. The certifications cover the 10^{-12}–10^{-3} atm range; for the complete series of materials, the temperatures corresponding to these pressures will vary from 350 to 3000 K. Gold has previously been certified over the temperature range 1300–2100 K[1]. This report describes the current certification of cadmium (350–594 K), and of silver (800–1600 K)*.

These vapor pressure standard reference materials will allow workers in the field to detect systematic errors and to evaluate their results quantitatively. The materials should be most useful for checking low vapor pressure measurement methods, such as the Knudsen, torque Knudsen, Langmuir, and mass spectrometric methods.

Experience in vapor pressure measurements, particularly at high temperatures, has shown that large systematic errors are common, even among experienced investigators. This report gives estimates of the uncertainties of the certified temperature/pressure values as well as estimates of the uncertainties of a 'typical' single laboratory's measurements.

The current certification of cadmium and silver, when taken in conjunction with the prior certification of gold, gives an indication of the temperature dependence of the uncertainties of vapor pressure measurements. These uncertainties are statistical in nature and reflect results for typical experienced investigators. The use of vapor pressure standard reference materials should aid in the detection and elimination of errors and should ultimately result in the decrease of the uncertainty limits that are herein reported.

Our results are based on interlaboratory tests (including NBS) made during 1968–9 (see list of the cooperating laboratories).

The results from the interlaboratory tests were used to obtain composite heats of sublimation ($\Delta H_{\text{sub}\,298}$) for cadmium and for silver at 298 K. The certified temperature/pressure values were then obtained by back-calculating through the third law equation

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

These calculations used composite $\Delta H_{\text{sub}\,298}$ of 26660 cal/mol (111550 J/mol) for cadmium, and 68010 cal/mol† (284550 J/mol)‡ for silver, along with the referenced free energy functions§. P is expressed in atmospheres. All temperatures for this report have been converted to the 1968 International Practical Temperature Scale (IPTS–68)‖.

The certified temperature/pressure values as well as the corresponding $1/T$ and $\log P$ values are listed in *Table 2*.

A broad cross section of measurement techniques was used by the cooperating laboratories; the techniques included the Knudsen (weight loss and condensation methods), torque Knudsen, and calibrated mass spectrometric methods. Temperatures were measured using either thermocouples or optical pyrometer. Summary information regarding the experimental details for each laboratory is given in *Tables 3* and *4*.

* The cadmium (SRM 746), silver (SRM 748) and gold (SRM 745) may be ordered from the Office of Standard Reference Materials, National Bureau of Standards, Washington, DC 20234. The respective prices for SRM 746, 748 and 745 are $65, $75 and $85 per unit; this price includes a 'Certificate of Analysis' containing specific recommendations for the material's usage as well as several statistical tests by which a laboratory may evaluate its results. All three materials are homogeneous and are in excess of 99.999 per cent pure. The cadmium and silver are in the form of rods 0.25 in. in diameter and 2.5 in. long, while the gold is in the form of wire 0.055 in. in diameter and 6 in. long.

† These $\Delta H_{\mathrm{sub}298}$ are in good agreement with the respective values 26770 and 68010 cal/mol, and 26720 and 67900 cal/mol quoted by: Wagman, D. D., Evans, W. H., Parker, V. P., Halow, I., Bailey, S. M. and Schumn, R. H., 'Selected values of chemical thermodynamic properties', *Tech. Notes Nat. Bur. Stand. (US). Nos 270-3* (Cd–1968) and *270–4* (Ag–1969); and by Hultgren, R., Orr, R. L. and Kelley, K. K., loose-leaf supplement to *Selected Values of Thermodynamic Properties of Metals and Alloys*, University of California and Lawrence Radiation Laboratory, Berkeley, California (Cd reviewed Sept. 1966; Ag reviewed April 1968).

‡ 1 calorie = 4.1840 joules

§ *Table 1.*

Temperature	Condensed phase[a] $-\frac{G_T^\circ - H_{298}^\circ}{T}$		Gas phase[b] $-\frac{G_T^\circ - H_{298}^\circ}{T}$	
K, (IPTS-68)	cal·mol⁻¹·deg⁻¹	(J·mol⁻¹·deg⁻¹)‡	cal·mol⁻¹·deg⁻¹	(J·mol⁻¹·deg⁻¹)‡
		CADMIUM		
298.15	12.38	(51.80)	40.065	(167.632)
400	12.63	(52.84)	40.260	(168.448)
500	13.10	(54.81)	40.628	(169.988)
594 (M. pt)	13.61	(56.94)	41·011	(171·590)
600	13.67	(57.20)	41.040	(171.711)
700	14.58	(61.00)	41.453	(173.439)
		SILVER		
298.15	10.169	(42.547)	41.320	(172·883)
600	11.378	(47.606)	42.295	(176.962)
700	11.899	(49.785)	42.708	(178.690)
800	12.408	(51.915)	43.107	(180.360)
900	12.898	(53.965)	43.487	(181.950)
1000	13.366	(55.923)	43.845	(183.447)
1100	13.815	(57.802)	44.184	(184.866)
1200	14.244	(59.597)	44.504	(186.205)
1235 (M. pt)	14.390	(60.208)	44.609	(186.644)
1300	14.767	(61.785)	44.807	(187.472)
1400	15.312	(64.065)	45.094	(188.673)
1500	15.822	(66.199)	45.366	(189.811)
1600	16.303	(68.212)	45.625	(190.895)
1700	16.755	(70.103)	45.871	(191.924)

[a] Converted to IPTS-68 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* (Cd–Sept. 1966; Ag–April 1968), and using data of Furukawa, G. T., Saba, W. G. and Reilly, M. L., *NSRDS-NBS 18* (Ag–April 1968). The data were converted to IPTS-68 using equations given by Douglas, T. B., *J. Res. Nat. Bur. Stand.* 73A, 451–69 (1969).

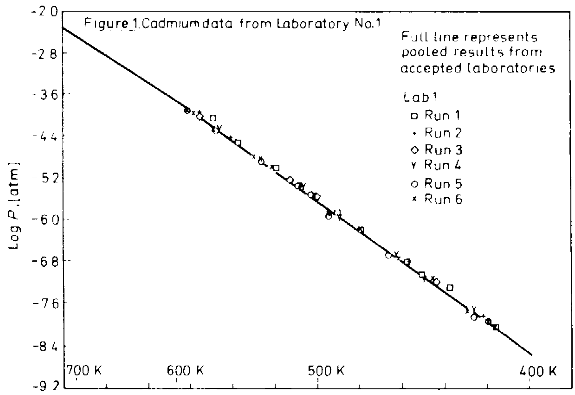
[b] From data of Hultgren, ibid.

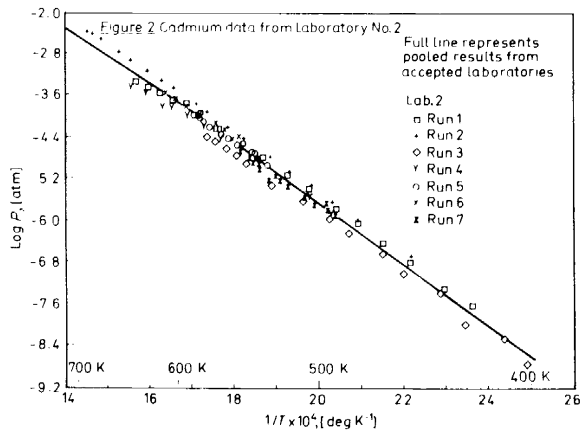
‖ The International Practical Temperature Scale of 1968, *Metrologia*, **5**, 35–49 (1969).

Table 2.

T(K)	P(atm)*	$(1/T) \times 10^4$ (K^{-1})	Log P* (atm)	T(K)	P(atm)*	$(1/T) \times 10^4$ (K^{-1})	Log P* (atm)
Cadmium				Silver			
350	2.49×10^{-11}	28.57	−10.603	800	1.35×10^{-12}	12.500	−11.870
400	2.97×10^{-9}	25.00	−8.528	900	1.48×10^{-10}	11.111	−9.830
450	1.20×10^{-7}	22.22	−6.922	1000	6.28×10^{-9}	10.000	−8.202
500	2.31×10^{-6}	20.00	−5.637	1100	1.33×10^{-7}	9.091	−6.875
550	2.56×10^{-5}	18.18	−4.592	1200	1.69×10^{-6}	8.333	−5.773
594 (M. pt)	1.51×10^{-4}	16.84	−3.820	1235 (M. pt)	3.71×10^{-6}	8.097	−5.431
				1300	$1{\cdot}35 \times 10^{-5}$	7.692	−4.868
				1400	7.80×10^{-5}	7.143	−4.108
				1500	3.53×10^{-4}	6.667	−3.452
				1600	1.31×10^{-3}	6.250	−2.881

* 1 atmosphere = 101 325 N . m^{-2}.





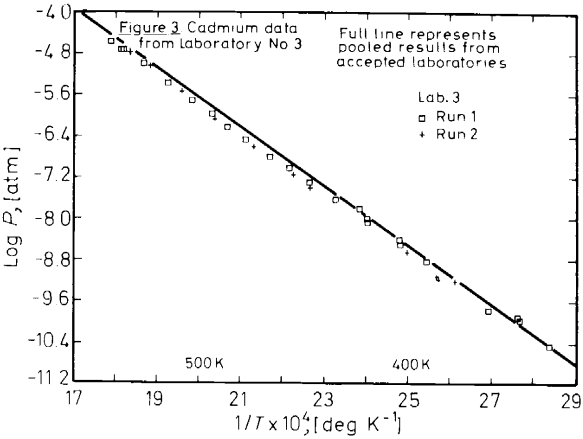


Figure 3. Cadmium data from Laboratory No 3

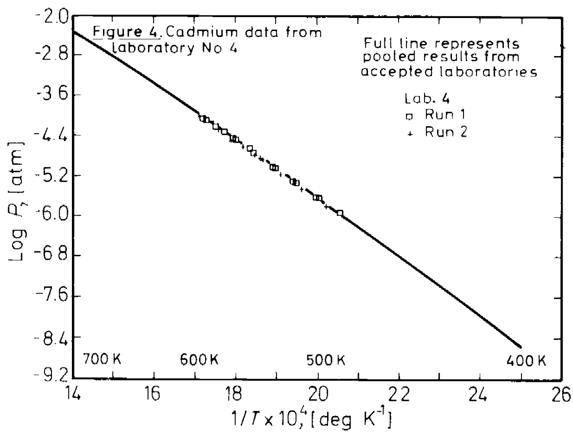


Figure 4. Cadmium data from laboratory No 4

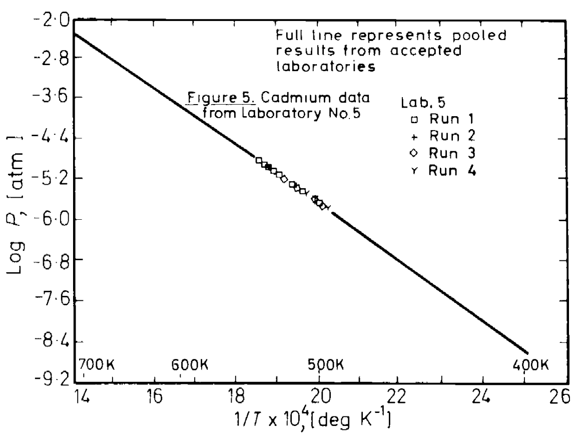


Figure 5. Cadmium data from Laboratory No.5

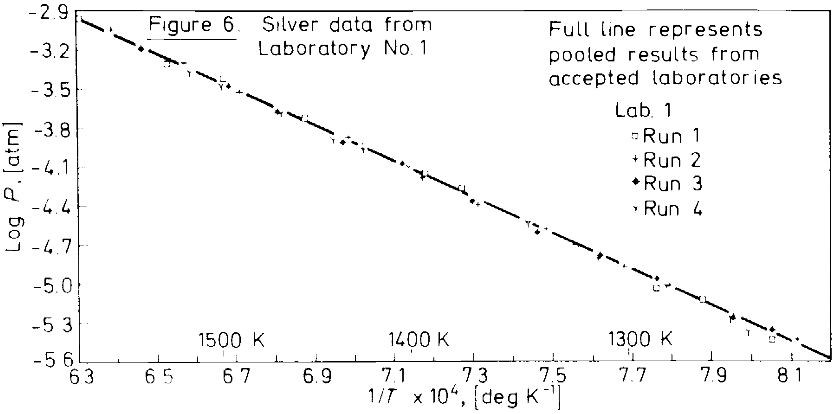


Figure 6. Silver data from Laboratory No. 1
Full line represents pooled results from accepted laboratories
Lab. 1
Run 1
Run 2
Run 3
Run 4
Log P, [atm]
-2.9
-3.2
-3.5
-3.8
-4.1
-4.4
-4.7
-5.0
-5.3
-5.6
1500 K
1400 K
1300 K
6.3
6.5
6.7
6.9
7.1
7.3
7.5
7.7
7.9
8.1
1/T x 10^4, [deg K^-1]

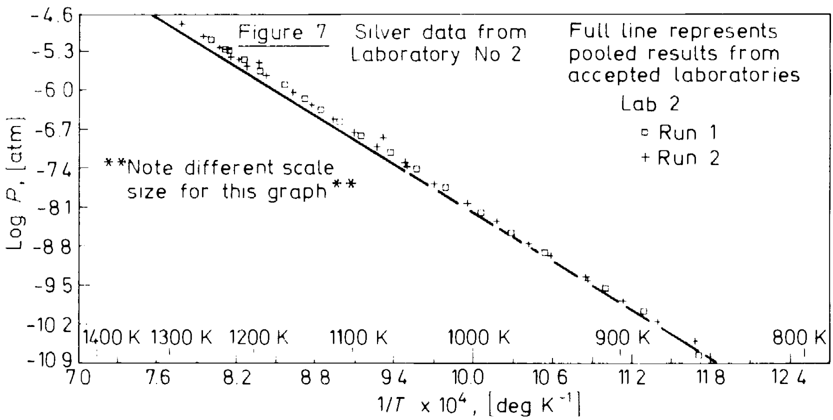


Figure 7 Silver data from Laboratory No 2
Full line represents pooled results from accepted laboratories
Lab 2
Run 1
Run 2
Note different scale size for this graph
Log P, [atm]
-4.6
-5.3
-6.0
-6.7
-7.4
-8.1
-8.8
-9.5
-10.2
-10.9
1400 K
1300 K
1200 K
1100 K
1000 K
900 K
800 K
7.0
7.6
8.2
8.8
9.4
10.0
10.6
11.2
11.8
12.4
1/T x 10^4, [deg K^-1]

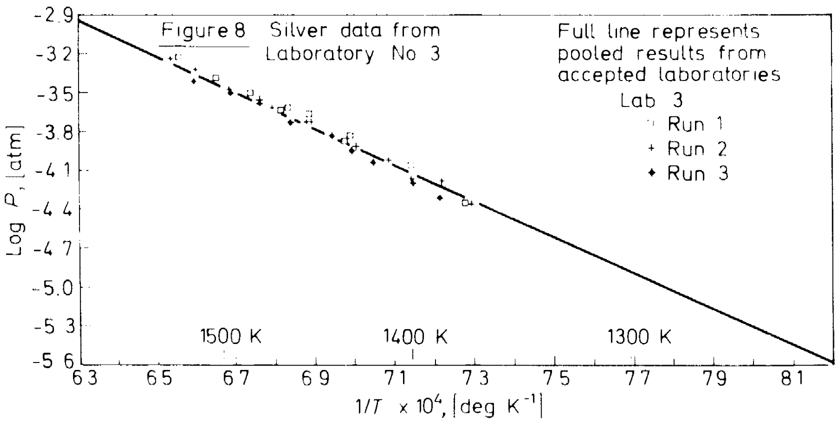


Figure 8 Silver data from Laboratory No 3
Full line represents pooled results from accepted laboratories
Lab 3
Run 1
Run 2
Run 3
Log P, [atm]
-2.9
-3.2
-3.5
-3.8
-4.1
-4.4
-4.7
-5.0
-5.3
-5.6
1500 K
1400 K
1300 K
6.3
6.5
6.7
6.9
7.1
7.3
7.5
7.7
7.9
8.1
1/T x 10^4, [deg K^-1]

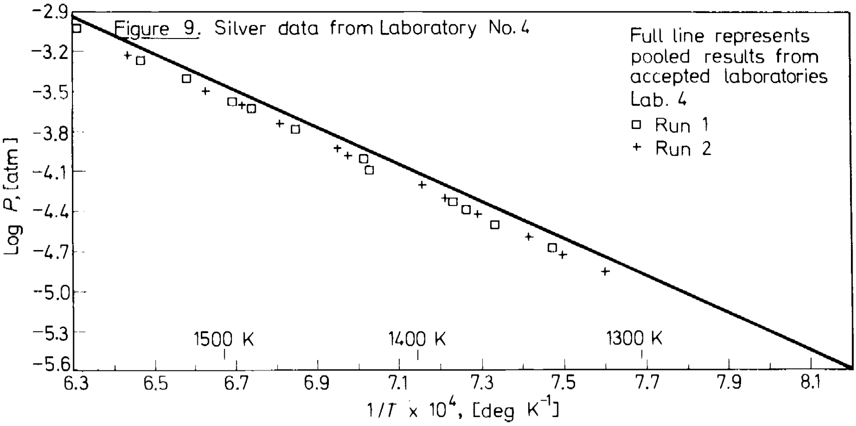


Figure 9. Silver data from Laboratory No. 4

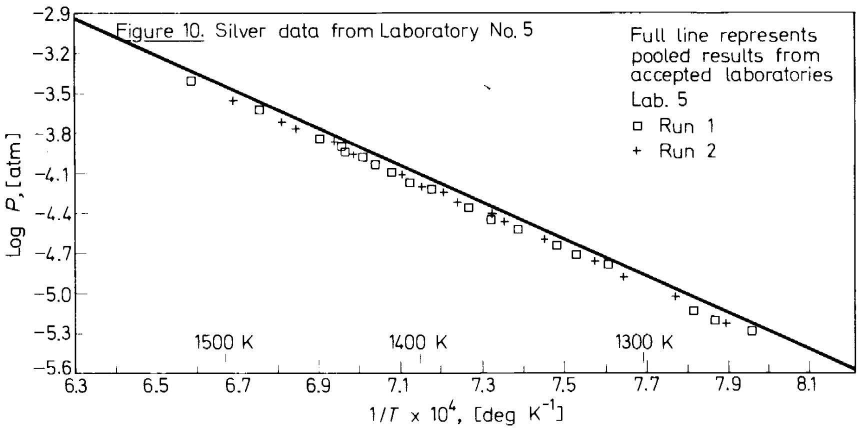


Figure 10. Silver data from Laboratory No. 5

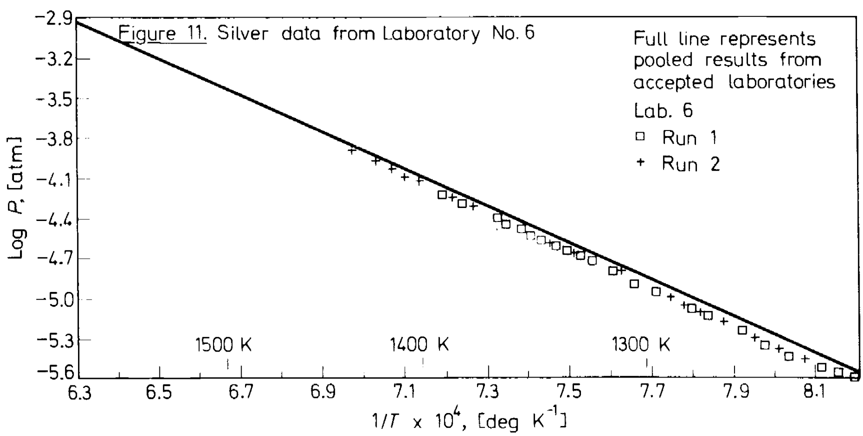


Figure 11. Silver data from Laboratory No. 6

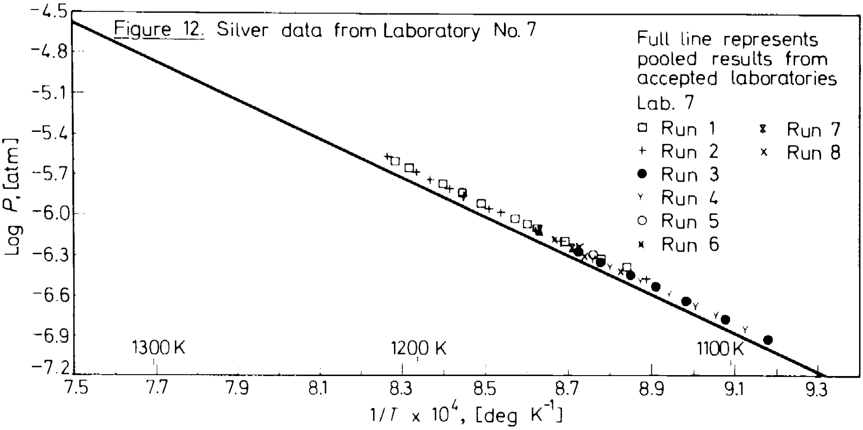


Figure 12. Silver data from Laboratory No. 7
Full line represents pooled results from accepted laboratories
Lab. 7
Run 1
Run 2
Run 3
Run 4
Run 5
Run 6
Run 7
Run 8
1300 K
1200 K
1100 K
Log P, [atm]
1/T x 10^4, [deg K^-1]

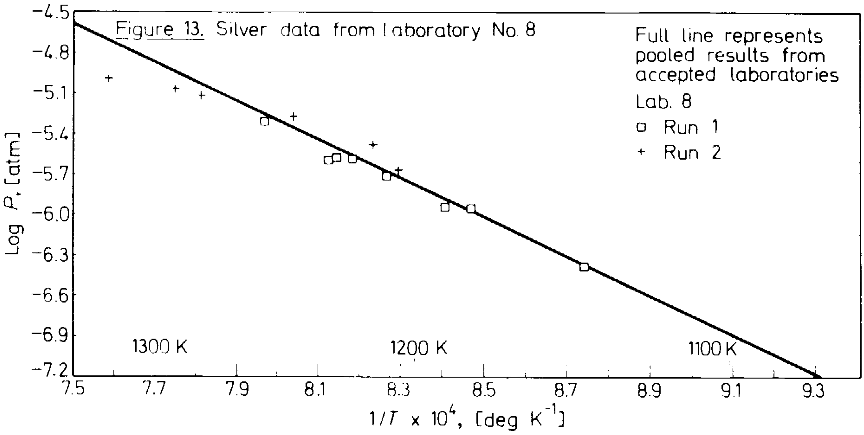


Figure 13. Silver data from Laboratory No. 8
Full line represents pooled results from accepted laboratories
Lab. 8
Run 1
Run 2
1300 K
1200 K
1100 K
Log P, [atm]
1/T x 10^4, [deg K^-1]

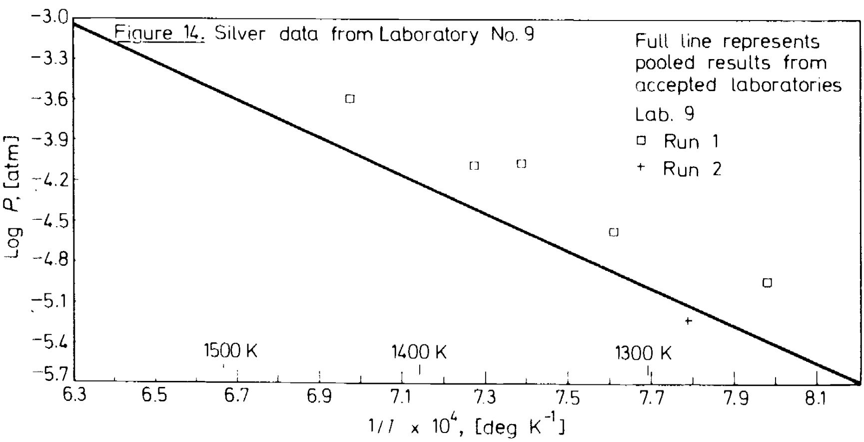


Figure 14. Silver data from Laboratory No. 9
Full line represents pooled results from accepted laboratories
Lab. 9
Run 1
Run 2
1500 K
1400 K
1300 K
Log P, [atm]
1/T x 10^4, [deg K^-1]

2. TREATMENT OF DATA

The detailed temperature/pressure data from the six laboratories for cadmium, and from the nine laboratories for silver, are given in *Tables 5* and *6*. Plots of the data for cadmium and for silver are given in *Figures 1* to *14* inclusive. The full lines in these figures represent the pooled curves for all accepted data from all laboratories. A total of 24 sets of cadmium data (runs) with over 250 temperature/pressure points, and a total of 27 sets of silver data with over 300 temperature/pressure points were available for consideration.

Each temperature/pressure run has been used to obtain both the second and third law heats of sublimation at 298 K. Equation (1) was used to calculate the individual third law $\Delta H_{\text{sub }298}$ values corresponding to each temperature/pressure point and the average $\Delta H_{\text{sub }298}$ value was calculated for each run. Available information would indicate that the evaporation coefficient for silver is unity. Cadmium, however, may have had evaporation-condensation coefficients less than unity[2]. Observations at NBS have indicated a considerable bouncing of cadmium vapors impinging on glass surfaces at room temperatures. Furthermore, remarks listed in *Table 3* for cooperating laboratories 1, 2 and 3 indicate possible effective evaporation-condensation coefficients of less than unity. Since Knudsen cells with relatively small orifices were used in *all* accepted experiments, we have not made corrections for possible non-unit evaporation coefficients.

The second law heat for each vapor pressure/temperature run was obtained by least-squares fitting the A and B constants in the equation:

$$\Delta\{-(G^\circ_T - H^\circ_{298})/T\} - R \ln P = A + B/T \tag{2}$$

where P is expressed in atmospheres. This calculational procedure is similar to the sigma method, and does not require the specification of a mean effective temperature[3,4]. The slope B is a second law heat of sublimation at 298 K. The intercept A will be zero for the ideal case where the measured pressures and the free energy functions are completely accurate. We have kept the intercept A in the least-squares equation to accommodate possible error. This second law procedure is very convenient to use when the calculations, including the interpolation of free energy functions, are made by computer. The OMNITAB computer language[5] was used in this work. Summaries of the second and third law results for cadmium and silver are are given in *Tables 7* to *10* inclusive.

3. STATISTICAL ANALYSES

The two OMNITAB programs written for the analyses of the gold (SRM 745) vapor pressure data were modified slightly and were used in the current work. The ultimate purpose of these programs was to obtain overall weighted average values of the second and third law heats of sublimation and estimates of the uncertainties.

The first OMNITAB program performed least-squares fits for each run to obtain the second law heats and the average third law heats. The program

Table 3. Cadmiun—Summary of experimental methods

Laboratory	Method	Temperature measurement technique	Temperature range, K	Container material	Effective orifice area × 10^3, cm^2	Remarks
1	Mass spectrometric, with Cd calibrations	Pt–10% Rh/Pt thermocouple	413–590	Iridium	4.70	No cadmium dimer observed ($P < 5 \times 10^{-9}$ atm at 580 K). Temperature calibrations made using cadmium melting-freezing point halts. Cadmium background was $\frac{1}{3} - \frac{2}{3}$ of primary cadmium signal.
2	Knudsen weight loss (runs 1–4); torque Knudsen (runs 5–7)	Pt–Rh/Pt thermocouple	423–690	Iron	7.48, 1.69, 124, 31.5, 14.5, 3.79 67.0 for runs 1–7, respectively	A very wide range of orifice areas was used and an effect of orifice area was noted. This may indicate an effective non-unit evaporation coefficient for the cadmium sample. A slight oxide coating on the sample could explain these results.
3	Mass spectrometric, with Cd calibration	Chromel/Alumel thermocouple	352–550	Spectroscopic grade graphite	8.84	Cadmium dimer observed to be less than 0.1% of monomer. Run temperature measurements made in one temperature direction only, i.e. temperatures were decreased. Initial pressure readings were low, presumably due to a slight oxide coating. Heating sample 15 min in vacuum at 460 K eliminated this problem.

4	Knudsen weight	Pt–10% Rh/Pt thermocouple	487–584	Alumina	2.65, 4.58	Orifices calibrated using vaporization of lead. Used Hultgren's data on lead (Nov. 1965).
5	Torque Knudsen	Pt–13% Rh/Pt thermocouple	495–539	ZTA graphite	6.11, 12.84	Temperature measurements made in one temperature direction only, i.e. decreasing temperatures.
6	Torque Knudsen	Pt–10% Rh/Pt thermocouple	500–600	Beryllia	0.86	Automatic data recording used by this laboratory to obtain hundreds of temperature/pressure data points. The resultant data were treated by the cooperating laboratory and third law $\Delta H_{\mathrm{sub}\,298}$ were submitted for use in this study.

Table 4. Silver—Summary of experimental methods

Laboratory	Method	Temperature measurement technique	Temperature range, K	Container material	Effective orifice area $\times 10^3$, cm^2	Remarks
1	Knudsen using condensation plates	Optical pyrometer sighting into blackbody hole (runs 1 and 3); Pt–10% Rh/Pt thermocouple (runs 2 and 4)	1 232–1 584	Tantalum	4.05	Temperature calibrations made using silver melting-freezing point halts.
2	Mass spectrometric, with Ag calibrations	Chromel/Alumel thermocouple	854–1 284	Graphite	10.21	Temperature tended to be measured in one direction only, i.e. decreasing temperatures.
3	Knudsen weight loss	Optical pyrometer sighting into blackbody holes	1 373–1 530	Graphite coated with pyrolytic graphite	2.11, 3.72, 4.17	Significant difference noted in second and third law heats.
4	Knudsen weight loss	Pt–Rh/Pt thermocouple, plus optical pyrometer as secondary temperature recorder	1 315–1 584	Quartz	0.29, 0.80	—
5	Knudsen weight loss	Pt–10% Rh/Pt thermocouple	1 256–1 494	Alumina (run 1); stackpole high density graphite (run 2)	4.58, 3.55	Orifice calibrated using vaporization of lead. Used Hultgren's data on lead (Nov. 1965).

6	Torque Knudsen	Optical pyrometer sighting into blackbody hole	1221–1433	Graphite	3.5, 1.6	Temperature measurements made in one temperature direction only, i.e. decreasing temperatures.
7	Torque Knudsen (runs 1–6), Knudsen weight loss (runs 7–8)	Pt–13% Rh/Pt thermocouple	1089–1209	ZTA graphite	6.12, 23.0	Temperature measurements made in one temperature direction only, i.e. decreasing temperatures.
8	Double cavity Knudsen cell used for absolute calibration of TOF mass spectrometer	Optical pyrometer sighting into orifice	1143–1318	Graphite	—	—
9	Knudsen weight loss	Optical pyrometer sighting on to bottom of cell and 0.77 emissivity correction made	1254–1434	AGSX graphite	2.45, 1.38	Temperature measurements made in one temperature direction only, i.e. increasing temperatures.

Table 5. Cadmium—List of experimental temperature/pressure data

Lab. 1, Run 1		Lab. 1, Run 2		Lab. 1, Run 3		Lab. 1, Run 4		Lab. 1, Run 5	
T, K	P, atm	T, K	P, atm	T, K	P, atm	T, K	P, atm	T, K	P, atm
525.0	1.010×10^{-5}	556.0	3.920×10^{-5}	550.0	2.740×10^{-5}	564.0	5.690×10^{-5}	567.0	5.160×10^{-5}
501.0	2.830×10^{-6}	475.0	5.780×10^{-7}	475.0	5.780×10^{-7}	487.0	1.060×10^{-6}	493.0	1.220×10^{-6}
475.0	6.370×10^{-7}	418.0	1.400×10^{-8}	416.0	1.120×10^{-8}	422.0	1.830×10^{-8}	422.0	1.380×10^{-8}
452.0	1.590×10^{-7}	503.0	3.100×10^{-6}	500.0	2.700×10^{-6}	508.0	4.630×10^{-6}	511.0	0.570×10^{-6}
413.0	8.640×10^{-9}	451.0	1.530×10^{-7}	457.0	1.840×10^{-7}	457.0	2.160×10^{-7}	461.0	2.030×10^{-7}
551.0	3.120×10^{-5}	528.0	1.060×10^{-5}	516.0	5.780×10^{-6}	535.0	1.450×10^{-5}	535.0	1.330×10^{-5}
503.0	2.980×10^{-6}	438.0	5.510×10^{-8}	438.0	6.250×10^{-8}	444.0	7.220×10^{-8}	445.0	8.680×10^{-8}
488.0	1.390×10^{-6}	580.0	1.190×10^{-4}	580.0	9.980×10^{-5}	584.0	1.140×10^{-4}	590.0	1.240×10^{-4}
569.0	8.970×10^{-5}								
432.0	4.890×10^{-8}								

Lab. 1, Run 6		Lab. 2, Run 1*		Lab. 2, Run 2*		Lab. 2, Run 3		Lab. 2, Run 4*	
T, K	P, atm	T, K	P, atm	T, K	P, atm	T, K	P, atm	T, K	P, atm
569.0	5.650×10^{-5}	569.3	6.461×10^{-5}	644.3	1.199×10^{-3}	529.5	4.947×10^{-6}	493.3	1.513×10^{-6}
493.0	1.310×10^{-6}	535.3	1.658×10^{-5}	614.1	4.763×10^{-4}	493.8	1.139×10^{-6}	522.8	642.1×10^{-6}
425.0	1.720×10^{-8}	506.0	4.211×10^{-6}	584.6	1.737×10^{-4}	464.9	2.395×10^{-7}	551.1	2.237×10^{-5}
510.0	4.390×10^{-6}	477.8	9.237×10^{-7}	560.4	6.145×10^{-5}	437.2	4.408×10^{-8}	578.6	6.303×10^{-5}
456.0	1.780×10^{-7}	451.1	1.645×10^{-7}	530.1	1.697×10^{-5}	410.1	5.868×10^{-9}	507.2	3.447×10^{-6}
539.0	1.670×10^{-5}	464.5	3.882×10^{-7}	504.1	4.934×10^{-6}	398.0	1.658×10^{-9}	537.1	1.355×10^{-5}
440.0	7.150×10^{-8}	423.1	2.500×10^{-8}	450.9	2.184×10^{-7}	426.1	1.129×10^{-8}	566.0	4.224×10^{-5}
589.0	1.280×10^{-4}	435.3	5.355×10^{-8}	477.8	1.099×10^{-6}	454.5	9.961×10^{-8}	592.8	1.092×10^{-4}
		490.0	1.750×10^{-6}	491.9	2.355×10^{-6}	482.5	6.092×10^{-7}	606.1	1.553×10^{-4}
		519.2	7.605×10^{-6}	518.1	9.132×10^{-6}	509.7	2.434×10^{-6}	614.1	1.632×10^{-4}
		549.4	3.079×10^{-5}	548.5	3.921×10^{-5}	538.2	9.487×10^{-6}	629.7	2.947×10^{-4}
		567.4	6.474×10^{-5}	576.4	1.234×10^{-4}	546.3	1.312×10^{-5}	643.7	3.947×10^{-4}
		580.5	1.070×10^{-4}	604.7	3.513×10^{-4}	554.2	1.855×10^{-5}		
		593.6	1.789×10^{-4}	628.4	7.500×10^{-4}	561.9	2.526×10^{-5}		
		605.4	2.039×10^{-4}	656.3	1.737×10^{-3}	570.2	3.395×10^{-5}		
		616.9	2.895×10^{-4}	674.9	3.118×10^{-3}	576.9	4.197×10^{-5}		
		627.7	3.671×10^{-4}	683.6	3.868×10^{-3}				
		639.4	4.724×10^{-4}	689.5	4.342×10^{-3}				

Table 5. Cadmium—List of experimental temperature/pressure data—continued

Lab. 2, Run 5		Lab. 2, Run 6*		Lab. 2, Run 7		Lab. 3, Run 1		Lab. 3, Run 2	
T, K	P, atm	T, K	P, atm	T, K	P, atm	T, K	P, atm	T, K	P, atm
574.1	6.368×10^{-5}	602.6	2.039×10^{-4}	531.3	6.276×10^{-6}	559.9	2.712×10^{-5}	441.7	3.948×10^{-8}
559.9	3.868×10^{-5}	593.2	1.579×10^{-4}	542.5	1.316×10^{-5}	552.5	1.875×10^{-5}	449.9	7.347×10^{-8}
553.1	2.895×10^{-5}	581.9	1.036×10^{-4}	537.4	9.908×10^{-6}	551.0	1.852×10^{-5}	469.8	2.584×10^{-7}
541.4	2.053×10^{-5}	569.0	7.355×10^{-5}	524.0	5.816×10^{-6}	536.9	1.008×10^{-5}	491.4	9.404×10^{-7}
532·3	1.213×10^{-5}	557.4	3.724×10^{-5}	508.6	2.829×10^{-6}	520.3	4.320×10^{-6}	482.1	9.847×10^{-7}
542.8	2.105×10^{-5}	550.7	3.447×10^{-5}	495.8	2.224×10^{-6}	505.1	2.014×10^{-6}	511.0	3.001×10^{-6}
548.4	2.961×10^{-5}	552.1	4.184×10^{-5}	490.5	1.314×10^{-6}	504.7	1.962×10^{-6}	511.3	3.076×10^{-6}
565.4	4.618×10^{-5}	562.4	5.632×10^{-5}	495.0	1.671×10^{-6}	493.0	1.113×10^{-6}	532.3	9.836×10^{-6}
577.9	7.605×10^{-5}	567.5	6.908×10^{-5}	502.8	2.118×10^{-6}	484.5	6.066×10^{-7}	546.1	1.893×10^{-5}
586.6	1.072×10^{-4}	578.3	9.711×10^{-5}	518.8	4.658×10^{-6}	473.4	3.463×10^{-7}	550.0	2.143×10^{-5}
582.3	9.487×10^{-5}	593.2	1.724×10^{-4}	526.8	7.487×10^{-6}	461.3	1.611×10^{-7}	429.6	2.289×10^{-8}
538.0	1.579×10^{-5}	603.3	2.158×10^{-4}	523.4	5.868×10^{-6}	451.8	9.498×10^{-8}	429.0	2.175×10^{-8}
		612.1	2.829×10^{-4}	538.3	1.270×10^{-5}	441.9	5.096×10^{-8}	416.3	8.229×10^{-9}
				544.2	1.632×10^{-5}	441.6	4.802×10^{-8}	400.4	2.409×10^{-9}
				551.3	2.026×10^{-5}	430.1	2.310×10^{-8}	389.0	7.021×10^{-10}
						419.9	1.563×10^{-8}	389.4	7.697×10^{-10}
						417.1	1.010×10^{-8}	382.9	6.033×10^{-10}
						416.5	8.234×10^{-9}		
						403.7	3.724×10^{-9}		
						403.1	3.188×10^{-9}		
						393.0	1.489×10^{-9}		
						371.4	1.713×10^{-10}		
						361.8	1.037×10^{-10}		
						362.2	1.181×10^{-10}		
						352.2	3.249×10^{-11}		

* Vapor pressure data above the melting point showed considerable deviations and were not used.

Table 5. Cadmium—List of experimental temperature/pressure data—Continued

Lab. 4, Run 1		Lab. 4, Run 2		Lab. 5, Run 1		Lab. 5, Run 2		Lab. 5, Run 3	
T, K	*P*, atm	*T*, K	*P*, atm	*T*, K	*P*, atm	*T*, K	*P*, atm	*T*, K	*P*, atm
581.0	9.165×10^{-5}	584.0	9.429×10^{-5}	539.5	1.577×10^{-5}	537.5	1.499×10^{-5}	528.8	9.869×10^{-6}
564.0	4.805×10^{-5}	569.0	5.575×10^{-5}	535.6	1.320×10^{-5}	533.2	1.174×10^{-5}	524.2	7.884×10^{-6}
545.0	2.217×10^{-5}	555.0	3.024×10^{-5}	532.9	1.161×10^{-5}	529.9	1.005×10^{-5}	520.7	6.613×10^{-6}
578.0	8.526×10^{-5}	541.0	1.685×10^{-5}	530.3	1.025×10^{-5}	522.2	6.965×10^{-6}	517.0	5.473×10^{-6}
555.0	3.369×10^{-5}	527.0	8.723×10^{-6}	527.2	8.865×10^{-6}	517.7	5.597×10^{-6}	513.2	4.511×10^{-6}
542.0	1.841×10^{-5}	513.0	4.594×10^{-6}	521.1	6.538×10^{-6}	512.0	4.240×10^{-6}	508.9	3.649×10^{-6}
528.0	9.574×10^{-6}	578.0	8.561×10^{-5}	514.6	4.918×10^{-6}			502.9	2.666×10^{-6}
515.0	5.073×10^{-6}	564.0	4.741×10^{-5}	500.3	2.323×10^{-6}			497.8	2.019×10^{-6}
501.0	2.421×10^{-6}	549.0	2.538×10^{-5}						
487.0	1.188×10^{-6}	536.0	1.393×10^{-5}						
500.0	2.311×10^{-6}	537.0	1.428×10^{-5}						
514.0	4.643×10^{-6}	523.0	6.984×10^{-6}						
529.0	9.791×10^{-6}	509.0	3.496×10^{-6}						
545.0	2.122×10^{-5}	494.0	1.684×10^{-6}						
557.0	3.650×10^{-5}	513.0	4.518×10^{-6}						
571.0	6.335×10^{-5}	528.0	9.397×10^{-6}						
		559.0	3.771×10^{-5}						
		543.0	1.943×10^{-5}						
		572.0	6.812×10^{-5}						

Table 5. Cadmium—List of experimental temperature/pressure data—Continued

Lab. 5, Run 4		Lab. 6, Runs 1, 2, and 3†	
T, K	P, atm	T, K	P, atm
521.1	6.777×10^{-6}	—	—
516.1	5.307×10^{-6}	—	—
511.6	4.199×10^{-6}	—	—
506.9	3.319×10^{-6}	—	—
503.1	2.705×10^{-6}	—	—
495.2	1.780×10^{-6}	—	—

† Automatic data recording was used by this laboratory to obtain hundreds of temperature/pressure data points. The resultant data were treated by the cooperating laboratory and only the third law $\Delta H_{sub\ 298}$ were practical to submit. The third law $\Delta H_{sub\ 298}$ are listed in *Table 8*.

Table 6. Silver—List of experimental temperature/pressure data

Lab. 1, Run 1		Lab. 1, Run 2		Lab. 1, Run 3		Lab. 1, Run 4		Lab. 2, Run 1	
T, K	P, atm	T, K	P, atm	T, K	P, atm	T, K	P, atm	T, K	P, atm
1454.6	1.870×10^{-4}	1336.3	2.630×10^{-5}	1340.3	2.460×10^{-5}	1313.3	1.530×10^{-5}	1248.8	7.704×10^{-6}
1375.4	5.450×10^{-5}	1258.1	5.320×10^{-6}	1496.7	3.330×10^{-4}	1424.5	1.080×10^{-4}	1228.0	5.012×10^{-6}
1393.5	7.060×10^{-5}	1431.6	1.350×10^{-4}	1257.1	5.390×10^{-6}	1518.8	4.230×10^{-4}	1210.2	3.370×10^{-6}
1499.7	3.780×10^{-4}	1367.4	4.110×10^{-5}	1312.3	1.630×10^{-5}	1367.4	4.250×10^{-5}	1232.2	5.166×10^{-6}
1288.2	9.190×10^{-6}	1490.7	3.030×10^{-4}	1370.4	4.300×10^{-5}	1251.1	4.170×10^{-6}	1192.6	2.151×10^{-6}
1344.3	3.180×10^{-5}	1564.9	9.110×10^{-4}	1434.6	1.240×10^{-4}	1467.7	2.050×10^{-4}	1166.8	1.191×10^{-6}
1584.9	1.090×10^{-3}	1232.1	3.740×10^{-6}	1404.5	8.430×10^{-5}	1344.3	2.850×10^{-5}	1146.3	6.837×10^{-7}
1423.5	1.160×10^{-4}	1302.2	1.360×10^{-5}	1469.7	2.110×10^{-4}	1500.7	3.280×10^{-4}	1130.4	4.257×10^{-7}
1269.2	7.450×10^{-6}	1394.5	6.600×10^{-5}	1546.8	6.380×10^{-4}	1401.5	7.700×10^{-5}	1112.2	2.534×10^{-7}
1323.3	1.890×10^{-5}	1521.8	5.050×10^{-4}	1242.1	4.370×10^{-6}	1439.6	1.280×10^{-4}	1092.4	1.469×10^{-7}
1521.8	4.940×10^{-4}	1283.2	9.720×10^{-6}	1288.2	1.080×10^{-5}	1284.2	9.380×10^{-6}	1066.6	7.173×10^{-8}
1242.1	3.660×10^{-6}							1044.6	3.670×10^{-8}
								1021.0	1.745×10^{-8}
								993.6	6.117×10^{-9}
								971.3	2.690×10^{-9}
								947.9	1.200×10^{-9}
								909.2	2.878×10^{-10}
								885.8	1.080×10^{-10}
								854.0	1.825×10^{-11}

Table 6. Silver—List of experimental temperature/pressure data—Continued

Lab. 2, Run 2		Lab. 3, Run 1		Lab. 3, Run 2		Lab. 3, Run 3		Lab. 4, Run 1	
T, K	P, atm	T, K	P, atm	T, K	P, atm	T, K	P, atm	T, K	P, atm
1072.6	1.369×10^{-7}	1467.7	2.329×10^{-4}	1515.8	4.816×10^{-4}	1516.8	3.855×10^{-4}	1336.3	2.130×10^{-5}
1194.6	2.988×10^{-6}	1431.6	1.474×10^{-4}	1479.7	2.776×10^{-4}	1462.6	1.855×10^{-4}	1383.4	4.790×10^{-5}
1193.1	3.015×10^{-6}	1503.7	4.132×10^{-4}	1451.6	1.895×10^{-4}	1479.7	2.632×10^{-4}	1376.4	4.260×10^{-5}
1284.8	1.571×10^{-5}	1463.6	2.408×10^{-4}	1428.6	1.224×10^{-4}	1430.6	1.118×10^{-4}	1384.4	4.930×10^{-5}
1258.0	8.829×10^{-6}	1484.7	3.171×10^{-4}	1400.5	6.842×10^{-5}	1386.4	4.868×10^{-5}	1424.5	9.390×10^{-5}
1237.9	5.687×10^{-6}	1433.6	1.329×10^{-4}	1371.4	4.342×10^{-5}	1399.5	6.316×10^{-5}	1460.6	1.691×10^{-4}
1207.4	2.619×10^{-6}	1525.8	6.000×10^{-4}	1530.8	5.816×10^{-4}	1440.6	1.461×10^{-4}	1492.7	2.788×10^{-4}
1216.4	3.415×10^{-6}	1400.5	8.816×10^{-5}	1496.7	3.395×10^{-4}	1495.7	3.132×10^{-4}	1545.8	5.915×10^{-4}
1225.7	3.910×10^{-6}	1452.6	2.132×10^{-4}	1472.7	2.421×10^{-4}	1419.5	9.079×10^{-5}	1584.9	1.024×10^{-3}
1185.8	1.749×10^{-6}	1373.4	4.474×10^{-5}	1453.6	1.882×10^{-4}			1518.8	4.204×10^{-4}
1158.3	8.958×10^{-7}			1411.5	9.474×10^{-5}			1483.7	2.554×10^{-4}
1139.7	5.382×10^{-7}			1385.4	6.579×10^{-5}			1425.5	1.054×10^{-4}
1118.4	2.941×10^{-7}							1363.4	3.370×10^{-5}
1098.6	1.722×10^{-7}								
1077.6	9.573×10^{-8}								
1053.8	4.896×10^{-8}								
1052.5	4.433×10^{-8}								
1029.7	2.066×10^{-8}								
1003.4	9.351×10^{-9}								
981.6	4.561×10^{-9}								
959.3	1.786×10^{-9}								
944.4	1.092×10^{-9}								
921.9	4.708×10^{-10}								
920.7	4.232×10^{-10}								
921.4	4.377×10^{-10}								
898.5	1.721×10^{-10}								
877.5	7.171×10^{-11}								
856.2	3.346×10^{-11}								

Table 6. Silver—List of experimental temperature pressure data—Continued

Lab. 4, Run 2		Lab. 5, Run 1		Lab. 5, Run 2		Lab. 6, Run 1		Lab. 6, Run 2	
T, K	P, atm	T, K	P, atm	T, K	P, atm	T, K	P, atm	T, K	P, atm
1334.3	1.970×10^{-5}	1314.3	1.725×10^{-5}	1432.6	1.151×10^{-4}	1387.5	6.056×10^{-5}	1433.6	1.277×10^{-4}
1371.4	4.060×10^{-5}	1328.3	2.039×10^{-5}	1468.7	2.097×10^{-4}	1381.4	5.447×10^{-5}	1421.5	1.089×10^{-4}
1348.4	2.610×10^{-5}	1271.2	6.627×10^{-6}	1440.6	1.378×10^{-4}	1362.4	3.983×10^{-5}	1414.5	9.380×10^{-5}
1385.4	5.050×10^{-5}	1279.2	7.778×10^{-6}	1286.2	9.961×10^{-6}	1360.4	3.795×10^{-5}	1407.5	8.456×10^{-5}
1434.6	1.112×10^{-4}	1336.3	2.414×10^{-5}	1309.3	1.438×10^{-5}	1352.4	3.328×10^{-5}	1399.5	7.784×10^{-5}
1467.7	1.891×10^{-4}	1353.4	3.165×10^{-5}	1328.3	2.071×10^{-5}	1349.4	3.149×10^{-5}	1384.4	5.485×10^{-5}
1508.8	3.402×10^{-4}	1328.3	2.027×10^{-5}	1268.2	6.291×10^{-6}	1344.3	2.899×10^{-5}	1376.4	5.026×10^{-5}
1553.9	6.176×10^{-4}	1256.1	5.139×10^{-6}	1399.5	6.606×10^{-5}	1338.3	2.571×10^{-5}	1362.4	4.057×10^{-5}
1488.7	2.646×10^{-4}	1364.4	3.728×10^{-5}	1380.4	4.998×10^{-5}	1333.3	2.389×10^{-5}	1352.4	3.305×10^{-5}
1437.6	1.217×10^{-4}	1376.4	4.684×10^{-5}	1360.4	3.552×10^{-5}	1327.3	2.129×10^{-5}	1339.3	2.625×10^{-5}
1396.5	6.650×10^{-5}	1393.5	6.332×10^{-5}	1340.3	2.575×10^{-5}	1322.3	1.924×10^{-5}	1333.3	2.394×10^{-5}
1315.3	1.450×10^{-5}	1403.5	7.311×10^{-5}	1320.3	1.833×10^{-5}	1313.3	1.645×10^{-5}	1326.3	2.085×10^{-5}
		1413.5	8.630×10^{-5}	1494.7	2.976×10^{-4}	1304.2	1.356×10^{-5}	1321.3	1.902×10^{-5}
		1422.5	9.955×10^{-5}	1462.6	1.888×10^{-4}	1295.2	1.173×10^{-5}	1311.3	1.656×10^{-5}
		1429.6	1.137×10^{-4}	1437.6	1.304×10^{-4}	1281.2	8.794×10^{-6}	1289.2	1.026×10^{-5}
		1437.6	1.266×10^{-4}	1407.5	8.059×10^{-5}	1275.2	7.766×10^{-6}	1283.2	9.124×10^{-6}
		1447.6	1.503×10^{-4}	1389.5	6.127×10^{-5}	1260.1	6.098×10^{-6}	1278.2	8.302×10^{-6}
		1256.1	5.256×10^{-6}	1363.4	3.981×10^{-5}	1251.1	4.615×10^{-6}	1269.2	6.953×10^{-6}
		1438.6	1.323×10^{-4}	1421.5	1.003×10^{-4}	1243.1	3.910×10^{-6}	1256.1	5.238×10^{-6}
		1518.8	4.260×10^{-4}	1438.6	1.339×10^{-4}	1229.1	3.007×10^{-6}	1247.1	4.458×10^{-6}
		1480.7	2.547×10^{-4}			1224.0	2.813×10^{-6}	1237.1	3.700×10^{-6}
						1221.0	2.478×10^{-6}		

***Table 6.* Silver—List of experimental temperature/pressure data—Continued**

Lab. 7, Run 1		Lab. 7, Run 2		Lab. 7, Run 3		Lab. 7, Run 4		Lab. 7, Run 5	
T, K	P, atm	T, K	P, atm	T, K	P, atm	T, K	P, atm	T, K	P, atm
1208.1	2.395×10^{-6}	1209.1	2.446×10^{-6}	1158.2	6.935×10^{-7}	1153.7	6.331×10^{-7}	1157.8	6.944×10^{-7}
1203.3	2.144×10^{-6}	1201.9	2.067×10^{-6}	1152.0	5.901×10^{-7}	1147.7	5.378×10^{-7}	1148.6	5.494×10^{-7}
1191.3	1.615×10^{-6}	1195.1	1.769×10^{-6}	1146.4	5.119×10^{-7}	1142.5	4.692×10^{-7}	1140.0	4.403×10^{-7}
1184.1	1.364×10^{-6}	1189.6	1.553×10^{-6}	1139.5	4.290×10^{-7}	1137.5	4.097×10^{-7}		
1177.5	1.164×10^{-6}	1183.7	1.349×10^{-6}	1130.9	3.419×10^{-7}	1126.8	3.189×10^{-7}		
1165.9	8.768×10^{-7}	1176.0	1.119×10^{-6}	1122.7	2.762×10^{-7}	1118.6	2.536×10^{-7}		
1162.3	8.000×10^{-7}	1171.9	1.012×10^{-6}	1112.9	2.128×10^{-7}	1110.9	2.025×10^{-7}		
1158.3	7.258×10^{-7}	1159.3	7.445×10^{-7}	1102.1	1.574×10^{-7}	1104.1	1.665×10^{-7}		
1150.5	5.947×10^{-7}	1151.0	6.028×10^{-7}	1089.5	1.105×10^{-7}	1096.3	2.356×10^{-7}		
1142.0	4.815×10^{-7}	1140.9	4.674×10^{-7}						
1132.2	3.729×10^{-7}	1126.1	3.204×10^{-7}						

Lab. 7, Run 6		Lab. 7, Run 7		Lab. 7, Run 8		Lab. 8, Run 1		Lab. 8, Run1 ctd	
T, K	P, atm	T, K	P, atm	T, K	P, atm	T, K	P, atm	T, K	P, atm
1154.1	6.263×10^{-7}	1157.8	6.849×10^{-7}	1154.1	6.224×10^{-7}	1143.8	4.100×10^{-7}	1222.0	2.650×10^{-6}
1144.0	4.806×10^{-7}	1148.6	5.347×10^{-7}	1144.0	4.771×10^{-7}	1180.9	1.090×10^{-6}	1227.1	2.730×10^{-6}
1132.9	3.626×10^{-7}	1140.0	4.345×10^{-7}	1132.9	3.604×10^{-7}	1189.0	1.180×10^{-6}	1229.1	2.730×10^{-6}
						1209.0	1.970×10^{-6}	1254.1	5.140×10^{-6}

Lab. 8, Run 2		Lab. 9, Run 1		Lab. 9, Run 2	
T, K	P, atm	T, K	P, atm	T, K	P, atm
1206.0	1.990×10^{-6}	1254.1	1.173×10^{-5}	1284.2	6.189×10^{-6}
1215.0	3.130×10^{-6}	1314.3	2.709×10^{-5}		
1244.1	5.060×10^{-6}	1354.4	8.601×10^{-5}		
1279.2	7.960×10^{-6}	1374.4	8.330×10^{-5}		
1291.2	8.530×10^{-6}	1434.6	2.588×10^{-4}		
1318.3	1.009×10^{-5}				

Table 7. Cadmium—Summary of second law results

Lab. No.	Run No.	No. of points	Intercept A (see eq. 2) $cal \cdot mol^{-1} \cdot deg^{-1}$	Slope B, 2nd law $\Delta H_{sub\ 298}$ (see eq. 2) $cal \cdot mol^{-1}$	f_1 (see eq. 4)	f_2 (see eq. 5)	S_{fit} (see eq. 3)
1	1	10	−1.381	27158	3.24	1570	0.2387
	2	8	−1.176	27109	3.26	1580	0.1511
	3	8	−0.474	26817	3.37	1630	0.1370
	4	8	−1.119	27128	3.27	1610	0.2501
	5	8	−0.798	27130	3.23	1590	0.2498
	6	8	−0.512	26922	3.17	1570	0.2734
2	1	14	0.180	26347	2.48	1250	0.0916
	2	10	−0.628	26488	3.91	2030	0.0682
	3	16	2.247	26005	2.07	1010	0.3027
	4	8	2.886	25247	5.86	3170	0.1035
3	1	25	2.758	25659	1.46	640	0.2507
	2	17	−0.204	27020	2.06	930	0.3527
4	1	16	−0.378	26840	4.72	2530	0.0533
	2	19	−0.123	26734	5.01	2700	0.0792
5	1	8	0.300	26523	15.19	7970	0.0212
	2	6	−0.084	26727	24.07	12640	0.0131
	3	8	−0.794	27076	18.24	9370	0.0074
	4	6	−0.383	26858	24.38	12410	0.0063
2	5	12	4.302	24239	9.10	5080	0.1434
	6	10	4.434	23913	12.24	6980	0.1835
	7	15	6.000	23765	7.06	3680	0.2687

Table 8. Cadmium—Summary of third law results

Lab. No.	Run No.	No. of points	3rd law $\Delta H_{sub\ 298}$ $cal \cdot mol^{-1}$	f_3 (see eq. 9)	S'_{fit} (see eq. 8)
1	1	10	26480	0·316	136·6
	2	8	26528	0.354	102.8
	3	8	26584	0·354	66·4
	4	8	26568	0.354	129.7
	5	8	26729	0.354	121.9
	6	8	26665	0.354	121.3
2	1	14	26439	0.267	45.5
	2	10	26159	0.316	44.4
	6	10	26444	0.316	119.1
3	1	25	26906	0.200	192.4
	2	17	26925	0.243	156.7
4	1	16	26636	0.250	29.7
	2	19	26668	0.229	43.1
5	1	8	26681	0.354	10.9
	2	6	26683	0.408	6.3
	3	8	26668	0.354	9.2
	4	6	26663	0.408	4.6
6	1	> 100	26704	< 0.1	See remark for laboratory 6 in *Table 3*
	2	> 100	26722	< 0.1	
	3	> 100	26749	< 0.1	
2	3	16	27122	0.250	192.4
	4	8	26816	0.354	114.4
	5	12	26642	0.289	109.9
	7	15	26898	0.258	176.3

Table 9. Silver—Summary of second law results.

Lab. No.	Run No.	No. of points	Intercept A (see eq. 2) $cal \cdot mol^{-1} \cdot deg^{-1}$	Slope B, 2nd law $\Delta H_{sub\,298}$ (see eq. 2) $cal \cdot mol^{-1}$	f_1 (see eq. 4)	f_2 (see eq. 5)	S_{fit} (see eq.3)
1	1	12	−0.922	69361	3.95	5460	0.1531
	2	11	−0.585	68842	4.00	5480	0.1336
	3	11	0.245	67817	4.37	5980	0.1063
	4	11	−0.516	68981	4.95	6850	0.0918
2	1	19	−2.432	69926	1.96	2070	0.1456
	2	28	−1.697	69080	1.56	1640	0.2939
4	1	13	−1.733	70958	5.52	7940	0.573
	2	12	−0.635	69412	5.82	8240	0.720
5	1	21	−0.194	68562	4.10	5610	0.0604
	2	20	−0.017	68295	4.92	6800	0.0602
6	1	22	−0.386	68678	5.41	7050	0.0425
	2	21	−0.432	68723	4.88	6490	0.0464
7	1	11	−0.444	68155	15.05	17600	0.0041
	2	11	−0.175	67840	13.97	16380	0.0067
	3	9	−0.430	68246	16.94	19100	0.0064
	4	9	−0.870	68705	19.61	22080	0.0226
	5	3	−0.806	68647	91.36	104950	0.0011
	6	3	−0.608	68444	76.33	87290	0.0110
	7	3	−0.719	68588	91.36	104950	0.0232
	8	3	−0.592	68442	76.33	87290	0.0216
3	1	10	−3.730	73169	10.44	15150	0.1485
	2	12	−2.560	71675	8.48	12280	0.1196
	3	9	−3.095	72829	11.66	16860	0.1384
8	1	8	1.973	65813	13.02	15690	0.1112
	2	6	16.483	47547	12.65	15900	0.3319
9	1	5	−0.143	66865	9.92	13320	0.4136

Table 10. Silver—Summary of third law results

Lab. No.	Run No.	No. of points	3rd law $\Delta H_{sub\,298}$ cal · mol^{-1}	f_3 (see eq. 9)	S'_{fit} (see eq. 8)
1	1	12	68076	0.289	219.4
	2	11	68034	0.302	185.7
	3	11	68155	0.302	137.3
	4	11	68263	0.302	121.4
2	1	19	67308	0.229	328.6
	2	28	67257	0.189	390.2
3	1	10	67747	0.316	259.8
	2	12	67963	0.289	206.9
	3	9	68347	0.333	229.2
4	1	13	68455	0.277	154.5
	2	12	68510	0.289	105.5
5	1	21	68295	0.218	80.4
	2	20	68272	0.224	79.5
6	1	22	68173	0.213	55.7
	2	21	68146	0.218	66.9
7	1	11	67636	0.302	11.9
	2	11	67634	0.302	8.8
	3	9	67761	0.333	12.0
	4	9	67726	0.333	29.5
	5	3	67620	0.577	7.2
	6	3	67749	0.577	11.0
	7	3	67762	0.577	20.0
	8	3	67764	0.577	12.0
8	1	8	68194	0.354	142.2
	2	6	68299	0.408	835.8
9	1	5	66309	0.447	480.7
	2	1	69240	1.000	-

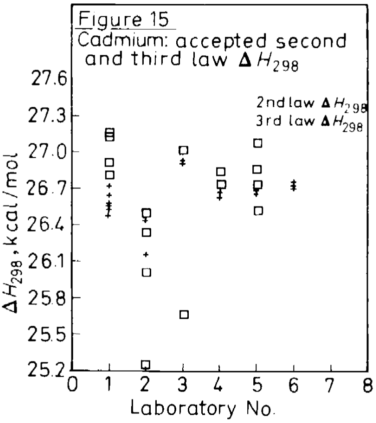
also made a preliminary test to detect laboratories that exhibited excessive scatter of points about the fitted curves (see below).

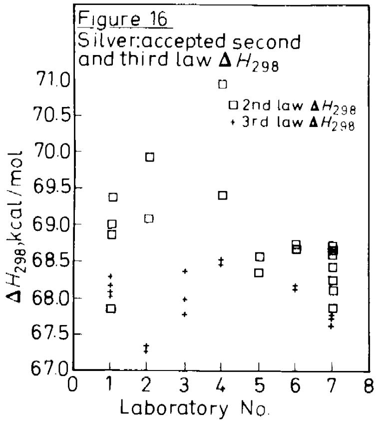
The authors then examined the results and made tentative decisions regarding the data to be excluded from the weighted averages and the estimated uncertainties*. The detailed criteria used in making these tentative decisions are given in the Appendix. Summaries of the accepted second and third law results are presented in *Figures 15* and *16*.

* A preliminary examination of the cadmium data, as well as an examination of the reports from the laboratories, have indicated the run 5, 6 and 7 second law results and the run 3, 4, 5 and 7 third law results from laboratory 2 should not be pooled with results from the other laboratories. The results from laboratory 2, however, are particularly valuable in supplying information regarding usable limits for orifice areas ($a < 1 \times 10^{-2}$ cm^2).

A preliminary examination of the silver data, as well as an examination of the uncertainties of the data, indicated that the second law results from laboratory 3 and the second and third law results from laboratories 8 and 9 should not be pooled with the results from the other laboratories.

A further discussion of results from the above laboratories is given in the Appendix.





The second OMNITAB program was next run to determine (1) the weighted average values of the second and third law heats of sublimation, (2) the uncertainties of the heats, and (3) the uncertainties expected for a typical in-control laboratory's measurements (see Appendix). In the second OMNITAB program the rejected data were not used for the calculation of the weighted averages and standard deviations, but were used in all other statistical tests. This procedure avoided distorting the overall results, but still allowed for further evaluation of all the data.

The statistical analyses for cadmium indicate the weighted average† and the *two* standard error limits of the *weighted averages* to be as follows:

$$A = 0.15 \pm 0.87 \text{ cal·mol}^{-1}\text{·deg}^{-1}$$

$$B = \text{2nd law } \Delta H_{\text{sub } 298} = 26610 \pm 380 \text{ cal·mol}^{-1}$$

$$\text{3rd law } \Delta H_{\text{sub } 298} = 26660 \pm 150 \text{ cal·mol}^{-1}$$

The A coefficient is essentially zero which indicates that the observed pressures and free energy functions are reasonably concordant. In the analyses it is tacitly assumed that the errors in the free energy functions are negligible. The second and third law $\Delta H_{\text{sub } 298}$ are observed to be in good agreement. We believe the third law $\Delta H_{\text{sub } 298}$ of 26660 cal mol^{-1} to be the preferred value.

A laboratory measuring a single temperature/pressure curve for cadmium may wish to compare its values with the weighted averages from this study. The total expected variance required for this comparison will be the sum of: (1) the between-curve component of variance, (2) the between-laboratory component of variance, (3) the variance of the weighted average. Assembling the numerical values corresponding to the components of variance in the above order we obtain for the single curve case:

† The results from six cooperating laboratories with 21 curves and over 200 temperature/pressure points were used to determine these weighted averages. The weighting procedure used, is given in the Appendix.

$$V(A) \qquad = 1.08 + 0.61 + 0.19 \qquad = 1.88$$

$$V(\text{2nd law}) = (16.3 + 12.7 + 3.6) \times 10^4 = 32.6 \times 10^4$$

$$V(\text{3rd law}) = (0.7 \quad + 3.2 \quad + 0.6) \times 10^4 = \quad 4.5 \times 10^4$$

The numerical values in the above variance equations have been derived using energy units of calories. The variance equations describe the typical uncertainties in the measurement of a single cadmium temperature/pressure curve. The equations are a summary of results for all accepted cadmium curves. The average temperature range for these curves is 120 K and the average number of points is thirteen.

The cadmium and silver data differ from the gold data[1] in that the between-curve components of variance are not realistically described by the products of the pooled standard deviations of fit ($\bar{S}_{\text{fit}}$) and the f factors (f_1, f_2 and f_3) which reflect the number and spread of $1/T$ values for the individual curves (see eqs 4 to 9 inclusive). *Tables 7* to *10* inclusive show a general lack of homogeneity of the S_{fit} values. The variations of the between-curve (within laboratory) A, B and third law values, however, are reasonably well behaved. The between-curve components of variance were therefore directly obtained from the analysis of variance[6] of the A, B and third law values.

The following limits for cadmium, which are equal to twice the square root of the above variances, can be used for the estimation of maximum allowable differences between the single curve results obtained by the 'typical' laboratory and the weighted averages. Approximately 95 per cent of the time, a *single curve* result obtained by the above described typical laboratory should fall within the following limits:

$$A$$

$$\text{2nd law } \Delta H_{\text{sub } 298} \quad = 26\,660 \pm 1140 \text{ cal}\cdot\text{mol}^{-1}$$

$$\text{3rd law } \Delta H_{\text{sub } 298} \quad = 26\,660 \pm 420 \text{ cal}\cdot\text{mol}^{-1}$$

Since the third law value is believed to be more accurate, we have replaced the second law weighted average by the third law weighted average, 26660 cal·mol^{-1}.

For silver, the weighted averages* and the *two* standard error limits of the *weighted averages* are as follows:

$$A = -0.79 \pm 0.58 \text{ cal}\cdot\text{mol}^{-1}\cdot\text{deg}^{-1}$$

$$B = \text{2nd law } \Delta H_{\text{sub } 298} = 68\,970 \pm 570 \text{ cal}\cdot\text{mol}^{-1}$$

$$\text{3rd law } \Delta H_{\text{sub } 298} = 68\,010 \pm 300 \text{ cal}\cdot\text{mol}^{-1}$$

A comparison of the two standard error limits with the weighted averages indicates some inconsistency in the second and third law results, i.e. the uncertainty limits do not quite allow an overlap of the second and third law heats. Furthermore, the value of the A coefficients cannot be assumed to be zero. The individual second and third law heats for each silver curve also

* The results from seven cooperating laboratories with 23 curves and over 250 temperature pressure points were used to determine these weighted averages.

indicate a consistent bias with 19 out of 20 accepted second law heats being higher than the corresponding third law heats (see *Tables* 9 and *10*). This problem has been examined in detail and it has been concluded that the higher second law heats are a result of the basic temperature/pressure data obtained from the cooperating laboratories, and are not a result of the treatment of the data. From a detailed analysis of possible error sources, it has been concluded that the silver second law results are most likely to be in error and that the third law results are essentially correct. A more detailed discussion of the problem is given in section 4.

For the silver *single curve* comparison with the weighted averages, the respective components of variance are as follows:

$$V(A) = 0.14 + 0.44 + 0.08 = 0.66$$

$$V(\text{2nd law}) = (25 + 40 + 8) \times 10^4 = 73 \times 10^4$$

$$V(\text{3rd law}) = (1.6 + 15.0 + 2.2) \times 10^4 = 19 \times 10^4$$

These single curve variances are a summary of results for all accepted silver curves. The average temperature range for these curves is 240 K and the average number of points is fifteen.

The following limits for silver, which are equal to twice the square root of the above variances, can be used for the estimation of maximum allowable differences between the single curve results obtained by the typical laboratory and the weighted averages. Approximately 95 per cent of the time, a *single curve* result obtained by the above described typical laboratory should fall within these limits:

$$A = -0.79 \pm 1.63 \text{ cal}\cdot\text{mol}^{-1}\cdot\text{deg}^{-1}$$

$$\text{2nd law } \Delta H_{\text{sub } 298} = 68\,010 \pm 1\,700 \text{ cal}\cdot\text{mol}^{-1}$$

$$\text{3rd law } \Delta H_{\text{sub } 298} = 68\,010 \pm 870 \text{ cal}\cdot\text{mol}^{-1}$$

Since the third law value is believed to be more accurate, we have replaced the second law weighted average by the third law weighted average, 68010 cal $\cdot$ mol^{-1}. The larger single curve uncertainties would, however, have easily overlapped the second and third law values.

An examination of the above cadmium and silver values of the components of variance for the typical single curve case is of considerable interest. For cadmium and silver, the between-laboratory components of variance are found to be an appreciable fraction of the total expected variance. Thus, a typical laboratory that measures $(n - 1)$ additional temperature/pressure curves will reduce only the between-curve variance by a factor of $1/n$, and will not affect the large between-laboratory component of variance.

Repetitive curve measurements within a single typical laboratory will not greatly diminish the overall uncertainties in the measured heats of sublimation. To paraphrase, we can say that a typical laboratory's ability to reproduce its own vapor pressure measurements exceeds its ability to reproduce other laboratories' measurements. This will be particularly true for measurements of the third law heat of sublimation.

4. DISCUSSION OF SILVER SECOND AND THIRD LAW RESULTS

Both the comparison of the standard error limits relative to the second and third law $\Delta H_{\text{sub}\,298}$ weighted averages, and the comparison of paired second and third law heats for individual pressure/temperature curves have indicated inconsistencies in the silver data. A more severe rejection of individual second law results would decrease the inconsistencies. Additional rejections were not felt to be justified since one of our primary goals was to evaluate 'typical' uncertainties of vapor pressure measurements made by experienced investigators. There is always a fundamental question of how much data to reject. For silver, it was felt that additional rejections would have unrealistically minimized the reported between-curve components of variance.

The differences in second and third law results are believed to be due to the basic temperature/pressure data submitted by the cooperating laboratories. A detailed inspection has shown that the calculational procedures and the OMNITAB computer programs have not artifically 'synthesized' the differences. The individual curve second and third law heats are found to be in good agreement with the results calculated by the cooperating laboratories. The cooperating laboratories results also showed the same trend of higher second law heats. To check the calculational procedures and programs further, temperature/pressure data from eleven randomly selected literature reports on silver were used to calculate second and third law heats. The results showed no trends of high individual second law heats. The overall average second and third law heats were 67 800 and 68 000 cal mol^{-1}, respectively.

Visits and discussions with several of the cooperating laboratories have not positively identified the source of the inconsistency. It appears most likely that the observed second law heats are too high and that this is caused by systematic errors in the measurement of the sample temperatures.

It seems very unlikely that the third law heat can be 900 cal $\cdot$ mol^{-1} too low. For this to occur it would be necessary that either (1) the free energy functions are in error by 0.6 cal $\cdot$ $\text{mol}^{-1} \cdot \text{deg}^{-1}$, or (2) the measured pressures were 35 per cent too high, or (3) the measured temperatures were 20 K too low, or (4) some combination of factors (1), (2) and (3) should prevail. It does not seem reasonable that either the free energy functions or the measured pressures can contain such large errors. Furthermore, the direct observation of melting-freezing point halts by laboratory 1 would seem to eliminate the possibility that the temperature scale was 20 K too low.

Let us now consider trended errors that could affect the second law heat by 900 cal $\cdot$ mol^{-1}. By trended errors we mean errors that either gradually increase or gradually decrease from one end of the measurement range to the other. Analysis of equation (2) shows that, for an average 240 K temperature interval, the factors in the left hand side of the equation would have to have a trended error of about 0.1 cal $\cdot$ $\text{mol}^{-1} \cdot \text{deg}^{-1}$. Such a trended error in free energy functions is highly unlikely since extremely large errors in heat capacity data would be required. A trended pressure error of five per cent would be equivalent to the 0.1 cal $\cdot$ $\text{mol}^{-1} \cdot \text{deg}^{-1}$; such an error is possible, but does not seem likely.

The formation of a dimer or higher polymer does not appear to offer an explanation for a trended pressure error. The literature[7–9] shows the total polymer concentration to be less than 0.5 per cent of the monomer at 1 600 K, the highest temperature used by the cooperating laboratories.

The most *probable* explanation of the 900 cal · mol^{-1} difference in second and third law results would appear to be a trended error in the measurement of temperatures. A trended error of 4 K over the 240 K interval, or 1 K out of 60 K, would be required. At temperatures of 800–1 600 K, gradients of 5–15 K within a Knudsen cell are far from uncommon. A shift of temperature gradients within the cell could account for an average trended temperature error of 4 K. The spectral and total emissivities of silver[10] are both less than 0.1. This could help exaggerate temperature gradients within the cell and could lead to temperature measurement errors and high second law heats.

After consideration of all the above factors, we favor the use of the third law $\Delta H_{sub\,298}$ value of 68 010 cal · mol^{-1}.

5. COMPARISON OF RESULTS FROM CADMIUM, SILVER AND GOLD

A comparison of results for the cadmium, silver and gold[1] standard reference materials allows for a partial examination of vapor pressure uncertainties as a function of the temperature at which measurements are made. The future certification of platinum and tungsten should allow a further examination of temperature effects. A summary of the currently available $\Delta H_{sub\,298}$ uncertainties is given in *Table 11*.

Table 11

Material	Average temp., K	$\Delta H_{sub\,298}$, cal · mol^{-1}	Two standard deviation limits of $\Delta H_{sub\,298}$			
			Weighted average		Typical single curve	
			2nd law	3rd law	2nd law	3rd law
Cadmium	500	26 660	±420	±150	±1 140	±380
Silver	1 300	68 010	±870	±300	±1 700	±570
Gold	1 700	87 720	±1 350	±420	±3 700	±1 000

As would be expected, the larger uncertainties in the second and third law heats are associated with the higher temperature measurements. It can also be noted that the uncertainties are roughly proportional to the size of the heat sublimation. The uncertainties for the second law results are appreciably larger than for the third law results.

By virtue of equation (1), an uncertainty in $\Delta H_{sub\,298}$ will cause a corresponding uncertainty in our knowledge of the relationship between temperature and pressure. *Table 12* shows the temperature/log pressure uncertainties resulting from a change in plus or minus two standard deviations in the third law $\Delta H_{sub\,298}$. The uncertainties in temperature are calculated assuming a fixed pressure, and the uncertainties in log pressure are calculated assuming a fixed temperature.

Table 12

Material	Average temp., K	$\Delta H_{sub\,298}$ cal·mol^{-1}	Two standard deviation limits corresponding to 3rd law $\Delta H_{sub\,298}$ uncertainties			
			Weighted average		Typical single curve	
			ΔT	or $\Delta \log P$	ΔT	or $\Delta \log P$
Cadmium	500	26 660	±3	±0.069	±7	±0.185
Silver	1 300	68 010	±7	±0.049	±20	±0.146
Gold	1 700	87 720	±9	±0.053	±30	±0.173

Inspection of the above $\Delta \log P$ values shows the values to be relatively independent of temperature. A consideration of the factors involved in the measurement of vapor pressure/temperature curves that would seem to indicate that the relative constancy of the $\Delta \log P$ values may be due to the combined change with temperature of (1) the uncertainties of temperature measurement and (2) the relative magnitudes of the various heats of sublimation.

Finally, it should be reiterated that the large uncertainty of a typical single curve measurement is primarily due to the large between-laboratory uncertainty. A single laboratory's evaluation of error may be greatly underestimated if systematic between-laboratory errors are not considered. The diligent use of vapor pressure standard reference materials should help in the detection and elimination of such systematic errors.

List of cooperating laboratories for cadmium

Bureau of Mines, A. Landsberg
Douglas Advanced 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

List of cooperating laboratories for silver

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 der Universität Wien (Austria), A. Neckel
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
National Chemical Laboratory (India), V. V. Dadape
Sandia Corporation, D. A. Northrop
Universita Degli Studi di Roma (Italy), V. Piacente and G. De Maria

The authors are greatly indebted to the above listed cooperating laboratories for their vapor pressure measurements. D. L. Hildenbrand of Douglas Advanced Research Laboratories should be given particular credit for the original impetus in the establishment of the vapor pressure standard reference materials. The authors also wish to acknowledge aid rĕceived from the following NBS staff members. E. R. Plante has contributed freely to discussions dealing with thermodynamic aspects of the analysis, and J. J. Diamond has made an extensive literature survey of the vapor pressure measurements on cadmium and silver. F. L. McCrackin has aided in the use of his computerized GRAPH routine.

6. APPENDIX

This Appendix gives additional details of the statistical analyses which were necessary for the evaluation of the cadmium and silver vapor pressure data. The two-part statistical analysis has been made in terms of two OMNITAB programs. An outline of the two parts is as follows:

6.1

1. The temperature/pressure data for each run were given least-squares treatments described below to obtain the second and third law values and the associated uncertainties. In all fits each data point was given unit weight.

(a) For the second law equation, the least-squares model was $Y = A + BX$, where $X = 1/T$. The standard deviation of the fit (S_{fit}) was obtained using the OMNITAB 'FIT' command. For the least-squares fitting of the N data points to a straight line curve,

$$S_{\text{fit}} = \sqrt{\left(\sum_i (Y_i - Y_{\text{fit}})^2\right)/(N-2)} \tag{3}$$

The standard deviations of the coefficients (S_A and S_B) can be expressed in terms of the standard deviation of the fit (S_{fit}):

$$S_A = f_1 \cdot S_{\text{fit}} \tag{4}$$

$$S_B = f_2 \cdot S_{\text{fit}} \tag{5}$$

where

$$f_1 = \left[\frac{1}{N} + \frac{(\bar{X})^2}{\sum_i (X_i - \bar{X})^2}\right]^{\frac{1}{2}} \tag{6}$$

$$f_2 = \left[\frac{1}{\sum_i (X_i - \bar{X})^2}\right]^{\frac{1}{2}} \qquad (7)$$

The f_1 and f_2 values provide a very convenient quantitative description of the number and spread of the $X(= 1/T)$ values. The f_1 and f_2 are independent of the measured Y_i values.

(b) The third law equation was also treated by least-squares. Here one obtains a single coefficient, C (the average of the individual $\Delta H_{\text{sub } 298}$ values), the standard deviation of the coefficient (Sc), and the standard deviation of the individual $\Delta H_{\text{sub } 298}$ values (S'_{fit}). For the third law case, it can be shown that:

$$S_C = f_3 \cdot S'_{\text{fit}} \qquad (8)$$

where

$$f_3 = 1/\sqrt{(\text{No. of points})} \qquad (9)$$

It can be noted that equation (8) has the same form as equations (4) and (5). The same general computational treatment was therefore used for both the second and third law results.

(c) The cadmium and silver results for the second and third law least-square fits are given in *Tables 7* to *10* inclusive.

2. The authors next examined all results in terms of criteria (i) to (v), listed below.

(i) The chi-square test. Comparisons were made of S_{fit} values from all curves.

(1) A tentative pooled $\tilde{S}_{\text{fit}}$ was first calculated from the individual S_{fit} values from all curves*.

(2) Each individual S_{fit} was compared to the pooled $\tilde{S}_{\text{fit}}$ using the approximate test:

$$\tilde{S}_{\text{fit}} \sqrt{\left(\frac{\chi^2_{\nu, 0\cdot025}}{\nu}\right)} \leqslant S_{\text{fit}} \leqslant \tilde{S}_{\text{fit}} \sqrt{\left(\frac{\chi^2_{\nu, 0\cdot975}}{\nu}\right)}$$

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* A special pooling procedure for standard deviations was used throughout this study. An example of the pooling procedure is as follows:

$$\text{pooled } S_{\text{fit}} = \sum_i \alpha_i S_{\text{fit}_i} / \sum_i \beta_i$$

where the sum is over the i curves and

$$\alpha_i = 2\nu_i + 1/(2 + 3\nu_i)$$

$$\beta_i = 2\nu_i - \tfrac{1}{2} + 2/(3 + 5\nu_i)$$

and ν_i = number of degrees of freedom. For a normal distribution, this pooling procedure for standard deviations will give results comparable to those obtained by the usual procedure of pooling variances. This procedure, however, has the advantage of being less sensitive to distortion by outlier values. The authors wish to thank B. L. Joiner of the National Bureau of Standards for the derivation of this pooling formula.

where χ^2 is the 0.025 or the 0.975 percentile of the chi-square distribution with ν degrees of freedom. A laboratory showing several curves for which the values of S_{fit} fell outside these two limits was noted for further evaluation.
(ii) The between-curve (within-laboratory) differences for both the second and third law results.
(iii) The overall differences for results from the different laboratories.
(iv) The possible drift of results with respect to time.
(v) The laboratory's experimental procedures.

3. Rejection of any laboratory's results was based on consideration of criteria (i) to (v). For cadmium, the run 5, 6 and 7 second law results and the run 3, 4, 5 and 7 third law results of laboratory 2 were not used in further calculations of averages and pooled standard deviations. The second law results for runs 5, 6 and 7 were not used due to the runs' small temperature intervals, and to minor difficulties in points (ii) to (v). Laboratory 2 has made a total of seven runs investigating the effect of orifice area (1.69×10^{-3} to 1.24×10^{-1} cm^2) and has contributed to our knowledge regarding the usable upper limits for orifice areas for cadmium. A consequence of this knowledge is that the cadmium third law results for the large orifice runs could not be used in our pooled results.

For silver, the results from laboratory 8 were not used because of difficulties in criteria (i) to (iii) and (v). The results from laboratory 9 were not used because of problems in criteria (i) to (iii).

Some laboratories did not randomly vary their temperatures during the measurement of the temperature/pressure curves. The S_{fit} values for these laboratories tended to be abnormally small. For this reason, the S_{fit} values of laboratories 3 (run 1) and 5 for cadmium, and of laboratories 6 and 7 for silver, were not used in the pooled S_{fit}. All other values from these laboratories were used in the further calculations.

6.2

1. In the second OMNITAB program, a comparison was made of runs within each laboratory. This comparison was made in terms of both the intercept A and the slope B for the curve fitted to each run, and in terms of the average third law heat derived from each run. Using the F test, the variance of the A values between curves within each laboratory was compared to the estimate of this variance derived from the pooled $\bar{S}_{\mathrm{fit}}$. The B and the third law heat values were similarly treated.

2. A comparison was made of laboratories with each other. First a pooled value was obtained for the between-curves (within-laboratories) standard deviation for each of the three parameters A, B and third law heat; an average value (for each of the three parameters) was also computed. Then, using Student's t test, the deviation of the average value of each laboratory from the overall weighted average was compared to the pooled standard deviation between curves (within laboratories). In this way, detailed information was obtained on the variability between laboratories in terms of the deviation of each individual laboratory from the consensus value.

3. An analysis of variance was made[6] for each of the three parameters, A, B and third law heat, using the estimated values of these parameters accepted after application of the first OMNITAB program. The ultimate purpose of the analysis was to estimate the components of the within- and the between-laboratory variance. An analysis of variance indicated the between-laboratory components of variance to be significantly greater than zero. The calculation of components of variance for this situation, where the number of curves is not the same for all laboratories, has been discussed elsewhere by the authors[11].

4. Overall weighted average (A, B and third law heat) values and the associated variances were determined. Since the laboratories did not submit the same number of runs, the overall weighted averages are dependent on the specific weighting procedure used. Statistically, a proper weighting procedure would be one that minimizes the variance of the weighted average. The weighting factors obtained by this procedure are functions of the ratio of the between- to within-laboratory components of variance. Denoting the ratio for A by ρ, it can be shown[11] that laboratory i with n_i curves has the weighting factor:

$$W_i = n_i/(1 + n_i\rho)$$

The value of ρ can be estimated from the results of the analysis of variance[11]. The weighted average $\tilde{A}$ will be:

$$\tilde{A} = \sum_i W_i\bar{A}_i/\sum_i W_i$$

where $\bar{A}_i$ is the average A value for laboratory i.
Using this procedure, the variance of $\tilde{A}$ will be smaller than for any other weighting procedure, and its approximate value will be:

$$V(\tilde{A}) = \frac{\text{'}A\text{' component of within-lab. variance}^{12}}{\sum_i W_i}$$

The values for the B and the third law heat were evaluated in an analogous manner using the ρ and n_i values corresponding to these parameters.

Two extreme cases for the weighting factor deserve special attention. For the situation where the ratio ρ of the between- to within-laboratory components of variance is large with respect to unity, essentially equal weight is given to each laboratory. For the situation where the ratio ρ is close to zero, each curve is given essentially equal weight. The cadmium and silver ρ values for A, B and the third law heat which we obtained from the analysis of variance are 0.568, 0.780 and 4.575, and 3.137, 1.590 and 9.546, respectively.

5. Finally, the components of variance were assembled from the analysis of variance to estimate the uncertainties for the pooled and single curve values.

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