

Tris(hydroxymethyl)aminomethane. Heat capacities and thermodynamic properties from 5 to 350 K

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Heat capacities of crystalline TRIS or THAM, $(\text{HOCH}_2)_3\text{CNH}_2$, were measured from 5 to 350 K by adiabatic calorimetry. No thermal anomalies were found in this region. The observed heat capacities yield for $C_p(298.15 \text{ K})$, $S^\circ(298.15 \text{ K}) - S^\circ(0)$, $\{H^\circ(298.15 \text{ K}) - H^\circ(0)\}/T$ and $\{G^\circ(298.15 \text{ K}) - H^\circ(0)\}/T$ values of 39.96, 41.93, 21.28, and $-20.65 \text{ cal}_h \text{ K}^{-1} \text{ mol}^{-1}$. The measurements are employed to establish limits of occluded solvent contamination of this reference material.

1. Introduction

The enthalpies of solution of crystalline tris(hydroxymethyl)aminomethane, $(\text{HOCH}_2)_3\text{CNH}_2$, commonly designated TRIS or THAM in dilute aqueous HCl and NaOH solutions are recommended and widely used for calibration tests in solution calorimetry.^(1,2) This investigation was initiated in part to ascertain the thermo-physical properties of the symmetrical-top molecule and partly to ascertain the possible presence of traces of occluded water and/or methanol in an important reference material. Extra care was therefore taken in the measurements near 273 K and 175 K.

2. Experimental

PREPARATION OF SAMPLE

The sample used was prepared at the Thermochemistry Laboratory at Lund (Lund designation, Sample F).^(1,3) Acidimetric titrations showed a purity of (99.96 ± 0.01) moles per cent. The sample was, after drying at 350 K for 36 h, stored in a glass bottle with plastic cap for at least six months. The crystallites had typical dimensions of 0.2 to 0.5 mm.

CALORIMETRY

Measurements were made by a quasiadiabatic intermittent heating technique in the Mark II calorimetric cryostat previously described.⁽⁴⁾ Above 50 K the adiabatic

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TABLE 1. Heat capacity of tris(hydroxymethyl)aminomethane
(cal_{th} = 4.184 J)

$\frac{T}{K}$	$\frac{C_p}{\text{cal}_{th} \text{ K}^{-1} \text{ mol}^{-1}}$	$\frac{T}{K}$	$\frac{C_p}{\text{cal}_{th} \text{ K}^{-1} \text{ mol}^{-1}}$	$\frac{T}{K}$	$\frac{C_p}{\text{cal}_{th} \text{ K}^{-1} \text{ mol}^{-1}}$
	Series I	31.95	4.803	269.79	36.41
		35.30	5.493	272.86	36.79
211.67	29.45	39.06	6.233	276.95	37.35
220.22	30.50	43.05	6.977	284.33	38.22
230.34	31.71	47.36	7.763		
241.07	32.99	52.64	8.680		Series VI
251.46	34.21	58.98	9.744		
259.22	35.17	63.54	10.502	271.45	36.78
264.47	35.76	67.85	11.180	273.57	36.92
271.70	36.77	74.17	12.152		
274.75	37.03	79.79	12.995		Series VII
278.77	37.51	85.61	13.892		
285.89	38.42	92.83	14.911	149.78	22.32
295.61	39.62	101.25	16.068	151.75	22.60
305.90	40.94			153.71	22.80
316.18	42.22		Series IV	155.16	23.02
326.51	43.51			156.12	23.03
336.93	44.80	42.47	6.882	157.07	23.21
346.01	45.89	46.85	7.691	158.01	23.31
		51.48	8.504	158.94	23.45
	Series II	56.51	9.324	160.34	23.59
		62.10	10.264	169.92	24.70
5.52	0.071	67.95	11.202	171.86	24.93
6.21	0.087	73.19	11.982	173.30	25.18
6.61	0.105	79.19	12.905	174.26	25.22
7.16	0.131	87.03	14.048	175.13	25.36
7.82	0.196	94.47	15.145	176.09	25.33
		103.69	16.393	177.51	25.60
	Series III	113.78	17.76	179.39	25.83
		124.25	19.14		
6.90	0.126	134.42	20.44		Series VIII
7.63	0.182	144.58	21.70		
8.54	0.247	154.69	22.92	269.14	36.33
9.46	0.336	164.76	24.11	271.16	36.65
10.25	0.426	171.26	24.78		
11.14	0.548	174.20	25.29		Series IX
12.28	0.769	177.09	25.56		
13.54	0.981	181.36	26.04	233.86	32.09
14.83	1.223	188.97	26.92	242.67	33.17
16.26	1.489	198.56	28.00	251.26	34.14
17.82	1.803	208.52	29.16	259.63	35.23
19.57	2.165	218.63	30.35	266.21	35.93
21.52	2.579			269.66	36.42
23.71	3.051		Series V	271.67	36.72
26.18	3.582			273.68	36.97
28.95	4.171	266.69	36.12	275.68	37.09

control was achieved with three channels of recording electronic circuitry, with proportional, rate, and reset control actions; below 50 K the control was done manually. The calorimeter (laboratory designation W-42, capacity 93 cm³), made of gold-plated copper, has horizontal, radial vanes for thermal equilibration within the sample space. The capsule-type, strain-free, platinum-resistance thermometer (laboratory designation A-5) was calibrated at the National Bureau of Standards. The crystalline sample was mechanically loaded in the calorimeter. Dry helium gas (53.5 Torr at 300 K)† was used to facilitate thermal equilibration in the sample space. The mass of the sample used was 59.124 g. Buoyancy correction was made on the basis of a sample density of 1.35 g cm⁻³.⁽⁵⁾ The heat capacity of the empty calorimeter together with the thermometer-heater assembly was determined in a separate series of experiments. Corrections were made for small differences in the amount of helium and Apiezon-T grease used in the empty and loaded calorimeter. No vaporization corrections were required. The heat capacity of the sample contributed about 91 per cent of the total apparent heat capacity at 10 K, 68 per cent at 103 K, and 80 per cent at 330 K.

The molar mass of TRIS was taken as 121.137 g mol⁻¹ on the basis of 1961 atomic weights. All determinations of mass, electric potential difference, current, and temperature are referred to calibrations performed at the National Bureau of Standards. The temperature calibration is considered to be in accordance with IPTS-68 within 0.03 K from 10 to 350 K; below 10 K a provisional scale was used.

3. Results

Table 1 lists the experimental, curvature-corrected, molar heat capacities in chronological order. The magnitude of the temperature increments used may be inferred from adjacent mean temperatures. The probable error is estimated at about 5 per cent at 5 K, 1 per cent at 10 K, and decreases to less than 0.1 per cent above 25 K. Table 2

TABLE 2. Thermophysical properties of tris(hydroxymethyl)aminomethane
(cal_{th} = 4.184 J)

$\frac{T}{K}$	$\frac{C_p}{\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}}$	$\frac{\{S^\circ(T) - S^\circ(0)\}}{\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}}$	$\frac{\{H^\circ(T) - H^\circ(0)\}}{\text{cal}_{\text{th}} \text{mol}^{-1}}$	$\frac{-\{G^\circ(T) - H^\circ(0)\}/T}{\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}}$
5	0.057	(0.017)	(0.063)	(0.004)
10	0.418	0.131	0.986	0.032
15	1.239	0.445	5.002	0.112
20	2.257	0.938	13.696	0.253
25	3.332	1.557	27.664	0.451
30	4.397	2.259	46.998	0.693
50	8.231	5.434	174.56	1.943
100	15.89	13.590	784.9	5.741
150	22.36	21.29	1745.0	9.654
200	28.17	28.52	3009.5	13.475
250	34.04	35.43	4563.5	17.18
273.15	36.86	38.57	5384	18.86
298.15	39.96	41.93	6344	20.65
300	40.20	42.18	6418	20.79
340	45.16	47.52	8126	23.62

† Torr = (101 325/760) kPa; cal_{th} = 4.184 J.

lists the smoothed, molar, heat capacities at selected temperatures obtained from polynomials computer-fitted through the experimental points. Below 5 K the Debye limiting T^3 law was used for extrapolation. The estimated error in the thermodynamic functions (also listed in table 2) obtained by integration of the smoothed heat capacities is less than 0.1 per cent above 100 K.

4. Conclusions

The lack of any significant deviations in the heat capacity near 175 K (compare figure 1) is such that even when the precision of the heat capacity measurements is assumed to be no better than 0.1 per cent, the maximum occluded methanol content

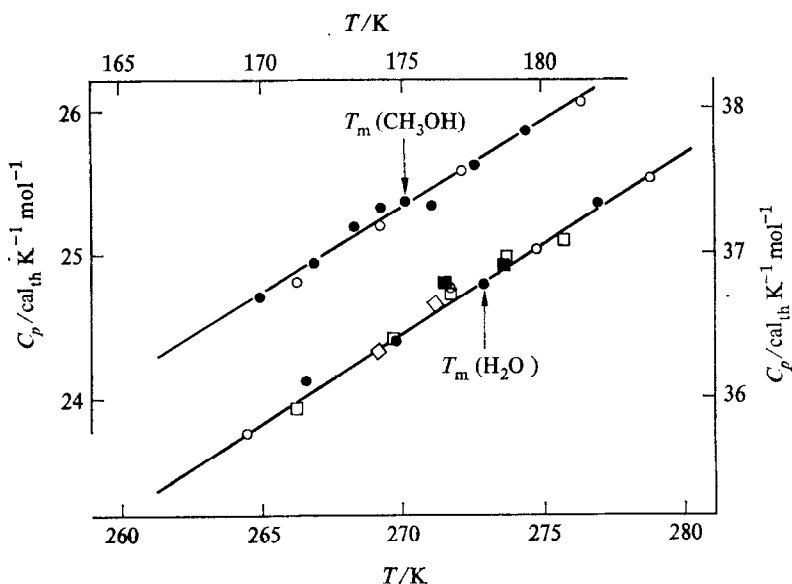


FIGURE 1. Experimental values for the heat capacity of tris(hydroxymethyl)aminomethane near the melting temperature of methanol (upper curve) and of water (lower curve). The different symbols differentiate the various series in table 1.

would then be about 2×10^{-3} mass per cent. Evaluation of the small "hump" below 273 K leads to an estimated maximum water content of about 2×10^{-3} mass per cent. The reliability of this method of determining traces of occluded, not chemically bonded, solvents from accurate heat capacity measurements, has been demonstrated in a recent paper.⁽⁶⁾ There, the amount of occluded water in succinic acid was determined by two completely different methods with very good agreement. One method utilized exactly the same calorimetric apparatus and technique used above; the other involved determinations of mass losses after careful drying.

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