

Thermodynamic Properties of Synthetic Sapphires ($\alpha\text{-Al}_2\text{O}_3$), Standard Reference Material 720 and the Effect of Temperature-Scale Differences on Thermodynamic Properties

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Comparison of the National Institute of Standards and Technology's Standard Reference Material 720 certificate values for heat capacity with those obtained from recent experimental determinations indicated the possibility of a systematic error in the certificate values. Selected experimental determinations of enthalpy increments and heat capacities were fitted in order to obtain a representation of the thermodynamic properties of $\alpha\text{-Al}_2\text{O}_3$, a sample of which is the standard reference material (SRM720) for calibration of some types of calorimeters. The fitted equation and calculated values of the heat capacity, the relative enthalpy, and the entropy are given. The new values are more accurate and result from a better representation of the experimental values than did the 1982 SRM720 certificate values. Additionally, the general problem of the effect of changes in practical temperature scales on thermodynamic properties is briefly discussed, using the results for $\alpha\text{-Al}_2\text{O}_3$. A recent report from the IUPAC Commission on Thermodynamics gave a method for the conversion of thermodynamic properties for changes in practical temperature scale. The IUPAC method is shown to be not generally correct. A better method for estimation of these changes is given.

Keywords: aluminum oxide; enthalpy; heat capacity; standard reference material; temperature scale; thermodynamic.

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1. Introduction

In order to retain a high degree of quality, the values assigned to a Standard Reference Material (SRM) require periodic re-evaluation. SRM720 is synthetic sapphire, $\alpha\text{-Al}_2\text{O}_3$, and is "intended for use in calibrating or checking calorimeters used to measure either enthalpy or heat capacity within the range of 10 to 2250 K."¹

The enthalpy and heat-capacity values given in the SRM720 Certificate were obtained entirely from NIST measurements. The SRM720 values from 8.6 to 273.15 K were obtained from three empirical functions piecewise fitted to experimentally determined heat-capacity values.² These heat-capacity values were measured by Chang by means of an adiabatic heat-capacity calorimeter.³ The SRM720 values for temperatures greater than 273.15 K were obtained from an empirical function fitted to enthalpy increments from 150 K to 2257 K.²

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The enthalpy increments for temperatures greater than 323 K were experimentally determined values.^{2,4} The enthalpy increments for lower temperatures were taken from the fitted adiabatic heat-capacity measurements.²

Recent experimental evaluations of the heat capacity of SRM720 have appeared in the literature.^{5,6} They are for temperatures that correspond to part of the temperature region spanned by the enthalpy-increment measurements that had been used for the assignment of heat capacity and enthalpy values to SRM720. The comparison of the new heat-capacity measurements to the SRM720 values in the two most recent studies suggested a systematic error in the SRM720 heat-capacity values. For example, Fig. 7 of Ref. 5 showed the differences of experimental values from the SRM720 values. These differences implied that the heat-capacity values given for SRM720 were approximately 0.1 to 0.2 percent smaller than the values determined by means of the three different adiabatic heat-capacity calorimeters of Refs. 5–7 for the temperature range of 300 to 500 K. Figure 6 of Ref. 4 also showed the SRM720 heat-capacity values to be, on average, smaller than the earlier heat-capacity determinations of Martin and Snowdon,⁸ of Grönvold,⁹ and of West and Ginnings¹⁰ in the temperature range of 350 to 550 K, with the results of Grönvold showing greater imprecision than the other heat-capacity measurements. Those two figures, showing the difference of six different sets of heat-capacity results from the SRM720 values, suggested the possibility of a small systematic error in the SRM720 values. Whether this error was experimental, an artifact of the fitting method, or if it even existed at all was not definitely answered by the two figures. As part of NIST's commitment to establishing the best possible values for its SRMs, the thermodynamic properties of synthetic sapphire are re-examined here with the intention of eliminating the concern raised by the comparison of experiment and SRM values shown in Ref. 5.

2. Representation of Experimental Results

Because it was not clear whether the differences between the experimental heat-capacity values and the SRM720 values were due to experimental error or were due to an artifact of the fitting method, all of the experimental results given in Refs. 2–7, 9, 10 were fitted with a cubic-spline method described previously.¹¹ This method allowed the simultaneous fitting of heat-capacity measurements and enthalpy-increment measurements, the two types of measurements of interest here. Subsequent evaluation, discussed below, reduced the number of data sets included in the representation and allowed deductions as to the accuracies of the different experimental studies. All of the considered references involved measurements for either SRM720 samples or the Calorimetry Conference sample of aluminum oxide. Ditmars and Douglas⁴ found the Calorimetry Conference sample to be "calorimetrically indistinguishable" from the SRM720 samples. All temperatures were converted

to the International Temperature Scale of 1990, ITS-90.^{12,13}

Briefly, the cubic spline is fitted to a function $f(T)$, where:

$$f(T) = \{T \cdot (C_{p,m}^{\circ} / C_p^{\circ})^{-1/3} - bT\} / T^{\circ} \quad (1)$$

and where T is temperature, T° is 1 K, $C_{p,m}^{\circ}$ is the molar heat capacity, C_p° is 1.0 J·K⁻¹·mol⁻¹ and b is arbitrarily chosen to be 0.2 for the present case. The function $f(T)$ of Eq. (1) is fitted with a cubic spline using polynomials of the form:

$$f(T) = a_i(T - T_i)^3 + b_i(T - T_i)^2 + c_i(T - T_i) + d_i, \quad (2)$$

where the subscript i refers to the polynomial that contains the specified value of T and spans the temperature range T_i to T_{i+1} . A particular (T_i, d_i) pair is referred to as a "knot." "Natural spline" end conditions (i.e. second derivative equal to 0) were imposed at the two end knots. (For the purpose of calculation: $T_{i+1} > T > T_i$). The calculated heat capacity is thus:

$$C_{p,m}^{\circ} / C_p^{\circ} = \left(\frac{T}{T^{\circ} f(T) + bT} \right)^3. \quad (3)$$

Eq. (3) was integrated numerically to obtain the enthalpy. The spline function $f(T)$ was fitted to the experimental values with a nonlinear least-squares program. The vector of residuals was calculated using Eq. (3) for the heat capacity or the numerical integration of Eq. (3) to obtain the enthalpy increments. Representation of the experimental results, over the full range of temperature, required 15 variable knots. In previous use of this fitting method,¹¹ the initial knot position, corresponding to $T_{i-1} = 0$ K, was assigned a value obtained from the Debye temperature and not varied in the least-squares procedure. In the current work, the initial knot position was treated as a variable knot and its value was determined from the nonlinear least-squares procedure. This procedure yielded an estimate of the Debye temperature of 990 K. The final knot positions are given in Table 1.

TABLE 1. Knot positions

T_i / K	d_i
0	46.3935
15	45.0727
30	40.7053
50	33.6265
70	28.1163
90	24.2467
135	18.6092
180	15.0860
255	11.3391
320	9.19794
400	7.31519
500	5.59568
700	3.15541
1200	-1.87757
2400	-19.4200

All of the experimental results were first fitted with square roots of the variances (herein s.r.v.) assigned to be 0.3 percent (variance assignment is used for calculation of weighting factors in the least-squares process¹⁴). Examination of the residuals obtained from this representation showed the results from Refs. 2, 3, 4, 7, and 10 all agreed in their regions of overlap, or points of connection, as the case may be, to better than 0.1 percent. Additionally, the results from Inaba⁶ also agreed with the results from this set of references, but with a somewhat greater imprecision. The experimental results from these six references were obtained with six different calorimeters. Of these calorimeters, four were adiabatic heat-capacity calorimeters; one of these was designed for temperatures less than 380 K,³ two were designed for temperatures greater than 300 K,^{7, 10} and the remaining heat-capacity calorimeter

was designed for both low and high temperature use.⁶ The remaining two calorimeters were enthalpy-increment calorimeters; one of the Bunsen type,⁴ the other an adiabatic receiving calorimeter.² All of the results not from these six references were removed from the data representation and the least-squares process was repeated with assignments of the s.r.v. that were more representative of the accuracies of the experiments. The values estimated for the s.r.v. are described below. Figure 1 shows the percent difference of the selected experimental results from the fitted equation. Also shown in Fig. 1 is the difference of the SRM720 heat-capacity values from the fitted equation.

The agreement of the adiabatic heat-capacity calorimeter results from Refs. 3, 6, 7, 10 with the Bunsen-type ice calorimeter,⁴ as shown in Fig. 1, was significant

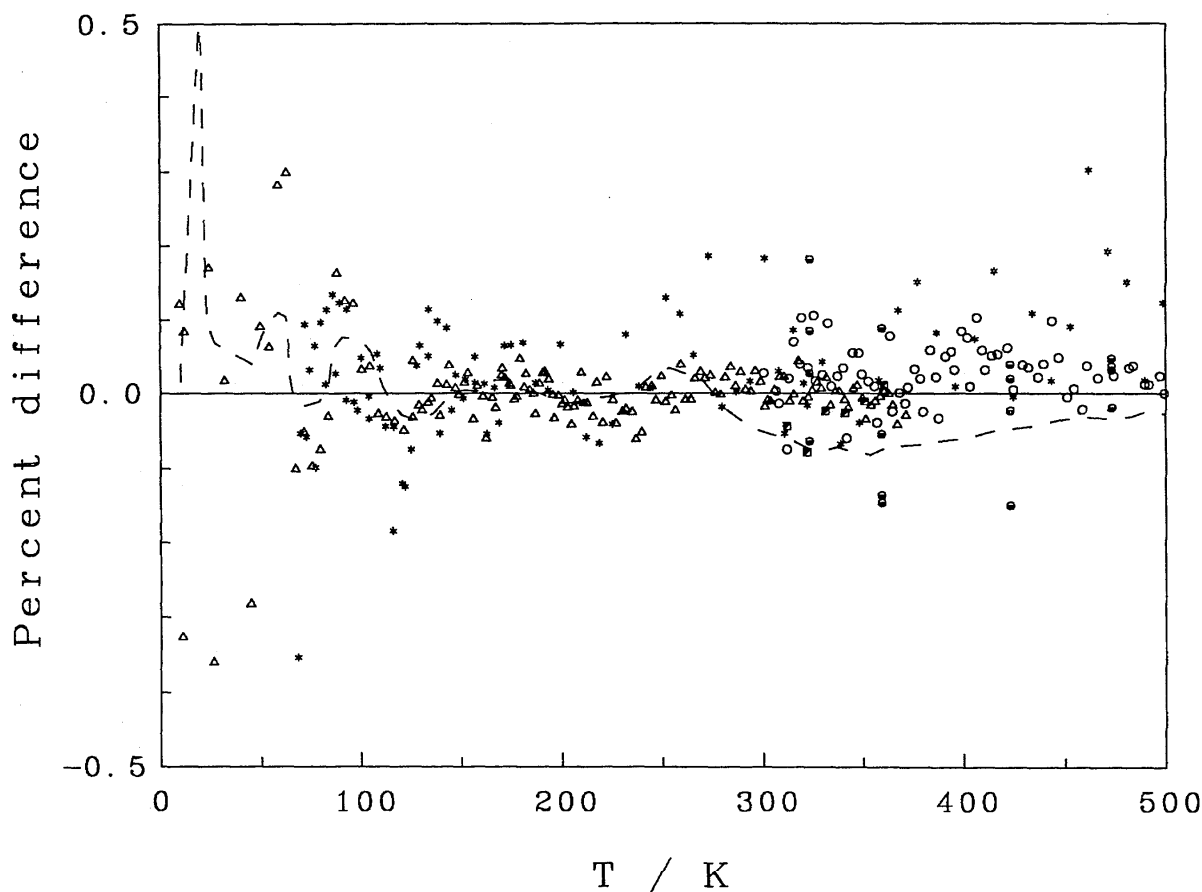


FIG. 1a. Percent difference of experimental results from fitted equation for temperatures of 10 to 500 K. The symbols are : O, Andrews *et al.*;⁷ Δ , Chang;³ *, Inaba;⁶ \bullet , Ditmars and Douglas;⁴ \blacksquare , West and Ginnings.¹⁰ The dashed line is the difference of the SRM720 values for heat capacity from the fitted equation.

for the following reason. Unaccounted apparent heat loss in the adiabatic heat-capacity calorimeters (an unaccounted non-adiabatic behavior of the calorimeter) results in an observed value that is greater than the actual value, whereas unaccounted heat loss in the Bunsen-type enthalpy-increment calorimeter results in an observed enthalpy increment that is smaller than the actual value. This means that if there is a significant unaccounted heat loss in either of these two types of calorimeter, or if there is a significant unaccounted heat loss in both of these two types of calorimeter, the residuals from the two types of calorimeters will not show an overlap, but instead a divergence, in the residual plot. (Some comments from reviewers regarding this point are of interest and are discussed in Appendix 1.) The chosen fitted results do overlap within their respective precisions.

The s.r.v. assigned to the heat-capacity results of Andrews *et al.*⁷ and of Inaba⁶ was 0.3 percent for all temperatures above 80 K. As seen in Fig. 1, the average deviation of both of these sets of results was slightly positive, indicating a very small systematic difference from the other results. The s.r.v. assigned to these results was larger than the precision so that the small systematic differences would not unduly affect the final representation. The s.r.v. assigned to the heat-capacity results from Chang³ was 0.1 percent for all temperatures above 100 K, 0.3 percent for $75 \text{ K} < T < 100 \text{ K}$, 0.5 percent for $40 \text{ K} < T < 75 \text{ K}$, 1 percent for $24 \text{ K} < T < 40 \text{ K}$ and 3 percent for $T < 24 \text{ K}$. The increasing s.r.v. at low temperatures resulted, in part, from the very small heat capacity of aluminum oxide for these temperatures. The heat-capacity results from West and Ginnings¹⁰ were assigned

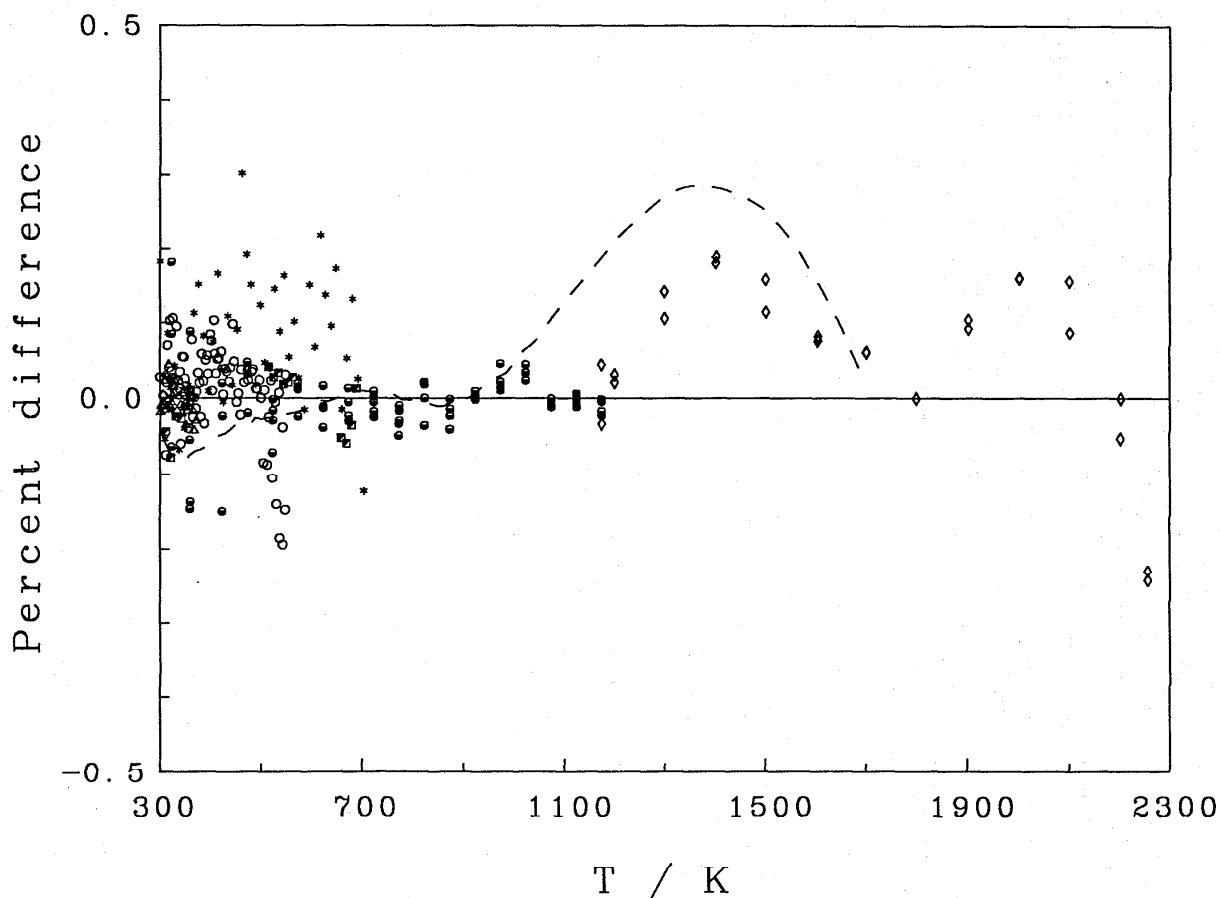


Fig. 1b. Percent difference of experimental results from fitted equation for temperatures of 300 to 2250 K. The symbols are: \circ , Andrews *et al.*⁷; \triangle , Chang³; $*$, Inaba⁶; \bullet , Ditmars and Douglas⁴; \square , West and Ginnings¹⁰; \diamond , Ditmars *et al.*² The dashed line is the difference of the SRM720 values for heat capacity from the fitted equation.

an s.r.v. of 0.1 percent. Figure 1 shows that the agreement of Chang's results with the fitted equation was within the assigned s.r.v. The differences of West and Ginnings' results from the fitted equation were somewhat smaller than the assigned s.r.v.; this suggests that their results may be more accurate than they claimed. The enthalpy-increment results from Ditmars and Douglas⁴ were assigned an s.r.v. of $25 \text{ J}\cdot\text{mol}^{-1}$. The $25 \text{ J}\cdot\text{mol}^{-1}$ s.r.v. results in a percentage s.r.v. that increased with decreasing temperature. Agreement of Ditmars and Douglas' values with the fitted equation was outside of the experimental precision only for the temperature 1023 K. The results for temperatures greater than 1173 K were obtained with an adiabatic lift calorimeter² and were assigned a s.r.v. of 0.3 percent. For these results, the temperature of the sample just prior to the enthalpy determination was determined with optical pyrometry with an accuracy of approximately 3 to 4 K. These small errors in calibration of the pyrometer could result in the systematic behavior of the differences of these results from the fitted equation.

One consideration for the present fitted equation was to maintain a reasonable behavior for the first temperature derivative of the heat capacity. Figure 2 shows values calculated from the present fitted equation and from the SRM720 equation.

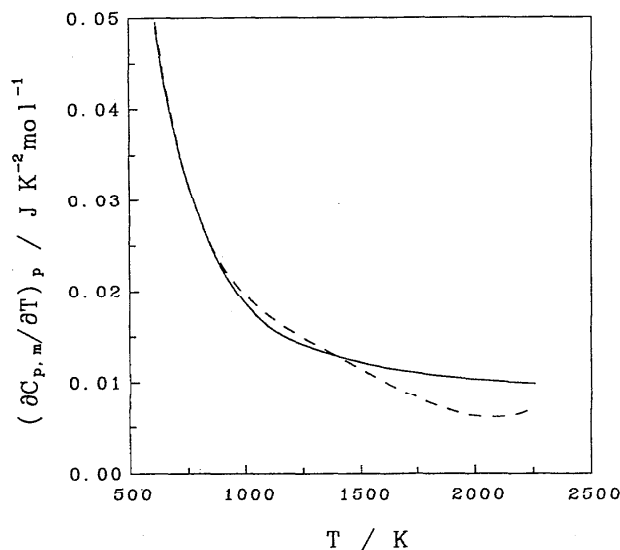


FIG. 2. The first temperature derivative of the heat capacity calculated from the present equation (solid line) and from the SRM720 equation (dashed line).

The present equation yielded a smoothly changing derivative for temperatures above 500 K. The SRM720 equation included polynomial terms in the temperature as large as T^5 . These large-order terms were probably incorporated to improve agreement with the high-temperature results. However, this agreement was obtained by incorporating a heat-capacity behavior that probably

varied more rapidly with temperature than does the true heat capacity. The enthalpy-increment measurements obtained at the two highest temperatures were smaller than values calculated from the fitted equation. This difference, combined with the first temperature derivative of the heat capacity shown in Fig. 2, is opposite to the effect expected from the physical behavior that occurs near the melting temperature, for example, vacancy formation or anharmonic effects.

It is seen in Fig. 1 that the SRM720 heat-capacity values were smaller than the observed heat-capacity values, including those of Chang,³ in the region of 300–500 K. Both the enthalpy-increment values from Ditmars and Douglas⁴ and the adiabatic heat-capacity values from Chang, upon which the SRM are based, agreed with the present fitted equation and with each other within experimental precision. This eliminates experimental systematic error as the cause of the differences of the SRM720 values from the heat-capacity results. It is concluded that the systematic difference arose from a fitting artifact that was present in the SRM720 equation and does not occur in the present fitted equation.

The differences from the present fitted equation of the heat-capacity results of Sorai *et al.*,⁵ of Martin and Snowdon,^{8,15} and of Grønvd⁹ are shown in Fig. 3. These three sets of adiabatic heat-capacity results were generally larger than the values calculated from the fitted equation, a condition that would be consistent with an apparent small and unaccounted heat loss in the calorimeter. Sorai *et al.*'s and Martin and Snowdon's⁸ earlier values showed a positive deviation that increased with increasing temperature. Martin and Snowdon's¹⁵ later values showed the same difference of the first derivative of the heat capacity with respect to temperature from the fitted equation, but the differences were systematically smaller than those observed for their earlier results. The results from Grønvd showed a systematic positive deviation that fell within his estimated inaccuracy of ± 0.3 percent. Also shown in Fig. 3, in the form of a dashed line, are values calculated from the residual plot given by Leadbetter.¹⁶ For most of their examined temperature range, Leadbetter's values do not show the positive deviations shown by the other sets of measurements. The heat-capacity results of Leadbetter and of West and Ginnings were not shown in Sorai *et al.*'s⁵ figure that showed differences of experimental heat-capacity results from the SRM720 values. Additionally, their figure did not take into account the enthalpy-increment measurements for SRM720.

Additional enthalpy-increment results exist in the literature. Ditmars and Douglas reviewed these results and compared them to their own results in their Fig. 7. Because of the accuracy of the Ditmars and Douglas enthalpy-increment results, the differences of these other experimental results from the present equation and from Ditmars and Douglas' fitted equation are very similar. Thus, the reader is referred to Ditmars and Douglas' Fig. 7 for comparison of these enthalpy-increment results.

Table 2 gives calculated values of the heat capacity, the difference in enthalpy between temperature T and 0 K, and the entropy of $\alpha\text{-Al}_2\text{O}_3$. A computer program that calculates these thermodynamic values for SRM720 is available from the author, for a limited time period. The heat-capacity values given in Table 2 are more accurate than those given previously for SRM720. In the region from 150 to 900 K the accuracy of the heat capacity is on the order of 0.05 percent and the accuracy of the relative enthalpy values is also approximately 0.05 percent over this temperature range. For temperatures of 900 to 2200 K, the relative enthalpy and heat capacity become less accurate, the inaccuracy reaching approximately 0.3 and 1.0 percent at 2200 K for relative enthalpy and heat capacity, respectively.

3. Effect of Practical Temperature Scale on Thermodynamic Properties

The periodic revisions of temperature scale prompt periodic discussion of what to do with models and tables of thermodynamic properties generated on the basis of the previous temperature scale. The current work provides a good test case for demonstration of these effects. In the current section of the paper, the differences between the IPTS-68 and the ITS-90 will be taken from the 1990 publication¹² for several reasons, despite the fact that these values were less accurate in the temperature region of 903 to 1337 K than the differences given in Ref. 13. The earlier and less accurate temperature-scale differences are used in this section because it is desired to

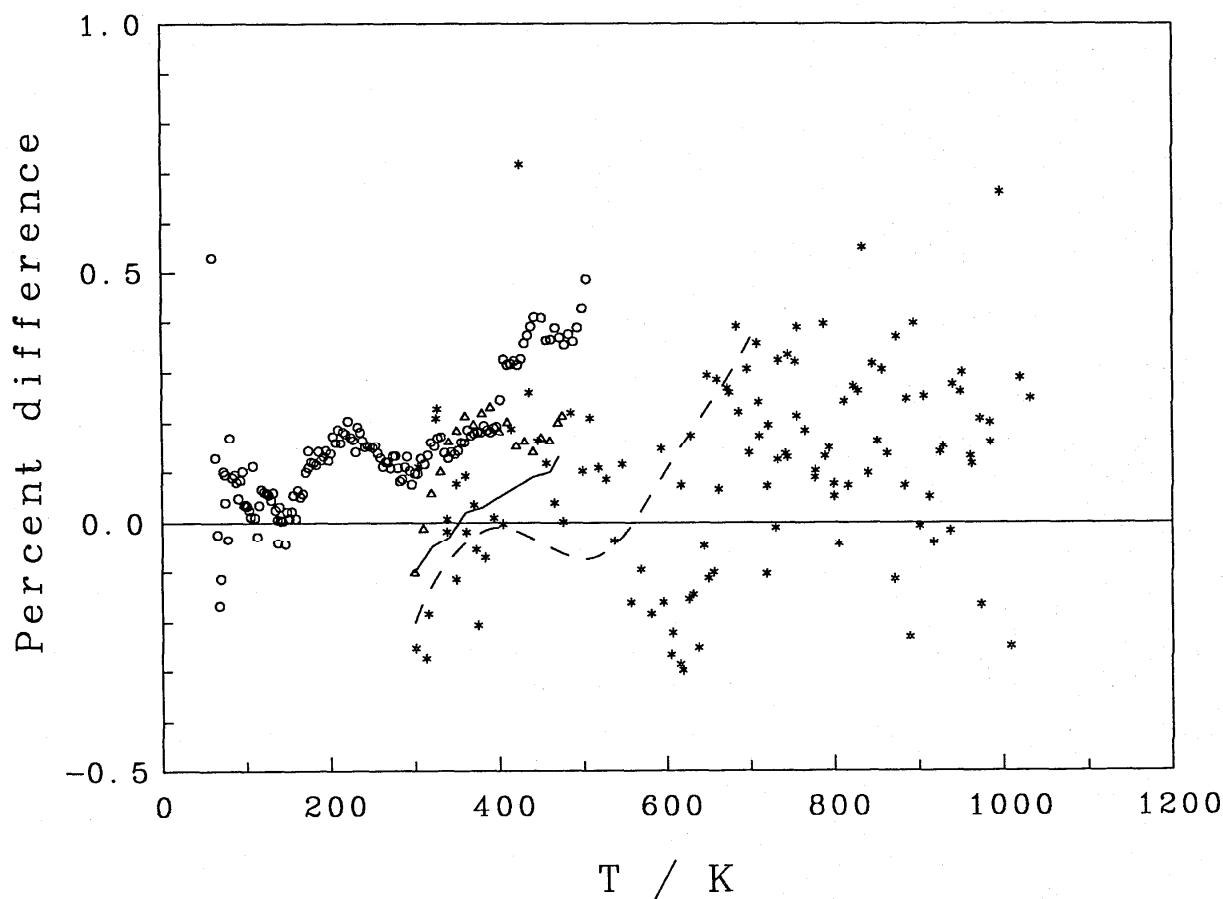


FIG. 3. Percent difference of experimental results, not included in the representation, from fitted equation for temperatures of 10 to 1000 K. The symbols are : O, Sorai *et al.*;⁵ Δ , Martin and Snowdon;⁸ *, Grönvold.⁶ The dashed line was calculated from values calculated from Fig. 3 from Leadbetter.¹⁶ The solid line was calculated from Martin and Snowdon's values.¹⁵

TABLE 2. Values of the heat capacity, the enthalpy relative to 0 K, and the entropy of α -Al₂O₃, calculated from the representation of the experimental results

$\frac{T}{K}$	$\frac{C_{p,m}^{\circ}}{J \cdot K^{-1} \cdot mol^{-1}}$	$\frac{H_{m,T}^{\circ} - H_{m,0K}^{\circ}}{kJ \cdot mol^{-1}}$	$\frac{S_m^{\circ}}{J \cdot K^{-1} \cdot mol^{-1}}$	$\frac{T}{K}$	$\frac{C_{p,m}^{\circ}}{J \cdot K^{-1} \cdot mol^{-1}}$	$\frac{H_{m,T}^{\circ} - H_{m,0K}^{\circ}}{kJ \cdot mol^{-1}}$	$\frac{S_m^{\circ}}{J \cdot K^{-1} \cdot mol^{-1}}$
10	0.01	0.000	0.00	480	104.51	27.068	95.11
20	0.07	0.000	0.02	490	105.35	28.117	97.27
30	0.27	0.002	0.08	500	106.15	29.175	99.41
40	0.70	0.006	0.21	510	106.92	30.240	101.52
50	1.51	0.017	0.45	520	107.66	31.313	103.60
60	2.79	0.038	0.83	530	108.36	32.393	105.66
70	4.59	0.075	1.39	540	109.04	33.480	107.69
80	6.90	0.132	2.14	550	109.69	34.574	109.70
90	9.67	0.214	3.11	560	110.31	35.674	111.68
100	12.84	0.326	4.29	570	110.90	36.780	113.64
110	16.34	0.472	5.68	580	111.48	37.892	115.57
120	20.07	0.654	7.26	590	112.03	39.009	117.48
130	23.95	0.874	9.02	600	112.56	40.132	119.37
140	27.93	1.133	10.94	610	113.07	41.260	121.23
150	31.94	1.433	13.00	620	113.56	42.393	123.08
160	35.94	1.772	15.19	630	114.03	43.531	124.90
170	39.89	2.151	17.49	640	114.48	44.674	126.70
180	43.74	2.570	19.88	650	114.93	45.821	128.47
190	47.50	3.026	22.34	660	115.35	46.972	130.23
200	51.12	3.519	24.87	670	115.76	48.128	131.97
210	54.61	4.048	27.45	680	116.16	49.288	133.69
220	57.95	4.611	30.07	690	116.55	50.451	135.39
230	61.14	5.206	32.72	700	116.92	51.618	137.07
240	64.17	5.833	35.38	710	117.29	52.790	138.73
250	67.06	6.489	38.06	720	117.64	53.964	140.37
260	69.80	7.174	40.75	730	117.99	55.142	142.00
270	72.41	7.885	43.43	740	118.32	56.324	143.60
280	74.88	8.621	46.11	750	118.65	57.509	145.19
290	77.23	9.382	48.78	760	118.96	58.697	146.77
300	79.45	10.166	51.43	770	119.27	59.888	148.32
310	81.56	10.971	54.07	780	119.57	61.082	149.87
320	83.55	11.796	56.69	790	119.87	62.279	151.39
330	85.44	12.641	59.29	800	120.15	63.480	152.90
340	87.23	13.505	61.87	810	120.43	64.682	154.39
350	88.92	14.386	64.42	820	120.71	65.888	155.87
360	90.52	15.283	66.95	830	120.97	67.097	157.34
370	92.04	16.196	69.45	840	121.23	68.308	158.79
380	93.48	17.123	71.93	850	121.48	69.521	160.23
390	94.84	18.065	74.37	860	121.73	70.737	161.65
400	96.14	19.020	76.79	870	121.97	71.956	163.06
410	97.37	19.988	79.18	880	122.21	73.177	164.45
420	98.55	20.967	81.54	890	122.44	74.400	165.83
430	99.67	21.958	83.87	900	122.67	75.625	167.20
440	100.73	22.960	86.18	910	122.89	76.853	168.56
450	101.74	23.973	88.45	920	123.11	78.083	169.90
460	102.71	24.995	90.70	930	123.32	79.315	171.24
470	103.63	26.027	92.92	940	123.53	80.550	172.56
950	123.73	81.786	173.86				
960	123.93	83.024	175.16				
970	124.13	84.265	176.45				
980	124.33	85.507	177.72				
990	124.52	86.751	178.98				
1000	124.70	87.997	180.24				
1010	124.89	89.245	181.48				
1020	125.07	90.495	182.71				
1030	125.25	91.747	183.93				
1040	125.42	93.000	185.14				
1050	125.60	94.255	186.34				
1060	125.77	95.512	187.53				
1070	125.93	96.770	188.72				
1080	126.10	98.031	189.89				
1090	126.26	99.292	191.05				
1100	126.43	100.556	192.20				

TABLE 2. Values of the heat capacity, the enthalpy relative to 0 K, and the entropy of $\alpha\text{-Al}_2\text{O}_3$, calculated from the representation of the experimental results — Continued

$\frac{T}{\text{K}}$	$\frac{C_{p,m}^\circ}{\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}}$	$\frac{H_{m,T}^\circ - H_{m,0\text{K}}^\circ}{\text{kJ}\cdot\text{mol}^{-1}}$	$\frac{S_m^\circ}{\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}}$	$\frac{T}{\text{K}}$	$\frac{C_{p,m}^\circ}{\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}}$	$\frac{H_{m,T}^\circ - H_{m,0\text{K}}^\circ}{\text{kJ}\cdot\text{mol}^{-1}}$	$\frac{S_m^\circ}{\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}}$
1110	126.59	101.821	193.35				
1120	126.74	103.087	194.49				
1130	126.90	104.356	195.61				
1140	127.05	105.625	196.73				
1150	127.21	106.897	197.84				
1160	127.36	108.170	198.94				
1170	127.51	109.444	200.04				
1180	127.66	110.720	201.12				
1190	127.80	111.997	202.20				
1200	127.95	113.276	203.27				
1250	128.66	119.691	208.51				
1300	129.35	126.142	213.57				
1350	130.02	132.626	218.46				
1400	130.67	139.143	223.20				
1450	131.29	145.692	227.80				
1500	131.91	152.272	232.26				
1550	132.51	158.883	236.60				
1600	133.09	165.523	240.81				
1650	133.67	172.192	244.92				
1700	134.23	178.889	248.92				
1750	134.78	185.614	252.81				
1800	135.33	192.367	256.62				
1850	135.87	199.147	260.33				
1900	136.40	205.954	263.96				
1950	136.92	212.787	267.51				
2000	137.44	219.646	270.99				
2050	137.95	226.531	274.39				
2100	138.46	233.441	277.72				
2150	138.96	240.376	280.98				
2200	139.46	247.337	284.18				
2250	139.96	254.322	287.32				

examine previous work based on those temperature-scale differences. Also the previous differences are larger than the more accurate values and thus provide a better test of the ability of different methods to accurately revise tables or equations that give thermodynamic properties.

Schematically, the process of creating thermodynamic tables can be described as follows. A set of thermodynamic measurements, Y_i , are obtained. Each Y_i has associated with it some number of random and systematic errors, the sum of which will be referred to as δY_i . The difference of temperature scale from thermodynamic temperature yields one of the systematic errors. One method of generating a thermodynamic table is to place the experimental results, obtained at approximately even temperature increments directly into the table. This will be called pathway A. This method retains all of the systematic experimental errors within the values given in the table. This was approximately the method of table generation of half a century ago, whether or not assisted by large pieces of graph paper. However, generation of thermodynamic tables is usually different now than compared to half a century ago. The more typical current practice can be described as pathway B. Pathway B incorporates some intermediate statistical treatment of the experimen-

tal results to yield the values placed in the table. This statistical treatment reduces the effect of the experimental random errors in the values calculated for a table. But the statistical treatment of the experimental results, under certain special conditions, may also reduce the influence of some systematic errors or some component of some systematic errors, removing some additional error from the δY_i . (The conditions under which this might occur are discussed later. Also, the statistical treatment may add a component of error that results from model bias to the δY_i .) The answer to the question: "What portion, if any, of a systematic error is removed by the statistical analysis that is used to generate a model of the thermodynamic function?" is found in a simple mathematical derivation, which is given next.

Consider a linear least-squares representation (linear in the parameters) of a set of i observations, Y_i . The least-squares estimated model is to be:

$$Y = \sum_{j=1}^p b_j X_j \quad (4)$$

(The nomenclature used here follows that given in Ref. 14.) For each b_k of the set of b_j there exists one equation of the set of p normal equations:

$$0 = \sum_{i=1}^n Y_i X_{i,k} - b_k \sum_{i=1}^n (X_{i,k})^2 - \sum_{j=1, j \neq k}^p b_j \sum_{i=1}^n X_{i,j} X_{i,k} . \quad (5)$$

The p normal equations are then used to determine the p b_j . Now, consider the effect of adding a small increment, ϵY_i , to each of the observed Y_i , the purpose of which is to correct for a small systematic error. By "small" we mean of a magnitude for which the applicability of the model's functional form remains valid. To maintain complete generality, the ϵY_i may or may not be dependent on the values of the X_j . (Of course, if the ϵY_i are independent of all of the X_j there will be difficulties in the matrix inversion. The usual statistical methods can be used to determine the validity of inclusion of any particular X_j .) Each adjusted observation Y_i^* is thus composed of Y_i and the adjustment, ϵY_i :

$$Y_i^* = Y_i + \epsilon Y_i . \quad (6)$$

Repeating the least-squares process using the adjusted Y_i^* gives slightly different values of the b_j , which may be expressed as $b_j + \epsilon b_j$. The normal equation for each ($b_k + \epsilon b_k$) for this case is thus:

$$0 = \sum_{i=1}^n Y_i^* X_{i,k} - (b_k + \epsilon b_k) \sum_{i=1}^n (X_{i,k})^2 - \sum_{j=1, j \neq k}^p (b_j + \epsilon b_j) \sum_{i=1}^n X_{i,j} X_{i,k} . \quad (7)$$

which, after substitution of Eq. (7), becomes:

$$0 = \sum_{i=1}^n (Y_i + \epsilon Y_i) X_{i,k} - (b_k + \epsilon b_k) \sum_{i=1}^n (X_{i,k})^2 - \sum_{j=1, j \neq k}^p (b_j + \epsilon b_j) \sum_{i=1}^n X_{i,j} X_{i,k} . \quad (8)$$

The set of p normal equations described by Eq. (8) is simply the sum of the p Eq. (5) and a set of p equations of the form:

$$0 = \sum_{i=1}^n (\epsilon Y_i) X_{i,k} - (\epsilon b_k) \sum_{i=1}^n (X_{i,k})^2 - \sum_{j=1, j \neq k}^p (\epsilon b_j) \sum_{i=1}^n X_{i,j} X_{i,k} . \quad (9)$$

The set of p equations typified by Eq. (9) is a set of normal equations for the least-squares model:

$$\epsilon Y = \sum_{j=1}^p \epsilon b_j X_j , \quad (10)$$

where ϵY is the change in the calculated dependent variable. In other words, the change in the model parameters, ϵb_j , can be calculated from the least-squares representation of the ϵY_i using the same $X_{i,j}$ as used for fitting the Y_i . This provides the general solution to the problem.

In order to use Eq. (10) for a specific application, values of ϵY_i must be obtained. A specific application is the effect that the difference in temperature scales has on statistically-treated thermodynamic properties obtained

from heat capacity measurements. The ϵY_i for an experimental heat capacity that results from the change in practical temperature scales can be approximated as:

$$\begin{aligned} \epsilon Y_i &= \{C_{p,m}(\text{ITS-90}) - C_{p,m}(\text{IPTS-68})\}_{i, \text{exp}} \\ &= - \{C_{p,m}(d(T_{90} - T_{68})/dT)\}_i , \end{aligned} \quad (11)$$

where the _{exp} has been added to designate the quantity that corresponds to the change in the i^{th} experimental measurement due to the change in the temperature scale. (The right-hand-side of Eq. (11) is not the correct treatment of the experimental results but it is a reasonable approximation of the effect.) Substitution of Eq. (11) for ϵY_i in Eqs. (9-10) gives the change of the model of the thermodynamic properties that adjusts for the difference in temperature scales. Other than the assumptions of Eq. (11) for the error in a heat capacity measurement, this result is mathematically rigorous. For the case of heat capacity, Eq. (10) and Eq. (11) give:

$$\{C_{p,m}(\text{ITS-90}) - C_{p,m}(\text{IPTS-68})\}_{\text{model}} = \sum_{j=1}^p \epsilon b_j X_j , \quad (12)$$

where the subscript _{model} has been added to distinguish these values from the experimental values. Eq. (12) is the change in the model, and thus also the change in the calculated heat capacity values given in a thermodynamic table, due to a change in the temperature scale. (For example, if the original model that had been fitted to the experimental results was: $C_{p,m} = a + bT + c/T^2$ then Eqs. 10-12 provides the ϵa , ϵb and ϵc that would be added to the original a , b , and c to obtain the new model.)

Equation (10), presented here as a method for obtaining the differences in thermodynamic properties that result from changes in temperature scales, is completely analogous to the previously described method for treating differences in thermodynamic properties of strong-electrolyte solutions that result from changes in Debye-Hückel coefficient.¹⁹ The mathematical treatment of the problem described above is exactly the same as that in Ref. 19; the only difference is the specific application of the general equations.

A simplified, but more practical, use of Eq. (10) can be obtained by using a vector of ϵY_i generated with a reasonable distribution within the range of temperature over which the original experimental values were fitted. This practical, but slightly approximate method, does not require the exact temperature distribution of the original data, i.e. the exact $X_{i,j}$, used in the original representation. This was shown previously with the electrolyte thermodynamic properties and can also be shown with the values for the calorimetric reference materials. This simplified method of use involves an approximation but it will still yield reasonable values. Equations (9-10) are applicable not only to the specific case of thermal properties but also to other models such as vapor pressure equations or equations of state. Because this method obviates the labor involved in gathering all of the experimental

results, adjusting their temperatures and refitting the model, it provides an excellent alternative to both that process and to a significantly less accurate method for "conversion of thermodynamic properties" given elsewhere and which is discussed next.

The IUPAC Commission on Thermodynamics (herein, IUPACCT) has published a "Technical Report," prepared by Goldberg and Weir,¹⁷ that gave a method for calculating the changes in thermodynamic properties that result from the change of earlier practical temperature scale to the ITS-90.^a That report also gave values for conversion of the thermodynamic properties of two calorimetric standard reference materials: α -Al₂O₃, SRM720, and Mo, SRM781, for the change in temperature scales. The Goldberg and Weir values for the change in heat capacity for these two substances were obtained by means of the equation:

$$C_{p,m}(\text{ITS-90}) - C_{p,m}(\text{IPTS-68}) = -(T_{90} - T_{68}) \\ (dC_{p,m}/dT) - C_{p,m}(d(T_{90} - T_{68})/dT) \quad (13)$$

where T_{90} and T_{68} are the practical temperature scale approximations of the thermodynamic temperature for the ITS-90 and the IPTS-68, respectively.

Equation (12), rigorously derived from the mathematics used to generate a thermodynamic table, is clearly different from Eq. (13). (The only assumption used in deriving Eq. (12) was the expansion and truncation of an error function about an experimental observation.) Because Goldberg and Weir's conversion method, as typified by Eq. (13), is quite different from the mathematically derived result it is concluded that their method is not mathematically correct for tables of thermodynamic properties generated from a statistical treatment of experimental results, such as those for the two calorimetric standard reference materials, aluminum oxide and molybdenum.

The accuracy of the IUPACCT conversions of the thermodynamic properties of SRM720 are examined by the following calculations. The previously described experimental results for aluminum oxide were fitted with all temperatures on the IPTS-68. Heat capacity values from this representation were calculated and can be considered as the $C_{p,m}(\text{IPTS-68})$ in Eq. (13). The experimental temperatures were then converted to the ITS-90 and the experimental results were fitted to yield a set of heat capacities based on the ITS-90, $C_{p,m}(\text{ITS-90})$. The difference between these two quantities is the difference in heat capacity due to the difference in temperature scales and is shown as a percentage error in Fig. 4. (This quantity can be considered as the error due to making no change in thermodynamic property for the change of the IPTS-68 to the ITS-90, if the ITS-90 is a better approximation of thermodynamic temperature than was the IPTS-68.)

^a The method described by Goldberg and Weir is meant to be used to alter the values of thermodynamic properties given in tables while retaining the same values for temperature given in the table.

Next, a set of $\delta C_{p,m}(\text{ITS-90, GW})$ were obtained by means of Goldberg and Weir's method. These $\delta C_{p,m}(\text{ITS-90, GW})$ were then added to the $C_{p,m}(\text{IPTS-68})$ to obtain $C_{p,m}(\text{ITS-90, GW})$. The $C_{p,m}(\text{ITS-90, GW})$ are thus the values of the heat capacity of SRM720 calculated from the values on the IPTS-68 and the method given by Goldberg and Weir. The difference between the $C_{p,m}(\text{ITS-90})$ and $C_{p,m}(\text{ITS-90, GW})$ is the error introduced by the Goldberg and Weir method and is also shown in Fig. 4. As can be seen from the figure, for approximately 80% of the temperature range from 200 to 1300 K, the Goldberg and Weir method introduces a larger error into the thermodynamic properties than if no conversion for temperature scales was made at all. Also, comparison of Fig. 4 with Fig. 1 indicates that for almost half of the temperature range shown in the figure, the Goldberg and Weir method introduces an error significantly larger than the expected uncertainty in the calculated heat capacity, by as much as a factor of five, or more, at some temperatures. Figure 4 indicates that it is better to ignore the change in thermodynamic property due to the change of the current temperature scale from the IPTS-68 than to apply the conversion method from the IUPACCT Technical Report, even for the very accurate experimental work for SRM720. Goldberg and Weir did not describe a test of their method, such as that of Fig. 4. Figure 5 shows values of the heat capacity of SRM720 against temperature, calculated by means of the Goldberg and Weir method. Also shown, are values calculated using the values from their Table 7, for comparison purposes, as well as the values for IPTS-68 calculated from the representation of experiment, as described in the previous paragraph. Clearly, the conversion method of Ref. 17 introduces an undesired behavior into the heat capacity values of this calorimetric standard. Because the discontinuity and other effects shown in Fig. 5 result from the combination of incorrect mathematical method and the temperature scale differences, they are a general effect and so also occur with molybdenum, SRM781.

That Ref. 17's method could show such a large discrepancy from the actual effect of changing practical temperature scales is readily explainable. Mathematically, their equation is an estimate of the difference due to temperature scales for an individual measurement of heat capacity. However, they applied their equation to values calculated from a statistical representation for Al₂O₃, which are not the same as the experimental results. As such, their method does not take into account the statistical treatment of experimental results. The large errors in their conversion values occurred because a significant component of the assumed temperature-scale differences in the individual measurements had been eliminated in the least-squares fitting to the experimental results. The subsequent application of their method reintroduces an error component that had been removed by the least-squares representation of the results. Further, the inaccuracies shown in Figs. 4 and 5 do not result from the difference of Ref. 17's "exact equations" (the infinite series expansion) from their "approximate equations"

(the truncated expansion); because both neglect the statistical treatment of the experimental results, their "exact equations" will also produce the behavior shown in Figs. 4 and 5.^b

Summarizing the preceding material, the following have been shown: 1) The Goldberg and Weir method for conversion of the thermodynamic properties of SRM720, specifically, and other substances, generally, can introduce significant errors into the values for the thermodynamic properties. 2) These large errors can be expected because their method does not take into account the statistical treatment of experimental results. 3) When the statistical treatment of the experimental results is taken into account, a much different equation than that given in Ref. 17 is obtained and this is indicative that their method is not mathematically correct for tables generated from statistical treatment of experimental results. It is concluded from these three things that the IUPACCT method for conversion of thermodynamic properties should not be used for this purpose.

Goldberg and Weir state: "We note that the fitting process tends to produce smooth results and, in doing this, it tends to minimize the effects of errors in the measurements, including any errors in the thermometry and in the temperature scale used in the study." This is not generally true and the mathematical treatment presented above does not indicate that such is the case. Consider the hypothetical difference between a temperature scale, T_x , and the thermodynamic temperature, T , that increases linearly with T_x :

$$T_x - T = b_T T_x, \quad (14)$$

over a particular range of temperature. If enthalpy-increment measurements were determined on the basis of T_x , $\Delta H_m(T_x - 273.15 \text{ K})$, over this same range of temperature, and were fitted with the model:

$$\Delta H_m(T_x - 273.15 \text{ K}) = b_1(T_x - 273.15 \text{ K}), \quad (15)$$

^b A reviewer has stated that the method used by Goldberg and Weir was that given by Douglas.¹⁸ This is not quite correct. It is true that Eq. (13) can be found within the first few pages of Douglas' paper. However, Douglas' paper contained significantly more procedure than was described by Goldberg and Weir. An example is as follows: Douglas correctly realized that Eq. (13) would give two values of the heat capacity at any temperature where the difference between two practical temperature scales had a discontinuity of the first derivative with respect to temperature. He gave a procedure by which the discontinuity that Eq. (13) introduces into the heat-capacity function (such as that shown in Fig. 5) could be avoided; this procedure was given on pages 466 and 467 of reference 18. Although there is a discontinuity in the first derivative of differences of ITS-90 from previous temperature scales, Goldberg and Weir neither described nor used Douglas' method to avoid the discontinuity in their calculated values (see, for example, their calculated values that are shown in Fig. 5.) Because Goldberg and Weir have used only part of Douglas' original method and because they used an equation of Douglas' for a condition for which Douglas described a different method, it seems not correct to describe Goldberg and Weir's method as "that derived by Douglas."

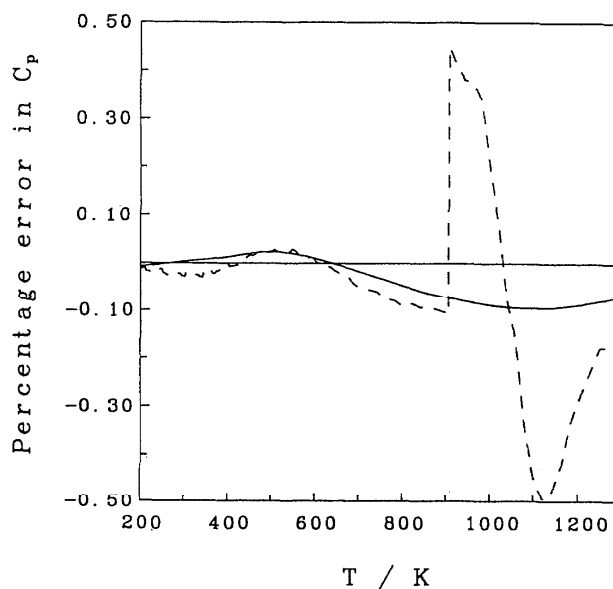


Fig. 4. Errors in thermodynamic values of SRM720 for two different treatments of the effects of changing practical temperature scales. The dashed line is the error introduced by the Goldberg and Weir equation into the calculated heat capacity values for SRM720. The solid curve is the error introduced into calculated heat-capacity values for making no change due to temperature scales.

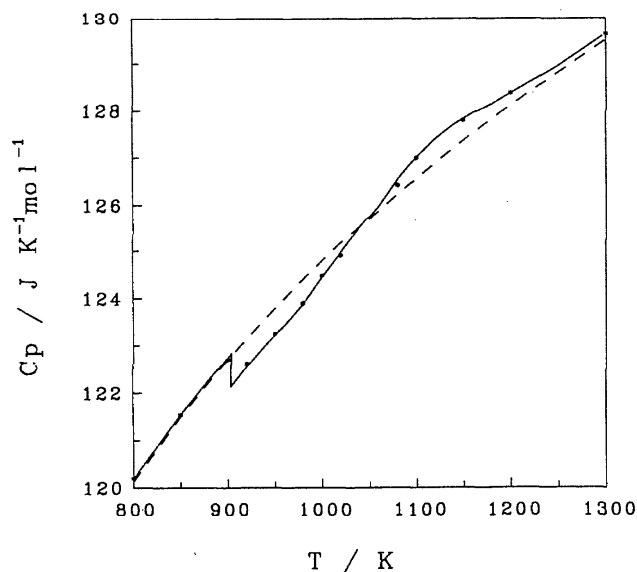


Fig. 5. Calculated values of the heat capacity of SRM720 against temperature. ---, calculated from the fit to the thermodynamic measurements on the basis of IPTS-68; - calculated from the dashed line and the conversion method given by Goldberg and Weir. *, calculated from values from Goldberg and Weir's Table 7 and the representation of experiment on the IPTS-68.

then clearly all of the difference between the temperature scale and the thermodynamic temperature is incorporated into the fitted model and none of it has been "minimized." This can be seen in the mathematical derivation given above. The rate of change of the temperature scale as compared to the rate of change of the fitted function is important. A large error in temperature scale that varies slowly with respect to temperature over the range of temperature included in the data representation is, of course, incorporated into the representation. This is apparent from Eqs. (6-10).

Finally, Goldberg and Weir state: "If the inaccuracies in the results are judged to be less than the approximate effects given in Table 7 (or Table 8), then a recalculation of the original results is clearly justified." Their Table 7 gives the errors shown in Fig. 4. It has already been demonstrated that the inaccuracies of the SRM720 results are smaller than Goldberg and Weir's conversion values and it has also been demonstrated that the true changes that result from the difference of temperature scales is within the inaccuracy of the calculated values for SRM720. Because the true values for conversion of the thermodynamic properties of SRM720 are less than the inaccuracy in the calculated results, the change due to temperature-scale differences could have been ignored. Thus, the implication that SRM720 and SRM781 need to be re-evaluated due to recent temperature-scale differences is not supported by the work of Ref. 17.

4. References

- ¹National Bureau of Standards Certificate, Standard Reference Material 720 (1982).
- ²Ditmars, D. A.; Ishihara, S.; Chang, S. S.; Bernstein G.; West, E. D. J. Res. Natl. Bur. Std. 1982, **87**, 159.
- ³Chang, S. S. Proc. Seventh Symp. Thermophys. Prop., (A. S. M. E. A. Cezairliyan ed. 1977).
- ⁴Ditmars, D. A.; Douglas, T. B. J. Res. Natl. Bur. Std. 1971, **75A**, 401.
- ⁵Sorai, M.; Kaji, K.; Kaneko, Y. J. Chem. Thermodyn. 1992, **24**, 167.
- ⁶Inaba, A. J. Chem. Thermodyn. 1983, **15**, 1137.
- ⁷Andrews, J. T. S.; Norton, P. A.; Westrum, E. F. J. Chem. Thermodyn. 1978, **10**, 949.
- ⁸Martin, D. L.; Snowdon, R. L. Can. J. Phys. 1966, **44**, 1449.
- ⁹Gronvold, F. Acta Chem. Scand. 1967, **21**, 1695.
- ¹⁰West, E. D.; Ginnings, D. C. J. Res. Natl. Bur. Std. 1958, **60**, 309.
- ¹¹Archer, D. G. J. Phys. Chem. Ref. Data 1992, **21**, 1.
- ¹²Preston-Thomas, H. Metrologia 1990, **27**, 3 and 102 (1990).
- ¹³Burns, G. W.; Strouse, G. F.; Mangum, B. W.; Croarkin, M. C.; Guthrie, W. F.; Marciano, P.; Battuello, M.; Lee, H. K.; Kim, J. C.; Gram, K. S.; Rhee, C.; Chattle, M.; Arai, M.; Sakurai, H.; Pokhodun, A. I.; Moiseeva, N. P.; Perevalova, S. A.; deGroot, M. J.; Zhang, J.; Fan K.; Wu, S. in Temperature Its Measurement and Control in Science and Industry (1992).
- ¹⁴Draper, N. R.; Smith, H. Applied Regression Analysis, (J. Wiley, New York 1981).
- ¹⁵Martin, D. L.; Snowdon, R. L. Rev. Sci. Instr. 1970, **41**, 1869.
- ¹⁶Leadbetter, A. J. J. Phys. C, Ser. 2 1968, **1**, 1481.
- ¹⁷Goldberg, R. N.; Weir R. D. Pure Appl. Chem. 1992 **64**, 1545.
- ¹⁸Douglas, T. B. J. Res. Natl. Bur. Std. 1969, **73A**, 451.
- ¹⁹Archer, D. G. J. Chem. Eng. Data 1990, **35**, 340.
- ²⁰Description of experimental uncertainties is in accord with: Guide for the Presentation in the Primary Literature of Numerical Data Derived from Experiments, (Report of the CODATA Task Group on Publication of Data in the Primary Literature, 1973).

Appendix 1

In the text of the paper it was noted that unaccounted heat losses in either the heat-capacity measurements or the enthalpy-increment measurements would result in opposite-signed residuals for the two types of experimental measurement. Considered here are comments from two reviewers and further exposition regarding the comments.

The first comment is: "There is no general bias to errors in results obtained with adiabatic heat-capacity calorimeters. If done correctly, 'heat loss' is compensated by extrapolation of temperature/time curves for the periods before and after a heat to the mid-time of the heating period. A common error involves the failure to reach equilibrium after a heating period, which results in extrapolation to an incorrect temperature. The direction of the error is a function of the relative positions of the heater and thermometer in the specific calorimeter." This comment is correct in as far as it goes. However, the situation is not always as simple as might be inferred from the comment. The extrapolation of the fore- and after-drift periods corrects for non-adiabaticity of the calorimeter in the drift periods, i.e. it is the correction for non-adiabaticity when the calorimeter proper is not being heated. This extrapolation corrects for such errors as the determination of the difference in temperature of the adiabatic shields from the calorimeter (offset voltages of the thermocouples), and heat transfers along the suspension device and along the electrical connections to the calorimeter. These heat transfers are about the same whether or not the calorimeter is being heated. Other heat exchanges may occur only during the heating of the calorimeter and not during the drift periods. These heat exchanges would not be minimized by the drift-period extrapolations. One such heat-exchange is caused by the time lag of the usual closed-loop adiabatic-shield controllers, whose response always lags the process variable. If the time-temperature profile observed when heat is first applied to the calorimeter is not the same (other than sign of the temperature difference) as when heating is first discontinued, then an asymmetric lagging response of the shield-controllers can create an unaccounted heat loss or gain. The magnitude of this error will depend, among other things, on how asymmetric are the initial and final temperature profiles (the asymmetry of these profiles is directly related to the time required to reach equilibrium) and the magnitude of the time lag of the controllers. When one considers the usual controller-response profile and the temperature-time profiles at the onset and the end of the calorimeter heating period the most likely case is a heat loss from the calorimeter and this heat loss would be unaffected by the extrapolations

described above. Because the temperature-time profiles of heating the empty and the filled calorimeter also will be different, the error associated with controller lag is further affected. With respect to the question of equilibration affecting the temperature assigned to the heat-capacity measurement, the differences of several of the experimental heat capacities, from the fitted equation and from study to study, seem to be too large to be explained by this effect. For example a difference of 0.3% between an experimental heat-capacity measurement and the fitted equation, for 400 K, corresponds to a 2.3 K error in the midpoint temperature or a 30 mK error in $T_{\text{final}} - T_{\text{initial}}$ for a 10 K heating interval. These values seem to the author to be a bit large. (This is not to be taken to mean that an error of this percentage is unlikely for situations where phase or glass transitions can affect the heat-capacity results in this way. The problems associated with slowly attained transitions are not a significant factor with the SRM720 samples.)

This reviewer also made the observation that "heat capacities" obtained by adiabatic calorimetry are not truly heat capacities, but instead, are enthalpy-increment values characterized by an enthalpy, an initial temperature and a final temperature, but are not always reported as such. "This causes conversion of the reported temperatures, which are $(T_{\text{final}} + T_{\text{initial}})/2$ a meaningless exercise." To this point, the author wishes to add that, on occasion, reported heat capacity values may have also been altered in some way with an appendage in the text that says: "corrected for curvature." Both of these alterations of what was actually determined in the measurement can introduce errors into further statistical treatment of these values. The author wishes to join the reviewer in his call to those reporting these calorimetric measurements to report the enthalpy increment, the initial temperature, and the final temperature.

Another reviewer observes: "In the design and operation of calorimeters, it is the intent to minimize 'heat leaks.' In the operation, the 'filled' and 'empty' measurements are carried out so that any heat leak would be nearly the same to minimize the effect of heat leak on the final results. Also, the errors of the final heat capacity or enthalpy can arise from the errors in the accounting of the container... With the 'receiving calorimeters' the transit periods of the filled and empty vessel may be different." This comment is correct. However, the intent to minimize heat leaks may not always be successful. There will always be some unaccounted heat leak which may or may not be insignificant. One such unaccounted heat leak, asymmetry of controller lag, was discussed above for the adiabatic heat-capacity calorimeters and is an example of an unaccounted error which is normally considered "minimized."