Thermodynamic Properties of the NaCl + H_2O System
I. Thermodynamic Properties of NaCl(cr)

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Received May 2, 1991; revised manuscript received October 1, 1991

The available experimental thermodynamic data for NaCl(cr) have been fitted in order to generate thermodynamic values as a function of temperature and for a nominal pressure of 0.1 MPa. Thermal measurements (heat-capacity values and enthalpy-increment values) have been fitted with a new method. The fitted function and calculated thermodynamic values are given. Estimates of the inaccuracies of the calculated thermodynamic values are also given.

Keywords: enthalpy, entropy, heat capacity, sodium chloride.

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1. Introduction

Sodium chloride is an important substance in the determination of a set of internally consistent thermodynamic values for a large set of substances. It is in this role that sodium chloride appears in the CODATA key values tabulation.[1] Because of the importance that has been assigned to sodium chloride, it would be expected that there exist accurate values for the thermodynamic properties of both the aqueous solution of sodium chloride and the crystal. Indeed, the values for the crystal that appear in compilations of thermodynamic values appear to

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0047-2689/92/010001-21/$12.00

support this expectation. For example, the following compilations list values of the 298.15 K heat capacity of NaCl(cr) as: Wagman *et al.*,[2] 50.50 J·K^{-1}·mol^{-1}, table dated 1980;[3] Gurvich *et al.*,[4] 50.500 J·K^{-1}·mol^{-1}; Chase *et al.*,[5] 50.509 J·K^{-1}·mol^{-1}, table dated 1964; Medvedev *et al.*,[6] 50.50 J·K^{-1}·mol^{-1}, table dated 1976; Pankratz,[7] 50.50 J·K^{-1}·mol^{-1}. The excellent agreement of the 298.15 K heat-capacity values given in these data evaluations (no more than 0.02 % deviation from the average value) reinforces the uncritical user's expectation that the tabulated values for NaCl(cr) are highly accurate.

Figure 1 shows the experimental values of the heat capacity in the temperature region about 300 K. Also shown are two small horizontal lines. The average of the compiled values listed above is midway between these two lines and the distance between the two lines, 0.02 J·K^{-1}·mol^{-1}, is twice the spread of the values. The heat- capacity value for 298.15 K given by Chase *et al.*[5] is the only one listed above that is dated in such a way that one would not expect the results of Leadbetter and Settatree[10] to have been included. Considering the differences in the experimental results available to all of the compilations listed above, with the exception of Chase *et al.*, it is perhaps surprising that so many different evaluations of the data of Fig. 1 resulted in values so nearly identical. This is especially so, as this value is significantly larger than the experimental data available to each of the compilations, (with the exception of Chase *et al.*)

The need to incorporate the thermodynamic values of NaCl(cr) in computer programs for other work, combined with the apparent systematic differences of the compiled heat capacities from the experimental values has prompted a re-examination of the thermodynamic properties for NaCl(cr).

2. Method of Representation

The representation of experimental heat-capacity results is interesting (NaCl(cr) is shown in Fig. 2). A method was desired that would; 1) allow a statistical representation of the various experimental results that contribute to the determination of the thermodynamic properties; 2) provide a function that could be used to generate a thermodynamic property and to generate other thermodynamic properties through some manipulation of the function; 3) introduce minimal model bias into the representation of the experimental results; and 4) incorporate the low-temperature T^3 dependence of heat

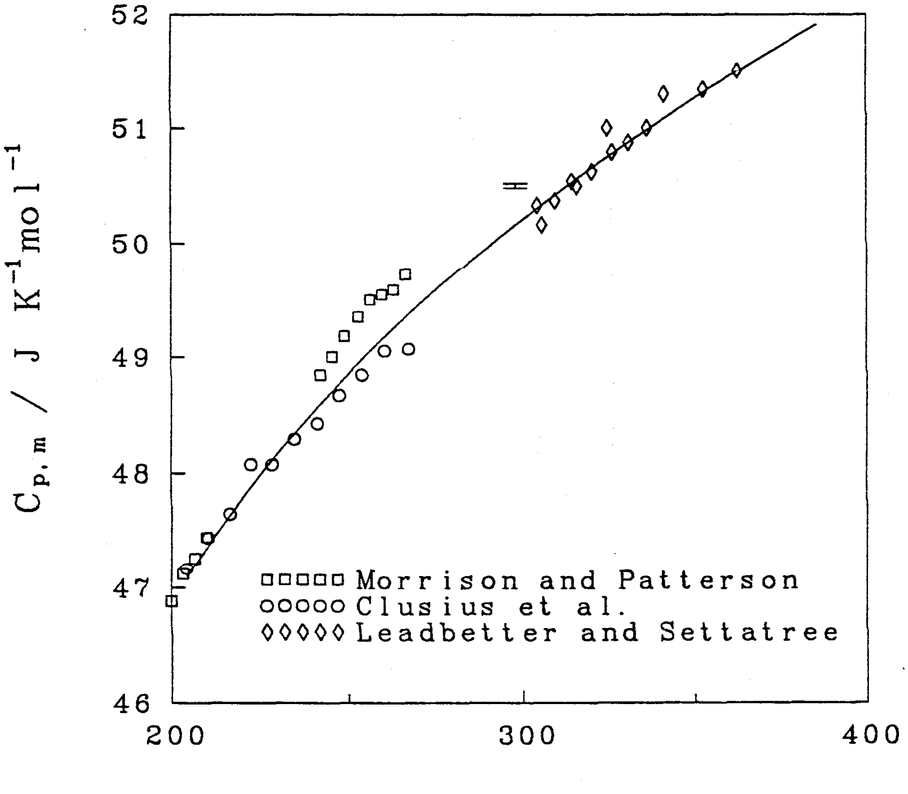

FIG 1. Experimental heat-capacity values of NaCl(cr) in the vicinity of 300 K. The two small horizontal bars are twice the spread of 5 recommended values.

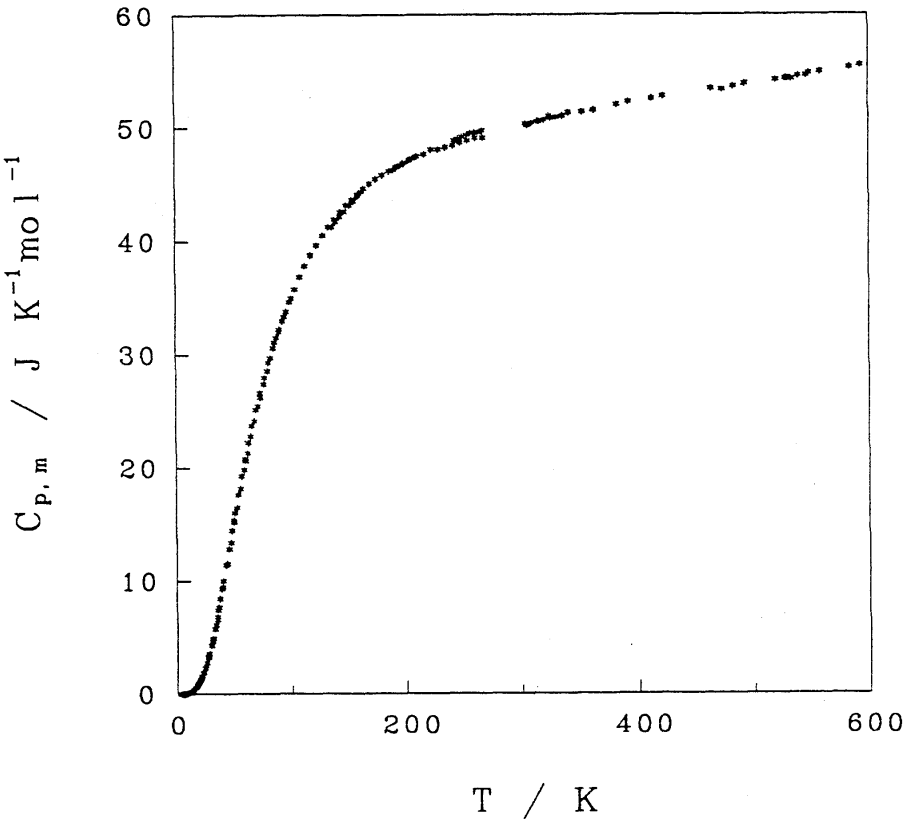

FIG 2. Experimental heat-capacity values for NaCl(cr).

capacity into the model. For temperatures approaching 0 K a polynomial in T with lowest order of three can represent experimental results. However as the temperature region included in the representation is increased such a polynomial becomes more difficult to fit to the experimental results. This is because the higher-temperature results are slowly varying functions of T when compared to the lower-temperature results. The high-order polynomial can thus be expected to oscillate about the higher-temperature experimental results. The reasons for this behavior are well understood[11] and will not be discussed here. The behavior of the higher-temperature data suggests a nearly first-order temperature dependence combined with a more exaggerated temperature dependence as temperature decreases. This suggests the use of an inverse-temperature power series combined with a first-order temperature term. This results in equations of the familiar type:

$$C^{\circ}_{p,m} = a + bT + cT^{-2} \tag{1}$$

However, the inverse-temperature power series exhibits the same problems as $T \to 0$ that the temperature power series does as T becomes large, that is $T^{-n} \to \infty$ as $T \to 0$ when $n > 0$; and so this method is also not applicable for the region of temperature to be considered here.

An alternate solution is to fit a cubic spline to the experimental values. In order to incorporate the low-temperature T^3 behavior the spline polynomials would take the form:

$$C^{\circ}_{p,m} = a_i(T^3 - T_i^3)^3 + b_i(T^3 - T_i^3)^2 + c_i(T^3 - T_i^3) + d_i, \tag{2}$$

and where a "natural spline" end condition would be adopted at the $T = 0$ end knot. This procedure was attempted for the NaCl(cr) data. A typical representation of the heat-capacity results for temperatures less than 300 K required about 10 knots. These least-squares evaluated splines represented the experimental results within expected error limits. However, plots of the first derivative of the heat capacity with respect to temperature showed small eccentricities superimposed on a function that appeared, on average, correctly behaved. The small eccentricities appeared from a combination of three causes: 1) the great flexibility of a spline with a significant number of knots; 2) the very rapid variations of the heat-capacity function against temperature; 3) the distribution of the experimental results against temperature. Cause 3 expresses the facts that the experimental results of Clusius *et al.*[8] and of Morrison *et al.*[9] differ by more than their precisions, and that the Morrison *et al.* results are distributed intermittently against temperature, whereas the results of Clusius *et al.* are distributed evenly against temperature. It is the combination of the three conditions listed above that hampered attempts to use the spline of Eq. (2), not either of the first two themselves. Thus, in order to improve the spline representation of the experimental results, one of the three causes described above must be mitigated. Of course, cause 3 is inherent in the data and cannot be altered. A more slowly changing function of temperature is a potential solution.

It is well known that at low temperatures the apparent Debye temperature is generally a more slowly changing function of temperature than is the heat capacity. A function, $f(T)$, similar to the Debye temperature, but not the Debye temperature, is:

$$f(T) = T\{(C^\circ_{p,m}/C^\circ_p)^{-1/3}\}/T^\circ, \tag{3}$$

where T° is 1 K and C°_p is 1.0 J·K^{-1}·mol^{-1}. Figure 3 shows the values of $f(T)$ calculated from the experimental heat-capacity values. At temperatures greater than 70 K, there appears to exist a first-order temperature dependence of $f(T)$. An estimate of the slope of this portion of $f(T)$, b, can be made and then $f(T)$ may be redefined as:

$$f(T) = \{T\cdot(C^\circ_{p,m}/C^\circ_p)^{-1/3} - bT\}/T^\circ \tag{4}$$

where b is 0.25. The values of the redefined $f(T)$, Eq. (4), calculated from the experimental heat capacities are shown in Figs. 4 and 5. The function $f(T)$ of Eq. (4) is splined using polynomials of the form:

$$f(T) = a_i(T-T_i)^3 + b_i(T-T_i)^2 + c_i(T-T_i) + d_i\,. \tag{5}$$

The calculated heat capacity is thus:

$$C^\circ_{p,m}/C^\circ_p = \left(\frac{T}{T^\circ f(T) + bT}\right)^3. \tag{6}$$

Equation (6) can be integrated numerically to obtain the enthalpy. Because Eq. (5) lends itself well to a recursive formulation this numerical integration does not require as much computational expense as might at first be expected. The spline function $f(T)$ is fitted to the experimental values with a nonlinear least-squares program. The vector of residuals is calculated using Eq. (6) and numerical integrations of Eq. (6).[a] This procedure allowed the experimental heat-capacity results and enthalpy-

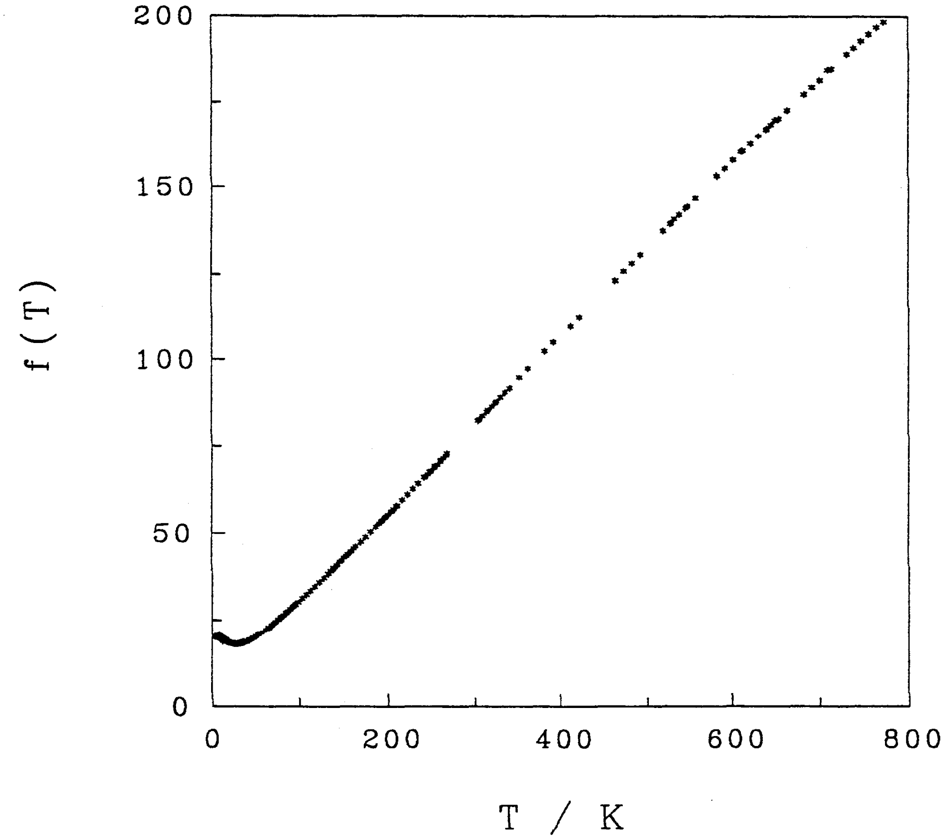

FIG 3. Values calculated from Eq. (3) and the experimental heat-capacity values.

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[a] In response to reviewers' comments, the import of the previous two sentences is described in Appendix 1.

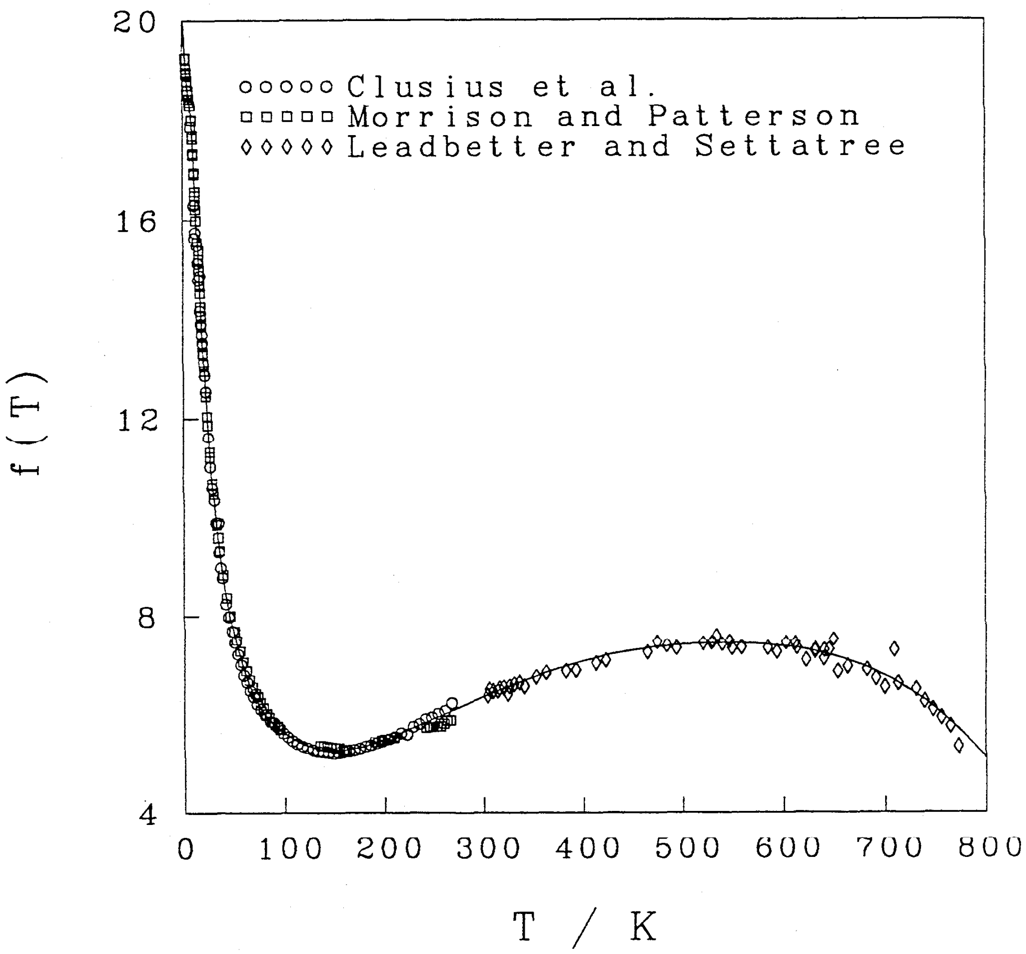

FIG 4. Values calculated from Eq. (4) and the experimental heat-capacity values from 0 to 800 K.

increment results to be fitted simultaneously from the lowest temperatures to the melting point of the crystal with 11 variable knots. The $T=0$ end knot was fixed at a value corresponding to a Debye temperature of 321 K.[12] "Natural spline" end conditions were adopted at each end knot. The first temperature derivative of the heat capacity was significantly better behaved with this method than when using splines of the type given as Eq. (2).

3. Representation of the Thermodynamic Properties of NaCl(cr)

Table 1 lists the sources of the experimental results that were used in the present work. Table 2 lists the experimental results included in the least-squares representation, the difference of the experimental value from the data representation, and the value of σ_i for each observation as it was used for the purpose of creating weighting factors. The σ are the square roots of the assumed variances. Basic statistical methods and expected experimental uncertainties were both used to obtain the assumed variances. The final knot positions are given in Table 3.

3.1. Representation of Heat-Capacity Values

The difference of the experimental heat-capacity values from the representation is shown in Figs. 6 and 7. Also shown is the difference of the values calculated by Kellermann[18] from a set of lattice frequencies for NaCl. It is seen in Fig. 6 that the values of Morrison and Patterson,[9] near 260 K, are larger than the results of the two other sets of heat capacities, one at the same temperature, the other extrapolated from somewhat higher temperatures. The results of Clusius *et al.*,[8] near 260 K, agree better with the extrapolation of the results of Leadbetter and Settatree,[10] than does either set agree with the Morrison and Patterson results. Leadbetter and Settatree's heat-capacity values show excellent agreement with Dawson *et al.*'s[13] enthalpy-increment measurements (see below). The agreement of these three sets of measurements suggests a higher probability that Morrison and Patterson's measurements are somewhat in error, at least near 260 K. Both Morrison and Patterson and Leadbetter[19] measured the heat capacity of the Calorimetry Conference sample of aluminum oxide with their respective calorimeters. Near 250 K, Morrison and

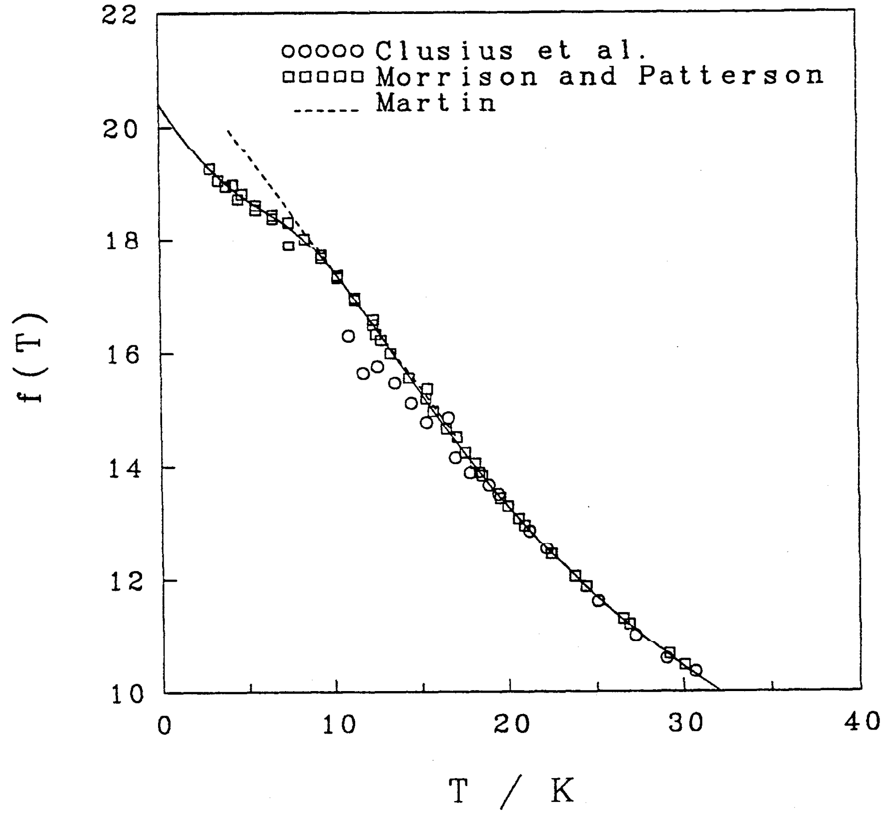

FIG 5. Values calculated from Eq. (4) and the experimental heat-capacity values for low temperatures. The solid line is calculated from the fitted equation. The dashed line represents values from Martin.[21]

TABLE 1. Literature sources for heat-capacity and enthalpy-increment results

Ref.	Type	Temperature range	Number	Year
8	$C^\circ_{p,m}$	2.9 K–266.5 K	93	1956
9	$C^\circ_{p,m}$	10.9 K–267.5 K	70	1949
10	$C^\circ_{p,m}$	304.4 K–772.5 K	54	1969
13	$\Delta H^\circ_m\ (T_2 \rightarrow T_1)$	672 K–1071 K	20	1963
14	$\Delta H^\circ_m\ (T_2 \rightarrow T_1)$	1002 K–1058 K	5	1973
15	$\Delta H^\circ_m\ (T_2 \rightarrow T_1)$	812 K–1058 K	6	1929
16	$\Delta H^\circ_m\ (T_2 \rightarrow T_1)$	430 K–1041 K	12	1935
17	$\Delta H^\circ_m\ (T_2 \rightarrow T_1)$	372 K–1035 K	11	1913

Patterson' s results are 0.2% larger than the values given by Ditmars *et al.*[20] and Leadbetter's values agree within 0.1% for temperatures near 300 K. Thus, the difference in Morrison and Patterson's results from the other results, again for temperatures near 260 K, cannot be attributed to a systematic calorimetric error present for all measurements. This leaves two other possibilities for rationalization of the discrepancies. These are: 1) an impurity in Morrison and Patterson's sample of NaCl; 2) a calorimetric error present in their highest temperature measurements. If the first case is correct then it would be reasonable to remove their entire set of measurements from the set of results to be fitted. If the second case is correct then it would be reasonable to remove the highest temperature results of Morrison and Patterson and perhaps the low temperature results of Clusius *et al.* (because of the demonstrated accuracy of Morrison and Patterson's calorimeter, at least above 80 K, through their aluminum oxide measurements.) However, information is not available that allows a preference of either of these cases. Thus, the Clusius *et al.* results were assumed to have the same standard errors as the Morrison *et al.* results with the exception of temperatures below 20 K; the Morrison *et al.* results from 242 to 267 K were not included in the fitted data set; and the standard error assigned to Leadbetter and Settatree's results was approximately 0.33 $J \cdot K^{-1} \cdot mol^{-1}$. The Clusius *et al.* results below 20 K were not included in the data set to be fitted for the following reason. The values of the Debye temperature calculated from the Clusius *et al.* results were smaller than those obtained from the Morrison and Patterson results. The values of the Debye temperature calculated by Martin[21] from his calorimetric heat-capacity values are somewhat larger than those reported by Morrison and Patterson, however, Martin's heat-capacity values were not published. Values of $f(T)$ estimated from a figure in reference 21 are shown in Fig. 5 as a dashed line. The crude net effect on the least-squares procedure of including Martin's larger values (which were not available) and

TABLE 2a. Experimental heat–capacity values included in the data representation[a]

$C^\circ_{p,m}$(exp.) / J·K^{-1}·mol^{-1}	$C^\circ_{p,m}$(calc.) / J·K^{-1}·mol^{-1}	[$C^\circ_{p,m}$(exp.) − $C^\circ_{p,m}$(calc.)] / J·K^{-1}·mol^{-1}	T / K	[$C^\circ_{p,m}$(exp.) − $C^\circ_{p,m}$(calc.)] / σ_i	σ_i / J·K^{-1}·mol^{-1}
		Morrison and Patterson[9]			
0.003222	0.003223	−0.000002	2.951	−0.019	0.00008
0.005021	0.004971	0.000049	3.405	0.394	0.00013
0.007117	0.007063	0.000054	3.825	0.431	0.00013
0.009594	0.009724	−0.000130	4.254	−0.912	0.00014
0.011912	0.011746	0.000165	4.531	0.919	0.00018
0.013539	0.013635	−0.000096	4.763	−0.468	0.00021
0.021548	0.021332	0.000215	5.539	0.668	0.00032
0.021309	0.021332	−0.000023	5.539	−0.072	0.00032
0.034213	0.034321	−0.000108	6.511	−0.215	0.00050
0.034585	0.034367	0.000218	6.514	0.434	0.00050
0.05058	0.05121	−0.00063	7.456	−0.831	0.00075
0.05138	0.05123	0.00015	7.457	0.197	0.00075
0.07280	0.07319	−0.00039	8.394	−0.514	0.00075
0.07284	0.07322	−0.00037	8.395	−0.494	0.00075
0.10180	0.10136	0.00044	9.327	0.434	0.00100
0.10108	0.10146	−0.00038	9.330	−0.376	0.00100
0.13891	0.13843	0.00048	10.291	0.347	0.00138
0.13828	0.13869	−0.00041	10.297	−0.295	0.00138
0.18715	0.18688	0.00027	11.287	0.146	0.00188
0.18648	0.18731	−0.00083	11.295	−0.441	0.00188
0.24815	0.24782	0.00033	12.288	0.134	0.00247
0.24539	0.24850	−0.00311	12.298	−1.259	0.00247
0.26359	0.25967	0.00392	12.460	1.487	0.00264
0.28368	0.28041	0.00326	12.747	1.147	0.00285
0.32618	0.32325	0.00294	13.292	0.900	0.00326
0.4201	0.4178	0.0022	14.326	0.533	0.00418
0.5217	0.5242	−0.0025	15.301	−0.470	0.00523
0.5318	0.5332	−0.0014	15.377	−0.271	0.00531
0.5766	0.5762	0.0004	15.727	0.064	0.00577
0.6766	0.6764	0.0001	16.478	0.019	0.00678
0.7523	0.7643	−0.0120	17.075	−1.591	0.00753
0.8351	0.8369	−0.0018	17.534	−0.236	0.00753
0.9301	0.9387	−0.0086	18.134	−0.939	0.00920
0.9795	0.9768	0.0027	18.347	0.277	0.00962
1.0104	1.0094	0.0010	18.525	0.102	0.01004
1.2138	1.2127	0.0011	19.557	0.092	0.01213
1.3008	1.3009	−0.0001	19.970	−0.011	0.01297
1.4385	1.4371	0.0014	20.573	0.098	0.01423
1.5238	1.5217	0.0021	20.930	0.137	0.01506
1.9230	1.9169	0.0060	22.451	0.313	0.01925
2.3045	2.3000	0.0045	23.754	0.197	0.02301
2.5033	2.5048	−0.0015	24.399	−0.058	0.02510
3.2329	3.2473	−0.014	26.522	−0.444	0.03222
3.3673	3.3753	−0.008	26.861	−0.239	0.03347
4.289	4.3139	−0.025	29.176	−0.605	0.04184
4.678	4.7071	−0.029	30.076	−0.703	0.04184
6.134	6.1943	−0.061	33.237	−0.965	0.06276
6.841	6.9122	−0.071	34.667	−1.066	0.06694
7.673	7.7543	−0.081	36.292	−1.073	0.07531
9.468	9.5715	−0.103	39.674	−1.072	0.09623
11.510	11.631	−0.121	43.397	−1.032	0.11715
13.422	13.574	−0.151	46.860	−1.131	0.13389
15.230	15.386	−0.156	50.090	−1.037	0.15062
16.477	16.649	−0.172	52.367	−1.057	0.16318
18.150	18.397	−0.247	55.588	−1.374	0.17991
19.803	20.053	−0.250	58.746	−1.270	0.19665
21.297	21.606	−0.310	61.842	−1.452	0.21338
22.803	23.072	−0.269	64.911	−1.168	0.23012
24.142	24.448	−0.306	67.957	−1.261	0.24267
25.447	25.748	−0.301	71.009	−1.177	0.25522
26.213	26.572	−0.359	73.046	−1.361	0.26359
27.388	27.710	−0.322	76.010	−1.184	0.27196
28.556	28.787	−0.231	78.990	−0.813	0.28451

TABLE 2a. Experimental heat–capacity values included in the data representation – Continued

$\frac{C^\circ_{p,m}(\text{exp.})}{\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}}$	$\frac{C^\circ_{p,m}(\text{calc.})}{\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}}$	$\frac{C^\circ_{p,m}(\text{exp.}) - C^\circ_{p,m}(\text{calc.})}{\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}}$	$\frac{T}{\text{K}}$	$\frac{C^\circ_{p,m}(\text{exp.}) - C^\circ_{p,m}(\text{calc.})}{\sigma_i}$	$\frac{\sigma_i}{\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}}$
28.543	28.813	−0.270	79.065	−0.949	0.28451
29.706	29.832	−0.126	82.067	−0.424	0.29706
30.585	30.669	−0.084	84.673	−0.276	0.30543
31.493	31.481	0.012	87.324	0.040	0.31380
32.225	32.233	−0.008	89.896	−0.025	0.32217
32.941	33.005	−0.065	92.648	−0.198	0.32635
33.794	33.790	0.004	95.573	0.011	0.33472
41.258	41.480	−0.222	135.505	−0.663	0.33472
41.685	41.932	−0.247	138.937	−0.737	0.33472
42.158	42.375	−0.217	142.509	−0.647	0.33472
42.614	42.808	−0.194	146.224	−0.579	0.33472
43.179	43.326	−0.147	150.994	−0.440	0.33472
43.535	43.694	−0.159	154.626	−0.476	0.33472
44.003	44.037	−0.034	158.219	−0.101	0.33472
44.359	44.356	0.002	161.771	0.007	0.33472
46.292	46.366	−0.074	190.225	−0.222	0.33472
46.547	46.549	−0.002	193.523	−0.007	0.33472
46.698	46.723	−0.026	196.794	−0.076	0.33472
46.886	46.889	−0.003	200.048	−0.010	0.33472
47.120	47.047	0.073	203.282	0.217	0.33472
47.262	47.199	0.063	206.497	0.190	0.33472
47.447	47.344	0.102	209.696	0.305	0.33472
48.844	48.596	0.248	242.093	*	*
49.003	48.711	0.292	245.549	*	*
49.183	48.822	0.361	248.990	*	*
49.350	48.946	0.404	252.915	*	*
49.497	49.051	0.446	256.333	*	*
49.543	49.153	0.390	259.737	*	*
49.585	49.252	0.332	263.128	*	*
49.718	49.349	0.370	266.504	*	*
		Clusius *et al.*[8]			
0.1883	0.1667	0.0216	10.90	*	*
0.251	0.211	0.040	11.71	*	*
0.293	0.265	0.028	12.54	*	*
0.368	0.341	0.027	13.50	*	*
0.460	0.430	0.030	14.45	*	*
0.561	0.529	0.032	15.34	*	*
0.669	0.697	−0.027	16.62	*	*
0.787	0.750	0.037	16.98	*	*
0.920	0.888	0.033	17.84	*	*
1.088	1.084	0.004	18.92	*	*
1.188	1.193	−0.004	19.46	*	*
1.590	1.588	0.002	21.2	0.126	0.01674
1.849	1.848	0.001	22.2	0.087	0.01674
2.761	2.738	0.023	25.1	0.786	0.02929
3.565	3.506	0.059	27.2	1.763	0.03347
4.301	4.239	0.062	29.0	1.491	0.04184
4.945	4.988	−0.043	30.7	−0.851	0.05021
5.782	5.690	0.092	32.2	1.577	0.05858
6.594	7.031	−0.437	34.9	−6.534	0.06694
7.422	7.289	0.133	35.4	1.772	0.07531
8.435	8.235	0.200	37.2	2.391	0.08368
9.301	9.150	0.151	38.9	1.644	0.09205
11.389	11.076	0.313	42.4	2.772	0.11297
12.853	12.584	0.269	45.1	2.073	0.12970
14.477	14.215	0.261	48.0	1.788	0.14644
16.033	15.726	0.307	50.7	1.931	0.15899
17.640	17.324	0.315	53.6	1.794	0.17573
19.246	18.935	0.311	56.6	1.618	0.19246
20.769	20.387	0.383	59.4	1.828	0.20920
22.217	21.975	0.242	62.6	1.089	0.22175
23.732	23.481	0.250	65.8	1.049	0.23849
25.129	24.987	0.142	69.2	0.567	0.25104

TABLE 2a. Experimental heat – capacity values included in the data representation – Continued

$\frac{C^\circ_{p,m}(\text{exp.})}{\text{J·K}^{-1}\text{·mol}^{-1}}$	$\frac{C^\circ_{p,m}(\text{calc.})}{\text{J·K}^{-1}\text{·mol}^{-1}}$	$\frac{C^\circ_{p,m}(\text{exp.}) - C^\circ_{p,m}(\text{calc.})}{\text{J·K}^{-1}\text{·mol}^{-1}}$	$\frac{T}{\text{K}}$	$\frac{C^\circ_{p,m}(\text{exp.}) - C^\circ_{p,m}(\text{calc.})}{\sigma_i}$	$\frac{\sigma_i}{\text{J·K}^{-1}\text{·mol}^{-1}}$
26.610	26.434	0.176	72.7	0.658	0.26778
27.957	27.855	0.102	76.4	0.365	0.28033
29.305	29.206	0.099	80.2	0.338	0.29288
31.087	30.988	0.099	85.7	0.319	0.30962
31.991	32.090	−0.100	89.4	−0.313	0.31798
33.338	33.346	−0.008	93.9	−0.023	0.33472
34.627	34.541	0.086	98.5	0.257	0.33472
35.765	35.651	0.114	103.1	0.340	0.33472
36.853	36.681	0.171	107.7	0.512	0.33472
37.823	37.637	0.187	112.3	0.557	0.33472
38.761	38.578	0.183	117.2	0.547	0.33472
39.648	39.495	0.153	122.4	0.456	0.33472
40.509	40.351	0.158	127.7	0.473	0.33472
41.254	41.077	0.177	132.6	0.528	0.33472
41.915	41.772	0.143	137.7	0.428	0.33472
42.543	42.421	0.121	142.9	0.363	0.33472
43.171	43.006	0.165	148.0	0.493	0.33472
43.664	43.552	0.112	153.2	0.335	0.33472
44.150	44.072	0.078	158.6	0.232	0.33472
44.618	44.539	0.079	163.9	0.235	0.33472
45.045	44.984	0.061	169.4	0.181	0.33472
45.447	45.392	0.054	174.9	0.162	0.33472
45.815	45.780	0.035	180.6	0.103	0.33472
46.175	46.137	0.038	186.3	0.113	0.33472
46.526	46.477	0.049	192.2	0.147	0.33472
46.861	46.791	0.070	198.1	0.209	0.33472
46.852	46.791	0.062	198.1	0.185	0.33472
47.170	47.091	0.079	204.2	0.236	0.33472
47.438	47.371	0.067	210.3	0.200	0.33472
47.647	47.634	0.014	216.4	0.041	0.33472
48.074	47.881	0.193	222.5	0.576	0.33472
48.074	48.113	−0.038	228.5	−0.115	0.33472
48.292	48.340	−0.048	234.7	−0.143	0.33472
48.426	48.566	−0.140	241.2	−0.419	0.33472
48.668	48.771	−0.103	247.4	−0.308	0.33472
48.844	48.977	−0.133	253.9	−0.396	0.33472
49.053	49.179	−0.125	260.6	−0.374	0.33472
49.070	49.377	−0.307	267.5	−0.917	0.33472
		Leadbetter and Settatree[10]			
50.33	50.31	0.02	304.4	0.076	0.33472
50.17	50.34	−0.17	305.8	−0.519	0.33472
50.38	50.43	−0.05	309.6	−0.149	0.33472
50.54	50.53	0.01	314.5	0.029	0.33472
50.50	50.57	−0.06	316.0	−0.193	0.33472
50.63	50.66	−0.03	320.3	−0.094	0.33472
51.00	50.75	0.25	324.6	0.760	0.33472
50.79	50.78	0.01	326.1	0.042	0.33472
50.88	50.88	0.00	330.8	0.002	0.33472
51.00	50.98	0.02	336.1	0.057	0.33472
51.30	51.09	0.21	341.3	0.623	0.33472
51.34	51.31	0.03	352.8	0.081	0.33472
51.51	51.50	0.01	362.7	0.022	0.33472
52.01	51.86	0.15	382.4	0.444	0.33472
52.26	52.04	0.22	392.5	0.654	0.33472
52.55	52.39	0.16	412.6	0.468	0.33472
52.72	52.57	0.15	422.6	0.446	0.33472
53.39	53.28	0.11	464.2	0.319	0.33472
53.30	53.44	−0.14	473.9	−0.417	0.33472
53.60	53.61	−0.01	483.6	−0.024	0.33472
53.85	53.77	0.08	493.3	0.247	0.33472
54.18	54.20	−0.02	520.0	−0.048	0.33472
54.31	54.33	−0.02	528.2	−0.065	0.33472
54.31	54.35	−0.04	529.6	−0.131	0.33472

TABLE 2a. Experimental heat – capacity values included in the data representation – Continued

$\frac{C^\circ_{p,m}(\text{exp.})}{\text{J·K}^{-1}\text{·mol}^{-1}}$	$\frac{C^\circ_{p,m}(\text{calc.})}{\text{J·K}^{-1}\text{·mol}^{-1}}$	$\frac{C^\circ_{p,m}(\text{exp.}) - C^\circ_{p,m}(\text{calc.})}{\text{J·K}^{-1}\text{·mol}^{-1}}$	$\frac{T}{\text{K}}$	$\frac{C^\circ_{p,m}(\text{exp.}) - C^\circ_{p,m}(\text{calc.})}{\sigma_i}$	$\frac{\sigma_i}{\text{J·K}^{-1}\text{·mol}^{-1}}$
54.22	54.41	−0.19	533.3	−0.557	0.33472
54.52	54.50	0.01	539.1	0.045	0.33472
54.56	54.62	−0.06	546.3	−0.168	0.33472
54.77	54.65	0.12	548.6	0.349	0.33472
54.89	54.80	0.10	558.0	0.287	0.33472
55.27	55.19	0.08	583.7	0.227	0.33472
55.48	55.34	0.14	593.0	0.423	0.33472
55.40	55.48	−0.09	602.3	−0.259	0.33472
55.52	55.63	−0.11	611.5	−0.315	0.33472
55.65	55.65	−0.01	613.2	−0.020	0.33472
56.02	55.80	0.23	622.3	0.673	0.33472
55.94	55.94	−0.00	631.1	0.000	0.33472
55.90	55.94	−0.05	631.3	−0.135	0.33472
56.19	56.08	0.11	639.9	0.321	0.33472
56.02	56.09	−0.07	640.4	−0.204	0.33472
56.07	56.17	−0.11	645.2	−0.316	0.33472
55.90	56.24	−0.34	649.5	−1.030	0.33472
56.61	56.32	0.29	653.9	0.873	0.33472
56.61	56.48	0.13	663.5	0.383	0.33472
56.86	56.82	0.04	682.4	0.135	0.33472
57.11	56.98	0.13	691.3	0.398	0.33472
57.36	57.14	0.22	700.1	0.655	0.33472
56.74	57.32	−0.58	709.1	−0.695	0.83680
57.40	57.40	0.01	713.2	0.024	0.33472
57.66	57.75	−0.09	730.5	−0.270	0.33472
57.95	57.92	0.03	738.9	0.078	0.33472
58.16	58.10	0.05	747.3	0.163	0.33472
58.37	58.29	0.08	755.7	0.234	0.33472
58.58	58.49	0.09	764.5	0.262	0.33472
58.99	58.67	0.32	772.5	0.955	0.33472

[a]σ_i is the estimated standard error of the measurement; a * indicates that the observation was not included in the least squares representation.

TABLE 2b. Experimental enthalpy – increment values included in the data representation

$\frac{\Delta H^\circ_m\ (T_2 \rightarrow T_1)(\text{exp.})}{\text{J·mol}^{-1}}$	$\frac{\Delta H^\circ_m\ (T_2 \rightarrow T_1)(\text{calc.})}{\text{J·mol}^{-1}}$	$\frac{\delta\Delta H^\circ_m\ (T_2 \rightarrow T_1)}{\text{J·mol}^{-1}}$	$\frac{T_1}{\text{K}}$	$\frac{T_2}{\text{K}}$	$\frac{\delta\Delta H^\circ_m\ (T_2 \rightarrow T_1)}{\sigma_i}$	$\frac{\sigma_i}{\text{J·mol}^{-1}}$
			Dawson *et al.*[13]			
20033	20032	1	672.2	298.15	0.025	41.84
20033	20032	1	672.2	298.15	0.025	41.84
22979	22967	11	723.6	298.15	0.245	46.02
22928	22961	−33	723.5	298.15	−0.720	46.02
25983	25992	−9	775.6	298.15	−0.179	50.21
25786	25821	−35	772.7	298.15	−0.704	50.21
28828	28852	−25	823.8	298.15	−0.421	58.58
28983	28936	46	825.2	298.15	0.788	58.58
31878	31845	33	873.1	298.15	0.522	62.76
31870	31784	86	872.1	298.15	1.367	62.76
34957	34997	−39	923.7	298.15	−0.552	71.13
34849	34858	−9	921.5	298.15	−0.130	71.13
38292	38317	−25	975.5	298.15	−0.328	75.31
38196	38258	−62	974.6	298.15	−0.828	75.31
41497	41581	−84	1024.9	298.15	−1.001	83.68
41062	41339	−278	1021.3	298.15	−3.318	83.68
44836	44783	53	1071.9	298.15	0.598	87.86
44652	44652	0	1070.0	298.15	−0.002	87.86
44861	44742	119	1071.3	298.15	1.295	92.05
44903	44749	154	1071.4	298.15	1.674	92.05

TABLE 2b. Experimental enthalpy – increment values included in the data representation — Continued

$\Delta H_m^\circ\ (T_2\to T_1)$(exp.) J·mol^{-1}	$\Delta H_m^\circ\ (T_2\to T_1)$(calc.) J·mol^{-1}	$\delta\Delta H_m^\circ\ (T_2\to T_1)$ J·mol^{-1}	T_1 K	T_2 K	$\delta\Delta H_m^\circ\ (T_2\to T_1)$ / σ_i	σ_i J·mol^{-1}
			Holm and Groenvold[14]			
40033	40055	−23	1002.0	298.15	−0.056	402.
41003	41836	−833	1028.7	298.15	*	*
42765	42538	227	1039.1	298.15	0.531	427.
43334	43231	103	1049.3	298.15	0.236	435.
43593	43853	−260	1058.4	298.15	−0.598	435.
			Roth and Bertram[15]			
28576	28406	171	812.15	293.15	0.300	569.
35003	34583	420	913.15	293.15	0.598	702.
37238	37766	−529	963.15	293.15	−0.710	744.
40685	40979	−294	1012.15	293.15	−0.362	811.
43581	43881	−300	1055.15	293.15	−0.345	870.
43547	44087	−539	1058.15	293.15	−0.620	870.
			Lyashenko[16]			
7272	7131	140	429.65	290.95	0.986	142.
8255	8294	−39	451.35	290.65	−0.245	158.
14870	15008	−138	575.95	291.15	−0.472	292.
16556	16396	160	601.15	291.25	0.478	334.
21343	21181	161	686.45	291.35	0.378	426.
25439	25407	31	760.15	291.75	0.062	510.
25723	25607	116	763.65	291.85	0.226	514.
33882	33566	316	896.15	292.25	0.466	677.
42350	42759	−409	1038.15	292.45	−0.484	845.
42530	42910	−380	1040.45	292.55	−0.447	849.
42581	42903	−323	1040.65	292.95	−0.380	849.
42355	42937	−583	1041.15	292.95	−0.689	845.
			Magnus[17]			
4147	4171	−24	372.15	290.15	−0.564	41.8
4157	4171	−14	372.15	290.15	−0.334	41.8
4141	4171	−30	372.15	290.15	−0.714	41.8
13217	13101	116	541.15	291.15	0.868	134.
13188	13101	87	541.15	291.15	0.649	134.
13209	13101	108	541.15	291.15	0.806	134.
29246	29524	−278	829.15	291.15	−0.950	293.
29430	29584	−154	830.15	291.15	−0.527	293.
41463	42756	−1293	1037.15	291.15	*	*
41752	42689	−937	1036.15	291.15	*	*
41350	42621	−1271	1035.15	291.15	*	*

[a] σ_i is the estimated standard error of the measurement; a * indicates that the observation was not included in the least squares representation; $\delta\Delta H_m^\circ\ (T_2\to T_1))$ is the difference between the experimental and the calculated value, $\Delta H_m^\circ\ (T_2\to T_1)$(exp.) − $\Delta H_m^\circ\ (T_2\to T_1)$(calc.)

TABLE 3. Least – squares estimated knot positions

T_i/K	d_i
0	20.4174
5	18.6946
7.5	18.2037
15	15.2827
20	13.2900
45	8.12535
90	5.77101
220	5.62745
400	7.04825
550	7.41175
800	5.08930
1100	−8.76890

Clusius' smaller values is to appproximately cancel each other in the determination of the variable parameters. One method that approximates this effect is to omit the Clusius *et al.* values for temperatures less than 20 K from the fit.

3.2. Representation of Enthalpy-Increment Values.

Figure 8 shows the difference of experimental enthalpy-increment values from the representation. The values are shown against the higher temperature of the measurements. Dawson *et al.*[13] reported enthalpy-increment values for both sodium chloride and aluminum oxide. Their results for aluminum oxide were 0.3% greater

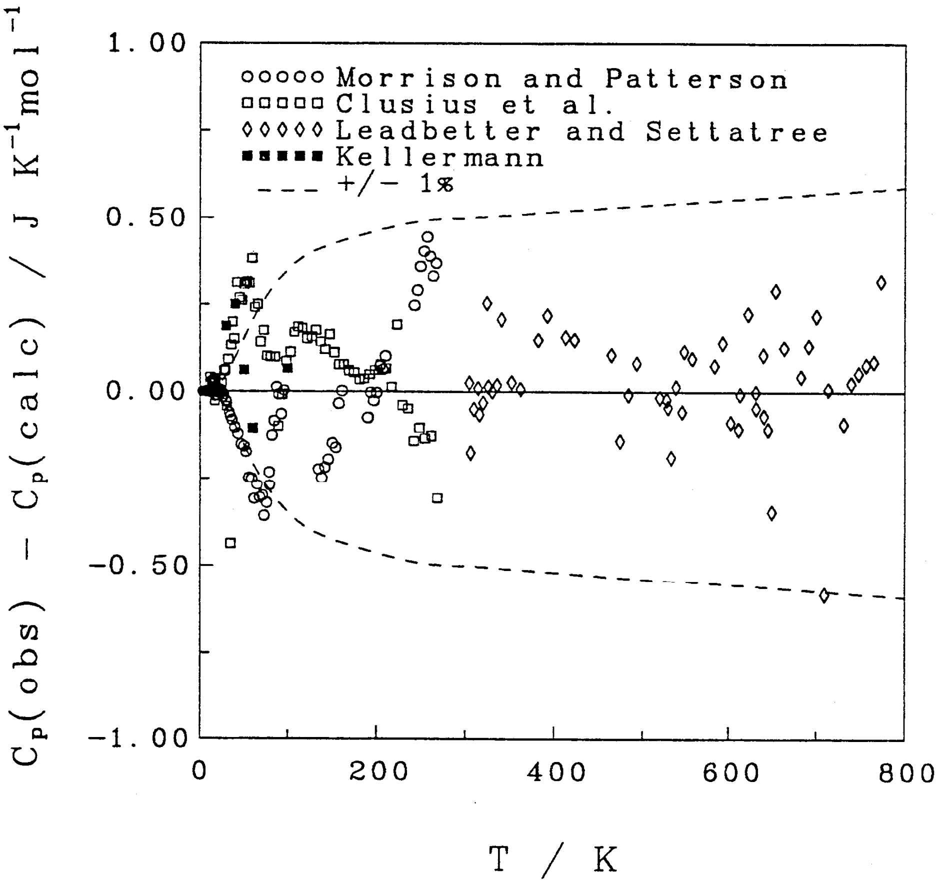

FIG 6. Difference of experimental heat-capacity values from the representation. The differences of Kellermann's calculated values from the fitted equation are also shown.

than the values given by Ditmars *et al.*[20] Assuming that this 0.3% difference represented a systematic calorimetric error, the enthalpy-increment values for NaCl(cr) were reduced by 0.3%. The thus-corrected enthalpy-increment values showed a root-mean-square error of 0.15% (omitting the largest residual) from the representation. The enthalpy-increment results from Roth and Bertram,[15] Holm and Groenvold,[14] and Lyashenko[16] were all fitted within expected error limits. The three highest temperature results from Magnus[17] were given no weight in the fit as these values disagreed significantly from the remainder of the values.

A systematic error in the heat-capacity values of Leadbetter and Settatree (which would have to exist if the Morrison and Patterson 260 K results were truly accurate to 0.2%) would generate a systematic error in a calculated enthalpy increment. No systematic difference of the observed enthalpy-increment values, especially those of Dawson *et al.* and those of Holm and Groenvold,[14] from those calculated from the representation, is seen in Fig. 8. This observation supports the suspicion of an unknown systematic error in the Morrison and Patterson heat-capacity results.

4. Thermodynamic Properties of NaCl(cr) and Estimated Errors

Values of the entropy, heat-capacity and enthalpy relative to 0 K, calculated from the fitted spline are given in Table 4. Calculated values of the heat capacity from 0 K to the melting point are shown in Fig. 9. Because of the discrepancies in heat-capacity measurements below 270 K (shown in Figs. 6 and 7) and because an impurity in Morrison and Patterson's sodium chloride sample cannot be eliminated from consideration, the 298.15 K entropy is known to no better than 1%. From 300 K to 800 K, the heat capacities given in Table 3 are accurate to approximately 0.3%; from 800 K to the melting point, the heat capacity values are probably accurate to 1%; between 20 and 300 K they are no more accurate than 1 to 5%.

No attempt was made to convert the temperatures of each experimental observation to a particular temperature scale for two reasons: 1) Only the temperatures for the results of Morrison and Patterson were reported with enough significant digits to give such a conversion significance; 2) When one considers the inaccuracies of the experimental results, as demonstrated in Figs. 6–8, such a correction is clearly much smaller than the uncertainties in the calculated values. As such, the values given in Table 3 could be taken as corresponding to any recent temperature scale.

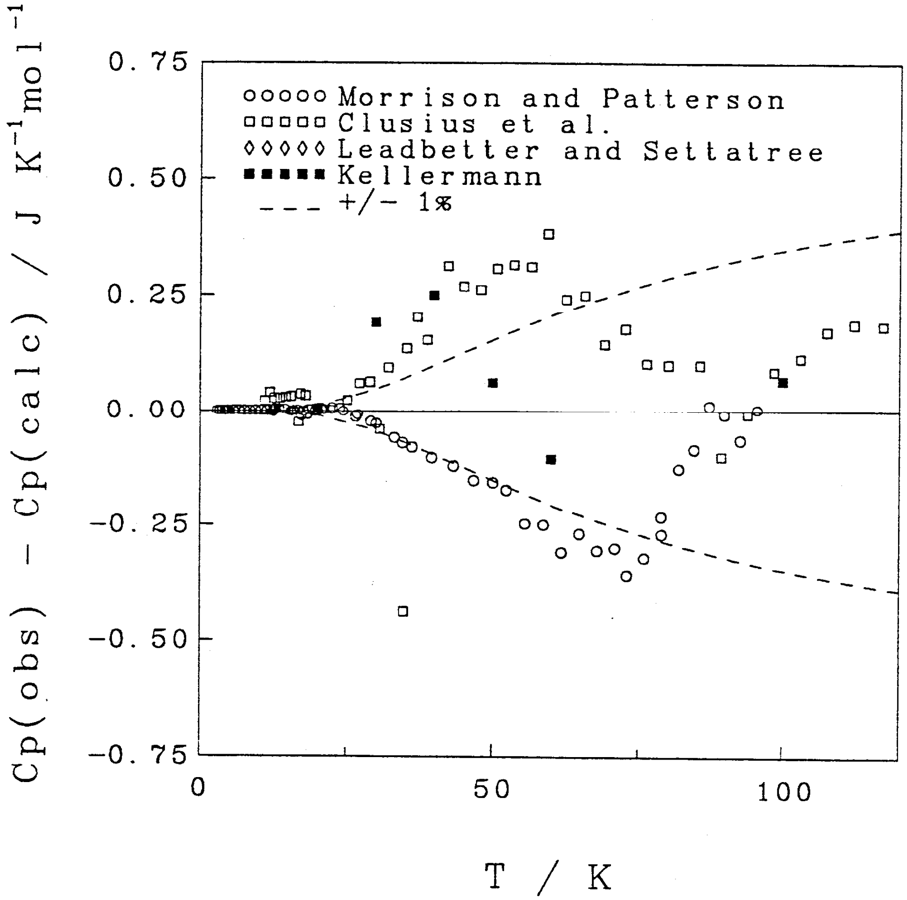

FIG 7. Difference of the low temperature heat-capacity values from the representation. The differences of Kellermann's calculated values from the fitted equation are also shown.

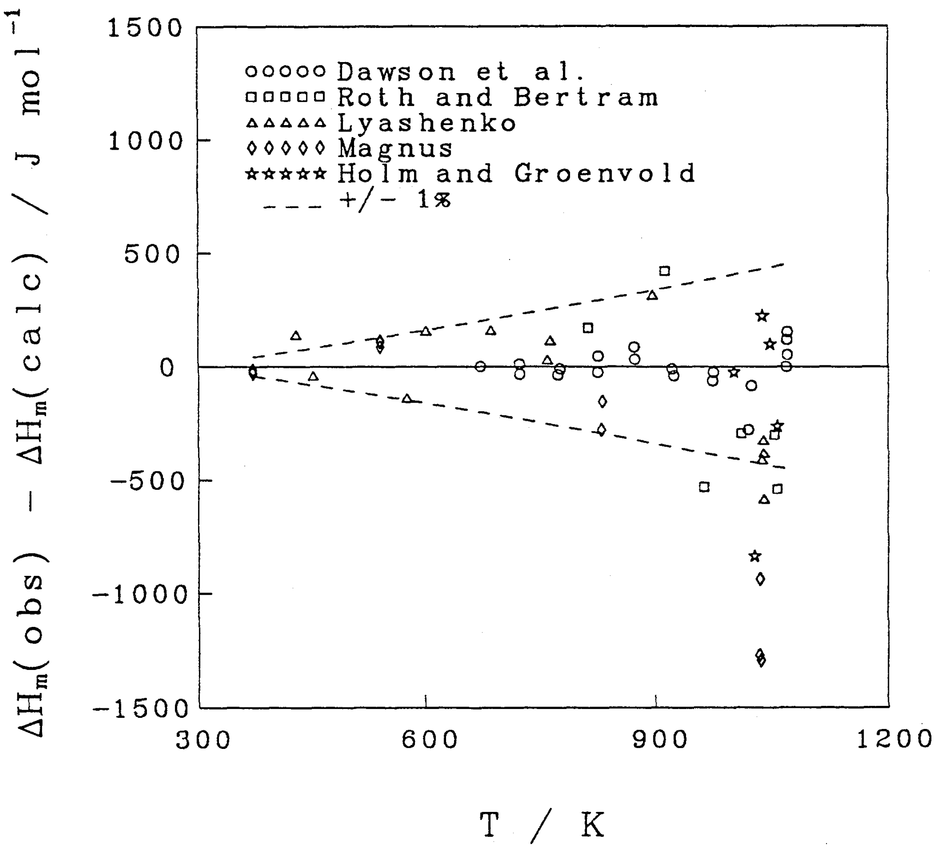

FIG 8. Difference of the experimental enthalpy-increment values from the fitted equation against the higher temperature for the increment.

TABLE 4. Thermodynamic values for NaCl(cr) calculated from the spline coefficients

$\frac{T}{\mathrm{K}}$	$\frac{C^\circ_{p,m}}{\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}}$	$\frac{S^\circ_m}{\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}}$	$\frac{H^\circ_m(T)-H^\circ_m(0\ \mathrm{K})}{\mathrm{kJ{\cdot}mol^{-1}}}$
20	1.31	.39	.006
40	9.75	3.49	.105
60	20.69	9.55	.411
80	29.14	16.73	.915
100	34.91	23.89	1.559
120	39.08	30.65	2.301
140	42.07	36.91	3.114
160	44.20	42.67	3.978
180	45.74	47.97	4.878
200	46.89	52.85	5.805
220	47.78	57.36	6.752
240	48.52	61.55	7.715
260	49.16	65.46	8.692
280	49.71	69.13	9.681
298.15	50.16	72.27	10.587
300	50.21	72.58	10.680
320	50.65	75.83	11.689
340	51.06	78.91	12.706
360	51.45	81.84	13.731
380	51.82	84.63	14.764
400	52.17	87.30	15.804
420	52.52	89.86	16.851
440	52.87	92.31	17.905
460	53.21	94.66	18.966
480	53.55	96.94	20.033
500	53.88	99.13	21.107
520	54.20	101.25	22.188
540	54.52	103.30	23.275
560	54.83	105.29	24.369
580	55.14	107.22	25.468
600	55.45	109.09	26.574
620	55.76	110.92	27.686
640	56.09	112.69	28.805
660	56.42	114.42	29.930
680	56.77	116.11	31.062
700	57.14	117.76	32.201
720	57.53	119.38	33.347
740	57.95	120.96	34.502
760	58.39	122.51	35.665
780	58.85	124.03	36.838
800	59.35	125.53	38.020
820	59.88	127.00	39.212
840	60.45	128.45	40.415
860	61.04	129.88	41.630
880	61.67	131.29	42.857
900	62.33	132.68	44.097
920	63.01	134.06	45.351
940	63.73	135.42	46.618
960	64.48	136.77	47.900
980	65.25	138.11	49.197
1000	66.06	139.44	50.510
1020	66.89	140.75	51.840
1040	67.76	142.06	53.186
1060	68.65	143.36	54.550
1073.80	69.29	144.25	55.502

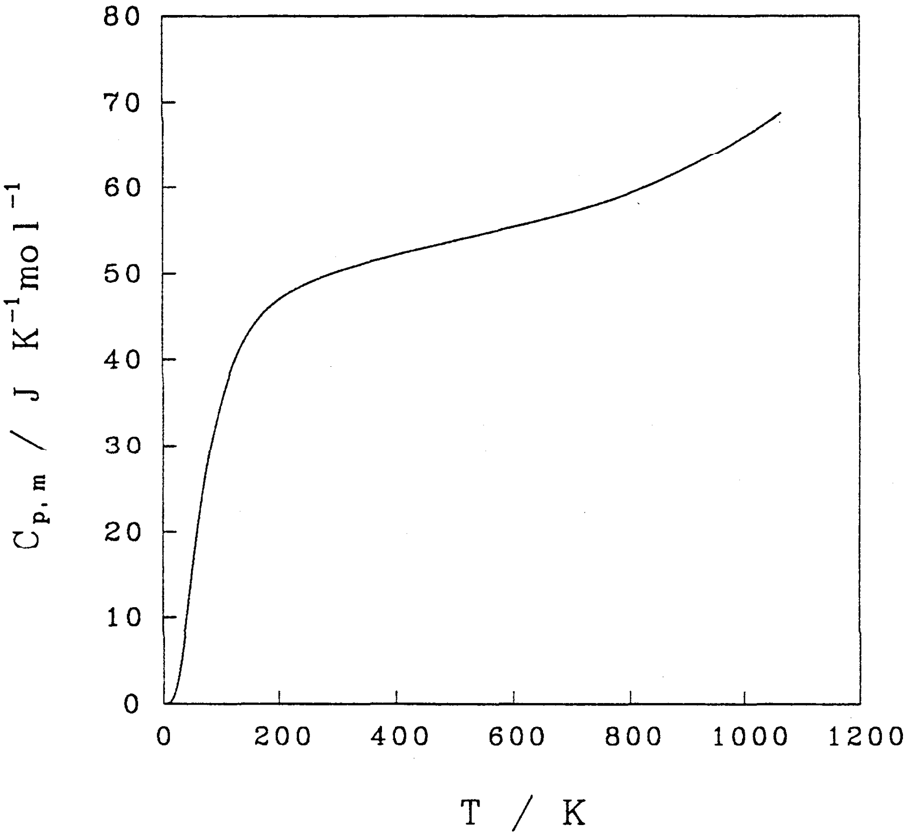

FIG 9. Calculated values of the heat capacity of NaCl(cr) from 0 K to the melting point.

5. Acknowlegment

The author wishes to thank Dr. David Garvin for helpful discussion.

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Appendix 1.

The mechanics of the least-squares representation of the enthalpy-increment and heat-capacity values is described here. Each knot position consisted of a d_i, T_i pair. The d_i of the variable knots that are adjusted by the least-squares routine are the degrees of freedom. A nonlinear least-squares routine was used to adjust the d_i until one or more convergence criteria for the sum of the squares of the errors was met. The sum of the squares of the errors, SSQ, was given by:

$$\mathrm{SSQ} = \sum_{i}^{N_1} \left(\frac{C^{\circ}_{p,m,\mathrm{obs}} - C^{\circ}_{p,m,\mathrm{calc}}}{\sigma_i} \right)^2 + \sum_{j}^{N_2} \left(\frac{\Delta H^{\circ}_{m,\mathrm{obs}} - \Delta H^{\circ}_{m,\mathrm{calc}}}{\sigma_j} \right)^2 \qquad \text{(A-1)}$$

where N_1 and N_2 are the numbers of heat-capacity values and enthalpy-increment values, respectively, and the σ_i and σ_j are the estimated standard errors of each observation (obs and calc indicate the observed value and the calculated value, respectively). For each calculation of SSQ required by the nonlinear least-squares routine, the $C^{\circ}_{p,m,\mathrm{calc}}$ of Eq. (A–1) were calculated from Eqs. (5, 6) and the knot positions. These knot positions included both the fixed knots and the variable knots, the latter having values of d_i selected by the least-squares routine. The values of $\Delta H^{\circ}_{m,\mathrm{calc}}$ were calculated from Eq. (5), integration of Eq. (6), and the values of d_i. A simple discussion of a cubic spline can be found in Applied Numerical Analysis 2nd ed. by C. F. Gerald (Addison Wesley, Reading, MA 1978).

Appendix 2.

One of the reviewers of this work objected to the weighting of the experimental results. The perceived incorrect treatment of the data, according to the reviewer, arises because of "problems with the temperature scale and/or thermometers used in..." the laboratory of Clusius and that the weighting of the experimental results does not take into account systematic errors that would result from these temperature measurement errors. The reviewer cited three cases, in which the results of Clusius were different from the results of others, as the evidence of the temperature measurement error. These three cases were the differences of the heat capacity measurements for germane (GeH_4) reported by Mountfield and Weir[22] from those of Clusius and Faber[23] and "Similar deviations occurred between the heat capacity results of Clusius[24] and those of Flubacher *et al.*[25] and of Clusius[24] and those of Beaumont *et al.*[26] for argon and krypton." The reviewer stated that the differences for NaCl (the results of Clusius *et al.*[8] compared to those of Morrison and Patterson[9]) in Figs. 6 and 7 "...reveals the same kind of deviation involving Clusius" as observed in the three cited cases. The reviewer stated that the results from Clusius for NaCl thus "...are suspect over a wide range and it is unsatisfactory for the author to exclude Clusius' data only below 20 K" and that all of the results of Clusius "...below 80 K should be eliminated." The reviewer further stated that, given the points described above, the variances that should be assigned to the results of Clusius "...are several times higher at temperatures above 80 K and the author should include these realistic errors in his numbers."

Summarizing the points of the reviewer:

1) There were systematic errors in determination of temperature by Clusius for temperatures below 80 K.
2) These systematic errors in temperature determination led to systematic errors in heat capacity measurements for temperatures below 80 K; and both are evidenced in the similarity of differences of the results of Clusius from the results of others for argon, krypton and germane.
3) These similar systematic errors below 80 K should cause all results from Clusius, for temperatures less than 80 K, to be eliminated from the fitted results and for temperatures greater than 80 K the results of Clusius should be assigned variances several times larger than those assigned to the Morrison and Patterson results.

Because of the significance of the reviewer's comments this appendix was added to examine more fully the points raised. It will be shown here that there is very little systematic similarity in the differences of the results above 20 K that were cited by the reviewer. The differences of the results of Clusius *et al.* from a fitted equation for each of argon, krypton and germane are shown for temperatures from 20 K to ~80 K in Fig. A1. Each fitted equation is based on the work cited by the reviewer. The methods used for fitting the results of Morrison and coauthors and of Mountfield and Weir are discussed later. The results from Clusius for Ar(cr) were smaller than those from Flubacher *et al.* by approximately 1.5 percent for all temperatures greater than 20 K. Clusius' results for Kr(cr) were larger than those from Beaumont *et al.* by approximately 0.5 per cent from 25 K to 80 K, while from 80 K to the triple point the agreement of the two sets of results was within the precision of the results from Clusius. The differences for germane were negative near 30 K, change sign near 40 K, were large and positive as the temperature passed 60 K, and then decreased to zero as temperature approached 75 K. In short, the pattern of differences is different for each of the three substances.

A small difference in temperature, ΔT_{calc}, that is related to a small difference in heat capacity can be approximated as:

$$\Delta T_{\mathrm{calc}} = (\partial C_{p,m}/\partial T)^{-1}\, \Delta C_{p,m} \, . \qquad \text{(A2.1)}$$

Through examination of Fig. A1 and Eq. (A2.1) it is clear that for the differences of heat capacity to be due to thermometer errors and/or differences in temperature scales then the difference in temperature scale and/or the thermometer error must have been different in each of the

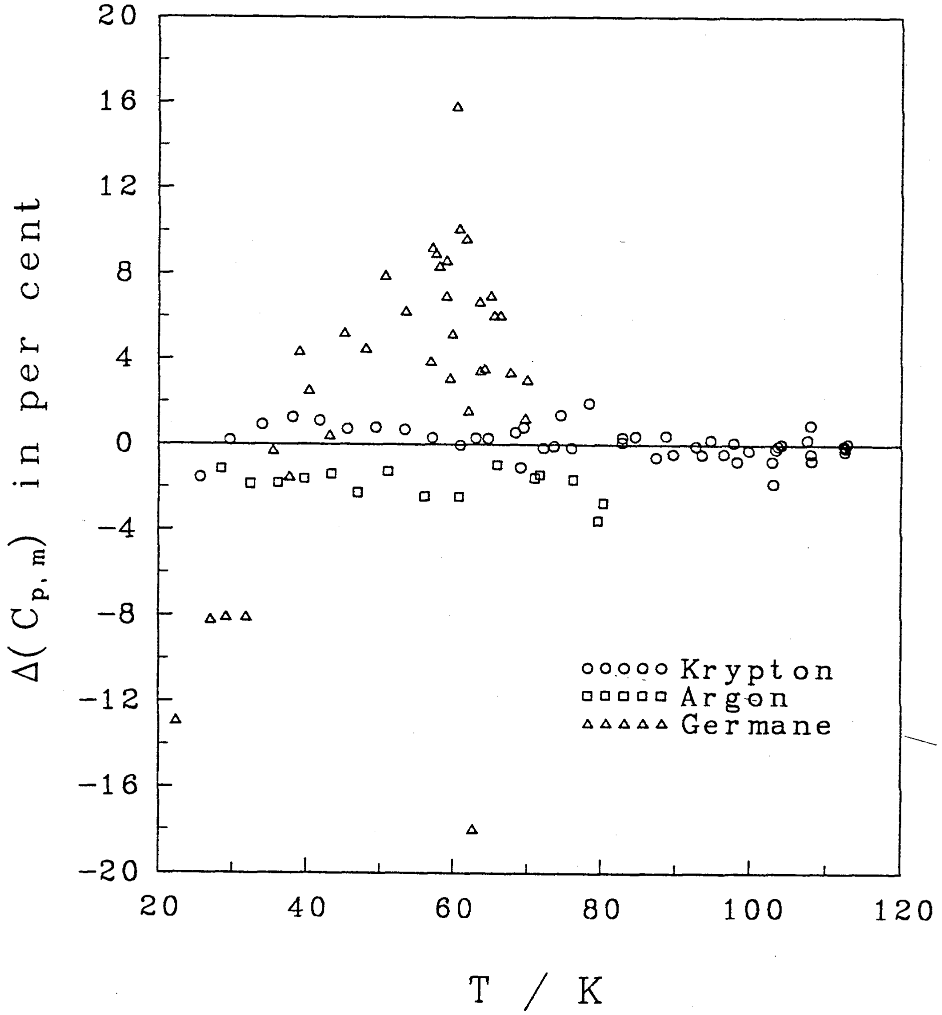

FIG A1. The differences between the heat capacity results of Clusius[24] for Ar(cr) and Kr(cr) and of Clusius and Faber[23] for germane from equations fitted to the results of Flubacher *et al.*,[25] Beaumont *et al.*[26] and Mountfield and Weir.[22]

three cases. The difference in temperature scale and/or thermometer error must have had opposite signs for the measurements of the heat capacities of argon and krypton, respectively. (This is because $(\partial C_{p,m}/\partial T)$ is positive for both of these substances between 0 K and the triple point.) This is not the behavior one expects from either a difference in temperature scales or a systematic error in the calibration or measurement of a thermometer.

The agreement for Kr(cr) can be considered to be within the combined uncertainties of the two studies. There are alternative explanations for the argon and germane differences. The differences for the heat capacity results for Ar(cr) (≈ -1.5 per cent) were approximately the same magnitude and the same sign as the difference in the heat of fusion (-1.3 per cent) of Ar reported in the two studies. This is particularly important in that the heat of fusion is measured at an approximately constant temperature and thus its magnitude is essentially independent of the temperature scale. The similarity in the differences of both the heat capacity results and the heat of fusion results suggests a calorimetric error or a sample error rather than a thermometer error or a large difference in temperature scale. The larger differences observed for germane, in this temperature region, might have been due to incomplete tempering of the crystal, or the presence of small amounts of decomposed (oxidized) germane, or other effects, rather than temperature scale differences or thermometer errors.

Values of transition temperatures are a better comparison of temperature scales and thermometer accuracies than are differences in heat capacity measurements. The best comparisons are first order transitions, however, second order transitions can also be useful. The differences of the triple point temperatures, in order of increasing temperature, for argon,[25] germane,[22] and krypton[26] from those from Clusius were: −0.04 at 83.8 K, 0.01 at 107.27 K, and −0.22 at 116 K. Mountfield and Weir reported transition temperatures for the three lambda transitions of germane as 62.8, 73.8, and 76.7 K. These differ from the values reported by Clusius by −0.1, 0.6, and 0.15. The neon triple point reported by Clusius as 24.55 K, compares with the IPTS–90 defined point of 24.5561 K , the value given by Furukawa[27] of 24.540 K, and the value given by Bigeliesen and Roth[28] (after correction for ice-point differences) of 24.582 K. These differences are representative of the thermometer errors in Clusius' laboratory. A value from Clusius *et al.*[29] of 24.66 K for the triple point of neon is different by about 0.12 K. This value was reported in 1960 and as such is much more recent than Clusius' other results considered here.

The differences in temperature measurements described above, when combined with Eq. A2.1, cannot explain the differences in heat capacity results for NaCl for temperatures greater than 30 K. Near the triple point of water, the thermometer error or temperature scale difference must be as large as 30 K to explain the differences in heat capacity for NaCl. Because neither the differences in temperature scales nor expected errors in thermometer measurement can account for the large differences in heat capacities for NaCl, sample differences or calorimetric errors must be considered as principal sources of error.

There is a similarity in the differences for the three substances for temperatures less than 20 K, and this was one of the reasons for not including the results of Clusius below this temperature. However, these differences have little effect on the entropy or enthalpy at 298 K, as shown below, and are rejected as a basis for setting weights at higher temperatures. The entropy at 20 K is 0.4 $J\cdot K^{-1}\cdot mol^{-1}$. A 10 per cent uncertainty in this quantity results in an error in the 298.15 K value of the entropy, 72.27 $J\cdot K^{-1}\cdot mol^{-1}$, of ± 0.04 $J\cdot K^{-1}\cdot mol^{-1}$. This uncertainty is clearly smaller than that which results from a systematic 0.1 per cent error in heat capacity. Because the heat capacity results for NaCl are significantly less accurate than ±0.1 per cent, even substantial errors in the heat capacity below 20 K have little effect on the properties of the crystal in the region of interest to the NaCl(aq) work, for which the present equation was prepared.

The possibility still remains that the results of Morrison and Patterson are accurate to ±0.2 per cent and that all of the other measurements, those of Clusius and of Leadbetter and Settatree, as well as the enthalpy increment values, were all less accurate than expected and that the agreement of these results was happenstance. Additional measurements would probably clarify matters for the interested parties.

Fitting of the experimental results

The heat capacity results of Flubacher *et al.* for Ar(cr) and of Beaumont *et al.* for Kr(cr) were fitted with the method described in the present work. The values of b and of the Debye temperature used in the representations for Ar(cr) and Kr(cr) were 0.25 and 0.30, and 92.6 and 72, respectively. The variances assigned to the reported heat capacity values were the values described in the references as "accuracy." These values were: ±2 per cent for $T < 20$ K, ±0.2 per cent for 20 K $< T <$ 60 K, and 0.5 per cent for $T > 60$ K, the last of these being an approximation to the phrase "...decreasing above 60 K to about 0.5% at the highest temperatures." The representation of the Ar(cr) results is particularly interesting. The weighted residuals, from 20 K to the triple point, calculated from the least-squares representation for Ar(cr) are shown in Fig. A2. (The weighted residual is the residual divided by the accuracy stated by the authors.) There appears to be a serial correlation pattern in these results. This is observed in groups of three to six residuals of closely spaced value followed by a large and negative residual. The second point to observe is that the accuracy cited by Flubacher *et al.* is about one-half to one-third the imprecision of the measurements, relative to a smooth function that does not have a wildly changing temperature derivative. The imprecision of the krypton results also appears to be about two to three times larger than the stated accuracy (not shown in the figure). The variances assigned to the results for NaCl from Morrison and Patterson are thus representative of the imprecisions seen in the argon and krypton results as well as the NaCl results, in the temperature range from 30 K to 100 K. The same type of serial correlation was not observed for the Kr(cr) results of Beaumont *et al.* (both sets of results were obtained in the same laboratory).

The results for germane, through the lowest-temperature lambda transition, from Mountfield and Weir were also fitted. These and the results from Clusius are shown in Fig. A3. The experimental results were weighted according to the authors' stated accuracies. Values of $b = 0.25$ and of the Debye temperature = 89.8 K were used. Four points, those of lowest temperature were deweighted in the fit because of the assumed presence of a Schottky anomaly at low temperatures. This will not affect our conclusions as we are interested in the comparison of heat capacities for temperatures significantly greater than these. The fitted function is shown in Fig. A3. In addition to the lambda transition shown in Fig. A3, there are an additional two lambda transitions that occur at approximately 73.2 and 76.5 K.

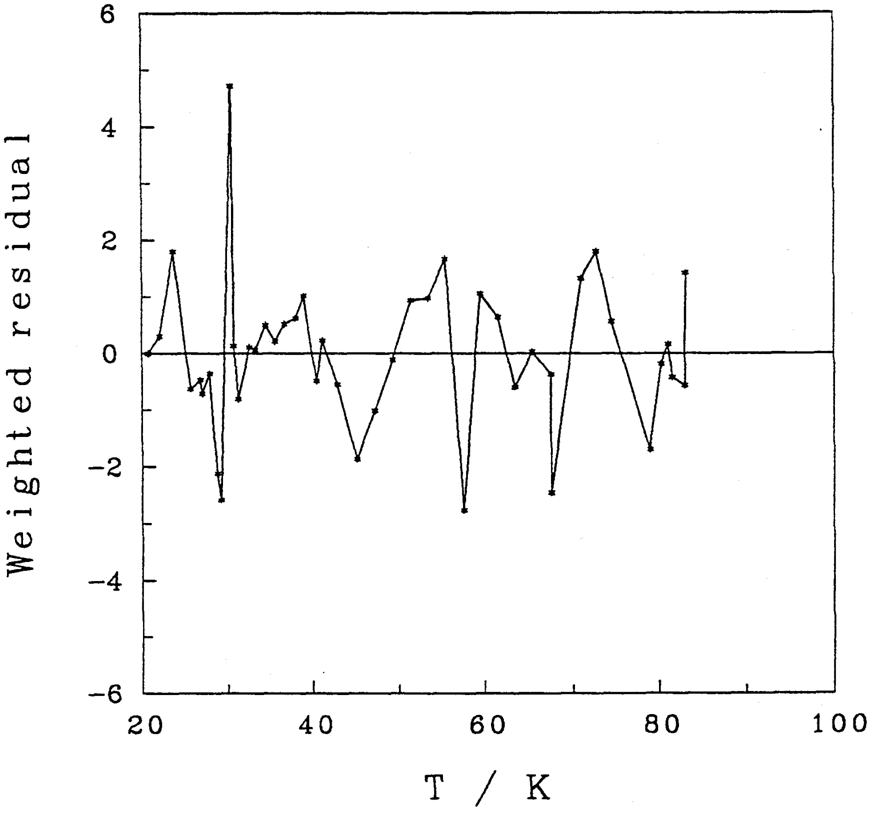

FIG A2. Weighted residuals for the fit to the results of Flubacher *et al.*[25] for Ar(cr).

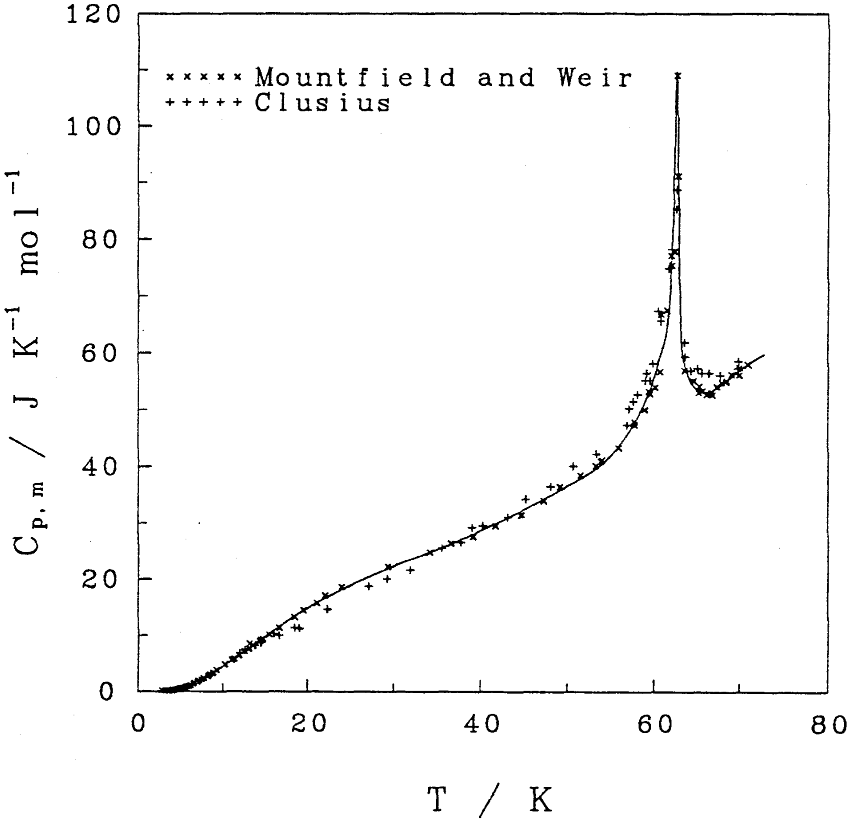

FIG A3. Observed values for the heat capacity of germane from Mountfield and Weir and from Clusius and Faber.[23] The line is the fit to the results from Mountfield and Weir.