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HEAT CAPACITY OF α QUARTZ FROM 298.15 TO 847.3 K, AND OF β QUARTZ FROM 847.3 TO 1000 K—TRANSITION BEHAVIOUR AND REVALUATION OF THE THERMODYNAMIC PROPERTIES *

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ABSTRACT

The heat capacity of two quartz mineral samples has been measured by adiabatic shield calorimetry in the range 298.15–1000 K. The α–β transition occurs continuously in a λ-like fashion with maximum heat capacity of about 1700 J K^{-1} mol^{-1} over a 0.02 K interval near 847.30 K. The transitional enthalpy is 518 ±5 J mol^{-1} over the range 820–865 K. The values of molar heat capacity $C_{p,m}$, enthalpy $[H_m^{\ominus}$ (1000 K) $- H_m^{\ominus}$ (298,15 K)] and entropy $[S_m^{\ominus}$ (1000 K) $- S_m^{\ominus}$ (298.15 K)] are 69.14 J K^{-1} mol^{-1}, 45633 J mol^{-1} and 75.00 J K^{-1} mol^{-1}, respectively. The results are compared with literature values and a revaluation of the thermodynamic properties of quartz in the range 298.15–1700 K is presented.

INTRODUCTION

The thermodynamic properties of quartz have been measured and evaluated by many investigators, but are still somewhat divergent especially in the α–β transition region. Furthermore, heat capacity results and drop-calorimetric results need to be evaluated in a common process.

In the subambient temperature range, the heat capacity results reported by Westrum [1] superseded earlier results by Koref [2], Nernst [3], Wietzel [4] and Anderson [5], and are the main basis for the CODATA [6] recommendations for standard entropy and enthalpy of α quartz at 298.15 K. More recent results by Gurevich and Khlyustov [7] are in close agreement with those of Westrum [1].

Enthalpy increments for quartz between temperatures in the range 273.15–298.15 K and at various higher temperatures up to 1676 K have been reported by numerous investigators during the last 100 years, with somewhat diverging results. The most recent drop-calorimetric results in the range 1000–1676 K by Richet et al. [8] and the DSC results from 300 to 1000 K by

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* Dedicated to Professor Edgar F. Westrum, Jr., on the occasion of his 70th birthday and in honour of his contribution to calorimetry and thermal analysis.

Hemingway [9] favour an intermediate value for the enthalpy increment $[H_m^{\ominus}$ (1000 K) $- H_m^{\ominus}$ (298.15 K)] of 45550 ± 30 J mol^{-1}, compared with the results from the 1960–1985 period [10–19], which give values from 44967 to 45848 J mol^{-1}.

Although not nesessarily the main cause of discrepancy in the experimental results for the thermodynamic properties of quartz, a structural transition complicates the picture near 850 K. The premonitory increase in dilation well below that temperature was first reported by Le Chatelier [20] and since then the transition has been intensely studied by virtually all physicochemical techniques. More recent structural studies, for reviews see [21–25], conclude that the symmetry of the structure changes from $P3_121$ or $P3_221$ in the low temperature α phase to $P6_422$ or $P6_222$ in the high temperature β phase. The way in which the transition process proceeds is still under discussion.

By using dark-field imaging electron microscopy, van Tendeloo et al. [26] and van Goethem et al. [27] observed a heterogeneous structure in a narrow temperature interval, and interpreted it in terms of microdomains of the Dauphiné twin type. These observations led Aslanyan and Levanyuk [28] to suggest the existence of an incommensurate phase resulting from coupling of elastic strains with spatial derivatives of the order parameter. The structures have been further studied by neutron diffraction and electron microscopy [29–32], and X-ray diffraction topography [33–34]. A theoretical interpretation [35,36] in terms of two distinct sets of domain walls having the same free energy has been advanced. The walls differ in orientation only, and this gives rise to the possibility of a macrodomain structure in quartz.

The first direct heat capacity measurements in the α–β transition region were made by Perrier and Roux [37,38]. They found that the heat capacity rose slowly for temperatures up to 846 K, becoming about 10% lower and approximately constant at temperatures above 849 K. For the intermediate 3 K range the total enthalpy increment was 1.0 kJ mol^{-1}. Perrier and Roux inferred that the heat capacity might rise to almost infinity in the 846–849 K range, but with only a very small isothermal enthalpy increment (latent heat). Such behaviour, they remarked, had passed almost unnoted in the large number of calorimetric investigations made by the classical method of mixture. The transitional heat capacity behaviour was studied more precisely by Moser [39], but he was only able to determine the heat capacity at 10 K intervals in the critical region. By extrapolating the available expansivity and compressibility data, Moser concluded that an isothermal enthalpy absorption of about 300 J mol^{-1} and a 0.45% volume discontinuity should occur at the critical temperature.

A subsequent heat capacity study by Sinelnikov [40] in the range 300–900 K, with special attention to the transition region, failed to show any isothermal enthalpy change. The heat capacity began to rise more rapidly at 826 K and reached its maximum value of around 170 J K^{-1} mol^{-1} at 847.3

K, and then decreased in a λ-like fashion. In the study by Mayer [41], the α–β transition was thoroughly discussed and the entropy of transition evaluated on the basis of Moser's heat capacity results [39]. A renewed interest in the transitional heat capacity of quartz arose after discovery of the incommensurate structures. Thus, Dolino et al. [42] observed a heat capacity rise in a temperature interval of 1.3 K before the retransformation of β quartz to α quartz occurred on cooling to about 844 K. This behaviour, observed by DSC with cooling rates of 0.3–1.35 K min^{-1}, was ascribed to the existence of an intermediate phase in the 1.3 K interval. The results were largely confirmed by Matsuura et al. [43] and by Hatta et al. [44] using AC light irradiation calorimetry. Here the temperature range of the intermediate phase was found to be 1.15 ± 0.05 K in the cooling experiments. Its absence in the ordinary heating runs was ascribed to hysteresis. The authors also asserted that the main phase transition was a first-order one.

The present study was primarily undertaken to delineate the heat capacity of quartz in the α–β transition region on a high purity sample, in order to see if any divergence or isothermal enthalpy change, related to the formation and disappearance of the incommensurate phase, was present in the heating mode. In addition, the need for revaluating the thermodynamic properties of quartz in the region 300–1000 K was present at the outset of this work. Meanwhile, DSC results have been reported by Hemingway [9] and the source of a recent discrepancy has been discovered. Nevertheless, results obtained by adiabatic shield calorimetry might assist in a further narrowing of the uncertainty limits.

EXPERIMENTAL

Samples

The two quartz samples studied were both from the Drag locality in Nordland, Norway. We thank Dr. Stig Lyng, Siv.ing. Åge Mykland and Siv.ing. Roald Gundersen of ELKEM A/S for placing the analyzed materials at our disposal.

The crushed and separated material with 150 μm crystallite size (sample A) contained the following impurities in ppm by mass: Al 40, Ca 115, Fe 70, K 20 and Na 70. The purified Minnor quality quartz (sample B) contains typically: Al 20, Ca 0.2, Fe 0.2, K 0.2, Li 4.5, Na 0.4, P 0.02, Sm 0.0001 and Ti 1.5. Other elements sought, but not detected, were: B < 0.4, Mg < 0.01, Cr < 0.002, Mn < 0.02, Co < 0.002, Ni < 0.01, Cu < 0.01, Zr < 0.002, La < 0.0005, Eu < 0.002, Tb < 0.0005, Th < 0.001 and U < 0.0005.

X-ray powder photographs of the Minnor sample were taken in an 80 mm diameter Guinier type camera with Cu $K\alpha_1$ radiation and silicon as an internal standard with $a(298.15\ \text{K}) = 543.1065$ pm [45]. Hexagonal unit cell dimensions were derived by the least-squares program CELLKANT [46]: $a = 491.3(1)$ and $c = 540.4(1)$ pm. The results agree within their limited accuracy with the precise determination by Miller and Du Mond [47]: $a(298.15\ \mathrm{K}) = 491.267(9)$ and $c = 540.459(11)$ pm. No lines from foreign phases were observed.

Calorimetry

The calorimetric apparatus and measuring technique have been described [48] along with the results obtained for the heat capacity of a standard sample of α Al_2O_3. The calorimeter is operated with adiabatic shields and intermittent energy inputs with temperature equilibration between each input. The 50 cm^3 sample container of silica glass has a well for the heater and platinum resistance thermometer, located axially in the cylindrical silver calorimeter. The calorimeter + sample assembly is suspended inside a double-walled silver shield system with enclosed heaters. Outside the shields is a heated guard system, also of silver. The whole assembly is placed in a vertical tube furnace.

The temperature differences between corresponding parts of calorimeter and shield are measured by means of Pt–(Pt + 10 mass% Rh) thermopiles. The amplified signals are recorded and also used for automatic control of the shield heaters to maintain quasi-adiabatic conditions during input and drift periods. The temperature of the guard body is automatically kept 0.4 K below that of the shield, while the temperature of the furnace core is kept 10 K lower to ensure satisfactory operation of the control units.

Heat capacity measurements of the empty calorimeter were carried out in a separate series of experiments. They represented between 57 and 60% of the total. Small corrections were applied for differences in mass of the empty and filled silica glass containers, and for "zero" drift of the calorimeter. The temperature excursions of the shields from the calorimeter temperature were of negligible importance. The thermometer resistance was measured with an automatically balancing ASL18 AC bridge, operated by a Hewlett–Packard 9835A computer. The energy inputs from a constant current supply were measured with a Hewlett–Packard 3455A digital voltmeter and a quartz clock to an accuracy of about 0.03%. Temperature recalibration of the resistance thermometer was carried out in situ with sealed samples of sodium sulphate decahydrate, tin, zinc and antimony. Temperatures are judged to correspond with the IPTS-68 to within 0.1 K at 1000 K.

RESULTS

The experimental heat capacities are given in Table 1 in chronological order. Series I–VIII refer to the Drag quartz after mechanical, magnetic and floation separation only, while those of Series IX–XI refer to the Minnor quality. Results obtained in the transitional region 820–865 K are reported in Table 2. Determination A represents a rather fast exploration of the transition region, compared to Detn. B (~ 2.7 compared with 0.2 K h^{-1}),

TABLE 1

Heat capacity of quartz

T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})	T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})	T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})
Sample A		704.63	69.49	475.13	58.57
		714.36	69.90	484.72	59.22
Series I		724.14	70.40	494.31	59.70
319.49	47.04	734.01	70.99	503.91	60.23
329.68	47.93	744.00	71.31	513.52	60.82
339.79	48.93	754.10	71.88	523.12	61.33
349.83	49.88	764.28	72.33	532.72	61.97
359.84	50.77	774.55	73.00	542.38	62.40
369.79	51.64	784.79	73.85	552.06	62.65
379.72	52.48	794.66	74.56		
389.61	53.25	804.46	76.06	Series VII	
399.47	54.04	814.27	77.15	322.97	47.17
409.30	54.77	$M(SiO_2) = 60.084$ g mol^{-1}		333.12	48.10
419.13	55.46	$\Delta_{trs} H_m$	Detn. A	353.26	49.97
428.94	56.12	865.06	68.20	363.15	50.82
438.75	56.77	867.63	68.26	373.00	51.61
448.56	57.41			382.80	52.55
458.38	58.11	Series IV		392.58	53.15
468.20	58.68	816.42	78.00	402.32	54.07
478.04	59.28	$\Delta_{trs} H_m$	Detn. B	412.05	54.65
487.89	59.81			421.76	55.47
497.78	60.11	Series V		431.47	55.94
507.67	60.72	310.32	45.75	441.16	56.72
		327.27	47.47	450.86	57.24
Series II		337.53	48.45	460.53	57.93
567.95	63.42	347.61	49.40		
577.48	64.05	357.62	50.32		
587.05	64.36	367.53	51.19		
596.63	64.64	337.40	51.92	Series VIII	
606.29	65.06	387.22	52.89	898.89	68.40
615.97	65.73	397.03	53.69	910.22	68.65
625.70	65.89	406.80	54.63	920.94	68.73
635.45	66.42	416.57	55.18	931.63	68.52
645.23	66.65	426.32	56.11	942.39	68.89
655.03	67.47	445.83	56.84	955.36	69.07
		455.48	57.50	970.54	68.84
Series III				983.66	69.14
685.15	68.79	Series VI		994.59	69.17
694.92	69.13	465.50	58.18	1005.58	69.03

TABLE 1 (continued)

T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})	T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})	T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})
Sample B		471.20	58.24	629.20	65.88
		483.31	58.88	641.32	66.49
Series IX		495.40	59.53	653.46	66.91
322.84	46.85	507.49	60.20	665.62	67.43
335.65	48.16	519.59	60.86	677.78	67.93
348.33	49.29	531.69	61.47		
360.95	50.40	543.78	62.01	Series X	
373.46	51.44	555.88	62.58	$\Delta_{trs} H_m$	Detn. C
385.88	52.43	556.76	62.73		
398.22	53.39	568.79	63.32	Series XI	
410.50	54.32	580.84	63.79	300.39	44.62
422.72	55.16	592.90	64.36	307.21	45.18
434.89	55.97	604.99	64.86	316.72	46.14
459.09	57.54	617.09	65.33	326.12	47.05

which results in a rather high heat capacity in the post-transition region for the former (97.59 J K^{-1} mol^{-1} at 849.54 K). The necessity of thorough equilibration was apparent in an unreported series of determinations in

TABLE 2

Fractional enthalpy for the α to β quartz transition

T (K)	ΔT (K)	$C_{p,m}$ (J K^{-1} mol^{-1})	$C_{p,m}$(n.t) [a] (J K^{-1} mol^{-1})	Δt_{stab} [b] (min)	$\Delta H_{m,exc}$ (J mol^{-1})	T_{final} (K)
		$M(SiO_2) = 60.0843$ g/mol^{-1}				
Detn. A,	Series III					
823.913	9.6245	79.56	79.09	47	4.5	828.725
833.485	9.5195	82.51	81.08	51	13.6	838.245
841.889	7.2878	90.94	83.13	50	56.9	845.533
846.976	2.8861	196.26	78.06	50	341.1	848.419
849.536	2.2346	97.59	68.17	55	65.7	850.653
851.916	2.5247	75.46	68.19	127	18.4	853.178
854.476	2.5971	71.70	68.21	119	9.1	855.775
857.089	2.6287	70.95	68.23	119	7.2	858.404
859.733	2.6582	69.64	68.25	118	3.7	861.062
862.391	2.6578	68.74	68.27	122	1.2	863.720
					521.4	
		$\Delta_{820\,K}^{865\,K} H_{m,exc} = 521.4 \pm 5$ J mol^{-1}				
Detn. B,	Series IV					
825.359	8.8895	79.79	79.36	41	3.8	829.804
834.153	8.6983	83.24	81.21	46	17.7	838.502
839.112	1.2194	86.91	82.40	39	5.5	839.721
840.330	1.2168	88.19	82.72	46	6.7	840.938
841.544	1.2110	89.37	83.07	45	7.6	842.149
842.749	1.1994	91.49	83.35	45	9.8	843.349

TABLE 2 (continued)

T (K)	ΔT (K)	$C_{p,m}$ (J K^{-1} mol^{-1})	$C_{p,m}$(n.t) [a] (J K^{-1} mol^{-1})	Δt_{stab} [b] (min)	$\Delta H_{m,\mathrm{exc}}$ (J mol^{-1})	T_{final} (K)
843.941	1.1845	94.16	83.68	45	12.4	844.533
845.111	1.1557	98.62	83.99	47	16.9	845.689
846.055	0.73209	108.9	84.25	45	18.0	846.421
846.674	0.50583	197.7	84.44	45	57.3	846.927
847.022	0.19049	669.1	84.54	45	111.4	847.117
847.248	0.26042	469.4	79.69	46	101.5	847.378
847.664	0.57270	155.8	68.17	45	50.2	847.950
848.323	0.74403	105.9	68.17	45	28.1	848.695
849.105	0.82132	87.55	68.18	45	15.9	849.516
849.947	0.86333	79.86	68.18	46	10.1	850.379
					472.9	
		$\Delta_{850.38\ \mathrm{K}}^{865\ \mathrm{K}} H_{m,\mathrm{exc}} = 42.5$				
		$\Delta_{820\ \mathrm{K}}^{865\ \mathrm{K}} H_{m,\mathrm{exc}} = 515.4 \pm 5$ J mol^{-1}				
Detn. C,	Series X					
846.371	0.28984	116.1	84.35	65	9.2	846.516
846.572	0.11270	125.4	84.41	67	4.6	846.629
846.705	0.15176	133.9	84.45	45	7.5	846.781
846.856	0.15066	143.9	84.50	41	8.9	846.931
846.991	0.11966	203.7	84.54	41	14.3	847.051
847.080	0.05823	505.5	84.56	46	24.5	847.109
847.127	0.03568	879.6	84.58	45	28.4	847.145
847.159	0.02820	1140	84.59	46	29.8	847.173
847.185	0.02430	1343	84.59	45	30.6	847.197
847.209	0.02388	1366	84.60	46	30.6	847.221
847.231	0.01927	1710	84.61	45	31.3	847.240
847.251	0.02043	1606	84.61	46	31.1	847.261
847.271	0.02110	1551	84.62	45	30.9	847.282
847.293	0.02260	1441	81.30	45	30.7	847.305
847.318	0.02693	1185	68.17	46	30.1	847.331
847.349	0.03464	874.7	68.17	45	27.9	847.366
847.395	0.05828	509.7	68.17	46	25.7	847.424
847.494	0.14025	164.5	68.17	46	13.5	847.565
847.657	0.18370	104.3	68.17	45	6.6	847.748
847.844	0.19094	97.92	68.17	46	5.7	847.939
848.037	0.19623	92.49	68.17	45	4.8	848.136
848.236	0.20112	87.47	68.18	46	3.9	848.337
848.440	0.20596	84.84	68.18	45	3.4	848.543
848.645	0.20433	83.43	68.18	46	3.1	848.747
848.851	0.20817	81.45	68.18	45	2.8	848.955
849.060	0.20964	80.82	68.18	45	2.6	849.164
849.271	0.21145	78.42	68.18	45	2.2	849.376
					444.7	
		$\Delta_{820\ \mathrm{K}}^{846.23\ \mathrm{K}} H_{(m,\mathrm{exc}} = 70 \pm 30$				
		$\Delta_{849.38\ \mathrm{K}}^{865\ \mathrm{K}} H_{\mathrm{m,exc}} = 25 \pm 10$				
		$\Delta_{820\ \mathrm{K}}^{865\ \mathrm{K}} H_{m,\mathrm{exc}} = 540 \pm 40\ J\ mol^{-1}$				

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[a] Non-transitional or reference heat capacity.

[b] Stabilization time.

between Series II and III, in which the sample was cooled from 850 to 842.5 K for 1 h before starting the measurements. The resulting transitional enthalpy was then only about 70% of those in Detns. A and B.

TABLE 3

Thermodynamic properties of quartz

T (K)	$C_{p,m}$ ($J\ K^{-1}\ mol^{-1}$)	$H_m^{\ominus}(T) - H_m^{\ominus}(298.15\ K)$ ($J\ mol^{-1}$)	$S_m^{\ominus}(T) - S_m^{\ominus}(298.15\ K)$ ($J\ K^{-1}\ mol^{-1}$)
		$M(SiO_2) = 60.084\ g\ mol^{-1}$	
298.15	44.50	0	0
300	44.70	82.51	0.276
320	46.73	996.9	3.226
340	48.68	1951.3	6.118
360	50.53	2943.6	8.954
380	52.27	3971.8	11.733
400	53.87	5033.4	14.455
420	55.33	6125.6	17.119
440	56.67	7245.8	19.725
460	57.89	8391.6	22.271
480	59.01	9560.7	24.759
500	60.05	10751	27.189
520	61.03	11962	29.563
540	61.98	13192	31.884
560	62.91	14441	34.156
580	63.84	15709	36.379
600	64.76	16995	38.559
620	65.68	18299	40.698
640	66.58	19622	42.797
660	67.47	20962	44.860
680	68.34	22321	46.887
700	69.20	23696	48.880
720	70.07	25089	50.842
740	71.01	26499	52.774
760	72.11	27930	54.682
780	73.53	29386	56.573
800	75.51	30875	58.458
820	78.39	32412	60.355
840	(82.62) *	(34020)	(62.292)
847.30α	(84.63)	(34630)	(63.015)
847.30β	(68.17)	(35148)	(63.627)
860	68.22	36014	64.641
880	68.33	37380	66.211
900	68.48	38748	67.748
920	68.64	40119	69.255
940	68.80	41493	70.733
960	68.94	42871	72.183
980	69.06	44251	73.606
1000	69.14	45633	75.002

* Predicted on the assumption that the transition is isothermal.

In order to make a meaningful comparison of the different runs through the transition region, non-transitional reference heat capacities had to be derived. For this purpose the least-squares fitted polynomial expressions for the heat capacities of α and β quartz were extrapolated to 847.30 giving values of 84.63 and 68.17 J K^{-1} mol^{-1}, respectively. With this background, the resulting mean transitional enthalpy for Detns. A and B is 518 ± 5 J mol^{-1}.

The enthalpy results for the Minnor sample (Detn. C) are less accurate because of uncertainty about the enthalpy contributions below 846.2 K and above 849.4 K. Even for this very pure sample, the heat capacity fails to approach infinity; instead, it remains surprisingly small, 1500 ± 200 J K^{-1} mol^{-1} over the range 847.17–847.31 K.

In order to check if this constancy could be due to longitudinal temperature gradients in the sample, another series of experiments was carried out. Here the temperature at the top of the shield was increased by 0.05 K to decrease any net upwards heat flow from the calorimeter to the shield. It resulted, as expected, only in a broadening and flattening of the peak with maximum $C_{p,m} \approx 800$ J K^{-1} mol^{-1} at around 847.26 K.

Smoothed values of the heat capacity $C_{p,m}$, enthalpy $[H_m^\ominus(T) - H_m^\ominus(298.15 \text{ K})]$, and entropy $[S_m^\ominus(T) - S_m^\ominus(298.15 \text{ K})]$ are given in Table 3 for selected temperatures. In the range 298.15–830 K the standard deviation in the heat capacity is 0.3% with the 8-term polynomial $C_P = A + BT + CT^2 + DT^3 + ET^4 + FT^5 + GT^6 + HT^7$. From 865–1000 K only the first four terms were used with a resulting 0.3% standard deviation for a single measurement.

DISCUSSION

When comparing the present heat capacity results with those in the literature, the results reported by Perrier and Roux [37] are worth mentioning as this was the first attempt to determine the heat capacity of quartz in the transition region, using small temperature increments. The results are, however, 11% higher than ours at 720 K and 3% higher at 820 K. Some evaluators have given considerable weight to the results obtained by Moser [39]. They are on the average 0.88% lower than ours outside the transition region. It has been noted, see Hemingway [9], that Moser's results for silver and nickel were 1.5–2% low, and that a similar trend was expected for quartz. The results of Sinelnikov [40] are shown only as a plot in his paper, and appear to be approximately equal to ours, but with a spread of more than 1%. More recently, Ghiorso et al. [49] and Hemingway [9] have provided heat capacity results for quartz by DSC. Those by Ghiorso et al. [49] are given as a hyperbolic equation over the range 400–842 K with a standard deviation of 0.7 J K^{-1} mol^{-1}. The curve deviates from ours by

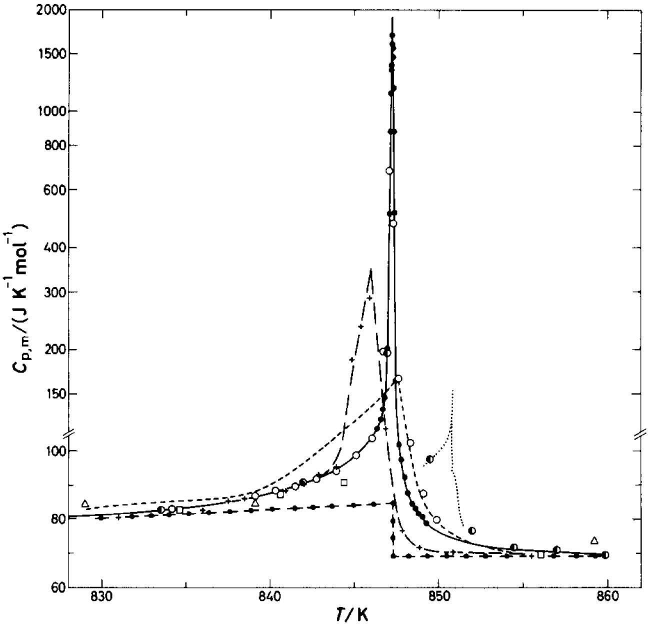

Fig. 1. Heat capacity of quartz in the transition region: ◐, ○ and -●- represent present results of Detns. A, B and C, respectively; Δ, Perrier and Roux [37]; □, Moser [39]; — — —, Sinelnikov [40]; …, Matsuura et al. [43]; –+–, Hemingway [9]; -●- -●-, reference heat capacity used in this study.

-0.55 J K^{-1} mol^{-1} at 480 K, and by $+0.59$ J K^{-1} mol^{-1} at 760 K. A 6-term polynomial representing the results by Hemingway [9] shows a maximum positive deviation of 0.50 J K^{-1} at 700 K and a negative deviation of -1.59 J K^{-1} mol^{-1} at 810 K. The heat capacity results by Moser [39], Ghiorso et al. [49], Cohn [50] and Hemingway [9] will be combined with ours in an attempt to revaluate the thermodynamic properties of quartz, see below. Further heat capacity results by Miehr et al. [51], Coenen [52], Leonidov et al. [53,54] and Shults et al. [55] are not accurate enough for our purposes.

The heat capacity behaviour of quartz in the α–β transition region is shown in Fig. 1. In addition to the present results for the Drag quartz (Detns. A and B), and for the Minnor quality (Detn. C), results by other investigators are also shown in the figure, and the enthalpy-determination results are collected in Table 4. The higher-order nature of the transition requires the non-transitional or reference heat capacity to be defined in order that meaningful comparisons can be made. Thus the value $\Delta_{trs}H_m = 625$ J mol^{-1} given by Hemingway [9] refers to a background 220 J mol^{-1} lower than that used here, so that our result would be 738 J K^{-1} with the background that Hemingway [9] used. Similarly, the total enthalpy over the range 847–850 K reported by Perrier and Roux [38] (3,83 cal g^{-1}) leads to a

TABLE 4

Enthalpy of transition of quartz

T_{trs} (K)	$\Delta_{\mathrm{trs}}H_m$ (J mol^{-1})	Method	Authors	Year
863 ± 10	760	Drop	Lashchenko [56]	1910
(848)	430 *	Drop	White [57]	1919
847–850	750	C_p	Perrier and Roux [37,38]	1923
848	1060 ± 50		Cohn [50]	1924
846.8/845.9 **	41	TA	Bates and Phelps [58]	1927
848	1070	Drop	Esser et al. [60]	1933
845.7 ± 0.2	780	Clapeyron	Gibson [59]	1928
847 ± 1	515	C_p	Moser [39]	1936
847.5		DTA	Sinelnikov [40]	1953
847.2 ± 0.5	452	Evaluation	Mayer [41]	1960
	338	Clapeyron	Young [61]	1964
846	326 ± 42	Clapeyron	Majumdar et al. [62]	1964
846	360 ± 85	DTA	Majumdar et al. [62]	1964
	828	DTA	Leonidov et al. [53]	1964
847/846.7 **	425 ± 42	Calvet-	Berger et al. [63]	1965
852/845 **	808 ± 50	microc.	Berger et al. [63]	1965
847.9/848.1 **	358 2 ± 4.6	DSC	Ghiorso et al. [49]	1979
848.6/847.5 **	450.6 ± 4.6	DSC	Ghiorso et al. [49]	1979
844	625	DSC	Hemingway [9]	1987
847.3	518 ± 5	C_p	Present	

* As evaluated by Sosman [21].

** First value on heating, second on cooling.

transitional enthalpy of about 750 J mol^{-1} in this region. Moser [39] reported a total enthalpy increment [$(H(600\,^{\circ}\mathrm{C}) - H(550\,^{\circ}\mathrm{C})$] of $16.8_3 \pm 0.1$ cal g^{-1}, which with the background used here yields $\Delta_{\mathrm{trs}} H_m = 515$ J mol^{-1}. Many transitional enthalpy values have been derived by the Clapeyron equation for a first-order transition

$$\Delta_{\mathrm{trs}H} = \left(\frac{\mathrm{d}p}{\mathrm{d}T_{\mathrm{trs}}}\right) T\,\Delta V_{\mathrm{trs}}$$

Here again the result depends on the value of ΔV_{trs} chosen for the transition, because the $(\mathrm{d}p/\,\mathrm{d}T_{\mathrm{trs}})$ value has been reliably determined to be $(3.69 \pm 0.20) \times 10^6$ Pa K^{-1} [64–67].

Both Berger et al. [63] and Ghiorso et al. [49] have reported that the $\Delta_{\mathrm{trs}}H$ values depend upon the origin and state of division of the quartz. In both investigations, the highest values refer to single crystals and the lowest to fine powders. Ghiorso et al. [49] observed a 92 J mol^{-1} difference between the results for single crystals and for 1 μm diameter particles, and related it to the corresponding surface enthalpy of the fine powder.

The present results are one order of magnitude higher in heat capacity in the transition region than those by previous investigators, see Fig. 1. The failure of the present results to approach infinity may possibly be due to local overheating of the sample during the energy inputs and to the fact that the β quartz formed does not revert to α quartz. This argument is weakened by the fact that superheating of α quartz by 0.5–1 K causes energy absorption and a comparable decrease in temperature after a few minutes [58,59]. More probably, therefore, the heat capacities are finite because of the permanent presence of an intermediate phase or phase mixture, as observed in the diffraction and imaging studies mentioned in the introduction. In principle, the finite heat capacities can also be ascribed to the slightly differing compositions of the two solid 2-component phases. The time–temperature existence range of the intermediate phase(s) needs further elucidation, as the equilibration is far from instantaneous. The fast heat capacity measurements made by other investigators [42–44] have revealed a plateau in the cooling mode, but only a kink in the heating mode, see Fig. 1, where the results by Matsuura [43] are shown. Results in the heating mode by Dolino et al. [42] showed a peak at about 846 K, which is where the intermediate phase formed in the cooling mode. Thus, they were unsure about the existence of the intermediate phase in the heating mode. The transition from the intermediate phase to α quartz on cooling occurred at 844 K and was characterized as a first-order transition. The heating results are not shown in Fig. 1 as the ordinate was not quantified.

We have not yet made further experiments concerning the retransformation of β to α quartz and are thus not yet able to confirm or disprove the stability range of 1.1–1.3 K of the intermediate phase on cooling. Dolino et al. [42] have calculated the heat capacity of the intermediate phase using one of the Pippard relations [68]

$$C_{p,m}T = \frac{V_m \alpha(T)}{(\mathrm{d}p/\,\mathrm{d}T)_\lambda} + h(p)$$

where V_m is the molar volume, $\alpha(T)$ the thermal expansivity and $h(p)$ a pressure-dependent constant. Dolino et al. [42] found good agreement between this expression and their DSC heat capacity in the cooling mode, which rose from about 75 J K^{-1} mol^{-1} at 846.0 K to about 220 J K^{-1} mol^{-1} at 844.5 K. The thermal expansivity of quartz has not been accurately studied closer than 3 K to the divergence temperature, therefore, we are unable to compare our results with the Pippard relation in this interesting range.

Above the α to β quartz transition the heat capacity results by Perrier and Roux [38] are about 6% higher than ours in the range 860–920 K. Those by Moser [39] are between 0.6 and 1.0% lower than ours, and those by Hemingway [9] show deviations from +1.2 to −0.8%.

A comparison of the present results can also be made with existing drop-calorimetric data, see Fig. 2, where the enthalpy-increment difference

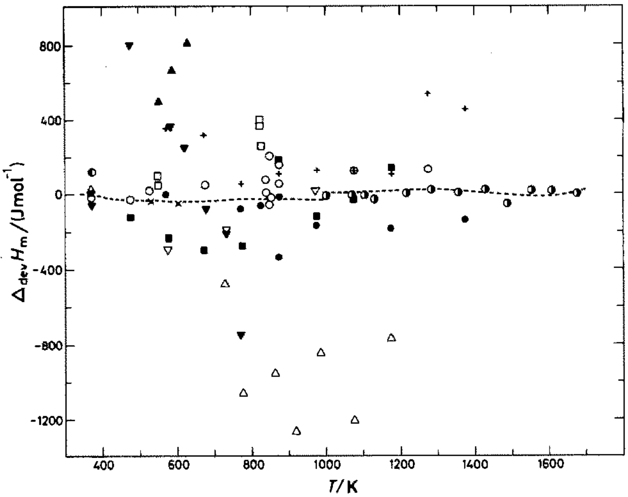

Fig. 2. Enthalpy increment deviations $[H_m^\ominus(T) - H_m^\ominus(298.15\text{ K})]$ between results of previous investigations and those obtained in this study: ◩, results by Neumann [69]; ◐, Regnault [70]; ▲, Pionchon [72]; □, Magnus [76]; ○, Wietzel [4]; △, Roth and Bertram [77]; +, Esser et al. [60]; ×, Mosesman, and Pitzer [78]; ▽, Holm et al. [79]; ◑, Richet et al. [8]; ■, Cohn [50]; ▼, Lashchenko [56]; — - — represents deviation of revaluated enthalpies from those determined experimentally in this study up to 1000 K, and those reported by Richet et al. [8], above.

$\Delta[H_m^\ominus(T) - H_m^\ominus(298.15\text{ K})]$ between the results of other workers and those of the present study are plotted. For temperatures above 1000 K, the heat capacities derived by Richet et al. [8] have been joined with ours and integrated.

With regard to the majority of the previous results, there are doubts about the basis for the calorie used, as well as concerning the temperature scale. For the former we have consistently used 1 cal = 4.184 J when not otherwise stated. Uncertainties about the temperature scale in the higher temperature range are of greater concern. In adjusting the temperatures, we have adhered to the changes made in the International (Practical) Temperature Scale during the last 60 years, and to the fix-point deviations for more local scales used before that time (Geophys. Lab, and PTR).

Concentrating first on the α quartz region, we find that the results reported by Pionchon [72], Bartoli [73], Weber [74], Lashchenko [56] and Schulz [75] appear to have large systematic errors. They are therefore of marginal interest in the revaluation process. Around 370 K, the results of Neumann [69], Regnault [70], Joly [71], Magnus [76], Wietzel [4], and Roth and Bertram [77] agree reasonably well with ours, but only those of White [57] fall within the narrow limits required for conforming with the heat capacity results up to this temperature. In the region 470–800 K, the results by Magnus [76], White [57], Wietzel [4], and Mosesman and Pitzer [78] agree reasonably well with ours, as do the heat capacity results by Moser [39], Ghiorso et al. [49] and Hemingway [9].

TABLE 5

Accepted and rejected enthalpy values [$H_m^\ominus(T) - H_m^\ominus$(298.15 K] for α and β quartz

Authors	α quartz results		β quartz results	
	Accepted	Rejected	Accepted	Rejected
Pionchon [72]	0	6	0	17
Lashchenko [56]	1	5	0	5
Magnus [76]	4	3	—	—
White [57]	4 (21) *	0	3 (14)	1 (2)
Wietzel [4]	9	0	5	4
Cohn [50]	2	3	4	1
Roth and Bertram [77]	1 (7)	2 (4)	0	5 (11)
Esser et al. [60]	1	2	4	2
Mosesman and Pitzer [78]	2	0	—	—
Holm et al. [79]	0	2	1	0

* Values in parentheses refer to the number of experiments carried out.

A statistical treatment [80–83] was carried out after combining the integrated heat capacity results with the available enthalpy results. They were all referred to 298.15 K. Integrated enthalpies from the heat capacities reported by Moser [39], Ghiorso et al. [49] and Hemingway [9], were included at intervals of 20 K over the region measured, while ours, because of their higher accuracy, were taken at 5 K intervals. This process resulted in a reassessment of the enthalpy results as summarized in Table 5, with a standard deviation of 42.6 J mol^{-1} for 1% probability that a rejected value should have been included. All integrated heat capacity results from the work of Ghiorso et al. [49], Hemingway [9] and those obtained by us were accepted, while those by Moser [39] above 700 K were rejected.

A least-squares treatment of the remaining enthalpies, fitted to a 7-term polynomial with the restriction that $C_{p,m}(298.15\ \text{K}) = 44.50\ \text{J K}^{-1}\ \text{mol}^{-1}$ and $[H_m^\ominus(T) - H_m^\ominus(298.15\ \text{K})] = 0$, gave the results presented in Table 6. Entropies and Gibbs energies are given on the basis of the CODATA [6] recommended values: $[H_m(298.15\ \text{K}) - H_m(0\ \text{K})] = (6916 \pm 20)\ \text{J mol}^{-1}$ and $S_m(298.15\ \text{K}) = (41.46 \pm 0.20)\ \text{J K}^{-1}\ \text{mol}^{-1}$).

In the α to β quartz region from 800 to 860 K, only the present results were used. The values for 820 and 840 K in Table 6 include the pre-transitional components. Results by some previous investigators show important variations depending upon crystallite size. Additional samples need to be accurately measured in order to clarify the situation.

For β quartz, the present results in the range 860–1000 K were used in combination with those reported by Ghiorso et al. [49] up to 900 K *, by

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* After addition of 760 J mol^{-1} of non-transitional enthalpy from 842 to 851 K which appears not to have been included, cf. Hemingway [9].

TABLE 6

Revaluated thermodynamic properties of quartz

T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})	H(T) − H(298.15) (J mol^{-1})	S(T) − S(298.15) (J K^{-1} mol^{-1})	$H(T) - H(0)$ (J mol^{-1})	S(T) − S(0) (J K mol^{-1})	− G(T) − H(298.15))/T (J K^{-1} mol^{-1})	−(G(T) − H(0))/T (J K^{-1} mol^{-1})
298.15	44.50	0	0	6916.0	41.46	41.460	18.264
300	44.74	82.55	0.28	6998.5	41.74	41.461	18.408
320	46.88	999.7	3.23	7915.7	44.69	41.571	19.958
340	48.66	1955.4	6.13	8871.4	47.59	41.840	21.499
360	50.31	2945.2	8.96	9861.1	50.42	42.239	23.027
380	51.92	3967.5	11.72	10883	53.18	42.742	24.542
400	53.50	5021.8	14.43	11937	55.89	43.332	26.042
420	55.03	6107.2	17.07	13023	58.53	43.993	27.526
440	56.45	7222.2	19.67	14138	61.13	44.713	28.995
460	57.77	8364.6	22.21	15282	63.67	45.482	30.447
480	58.95	9531.9	24.69	16447	66.15	46.291	31.883
500	60.02	10722	27.11	17637	68.58	47.135	33.302
520	60.99	11932	29.49	18848	70.95	48.005	34.705
540	61.91	13161	31.81	20077	73.27	48.898	36.091
560	62.80	14408	34.08	21324	75.54	49.809	37.459
580	63.70	15673	36.30	22589	77.76	50.735	38.810
600	64.62	16956	38.47	23872	79.93	51.672	40.146
620	65.58	18259	40.61	25174	82.07	52.618	41.464
640	66.56	19580	42.71	26495	84.17	53.571	42.765
660	67.55	20921	44.77	27837	86.23	54.529	44.051
680	68.50	22282	46.80	29197	88.26	55.492	45.321
700	69.41	23661	48.79	30576	90.26	56.457	46.577
720	70.27	25058	50.76	31973	92.23	57.423	47.818
740	71.13	26472	52.70	33387	94.16	58.390	49.044

TABLE 6 (continued)

T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})	H(T) − H(298.15) (J mol^{-1})	S(T) − S(298.15) (J K^{-1} mol^{-1})	$H(T) - H(0)$ (J mol^{-1})	S(T) − S(0) (J K mol^{-1})	− G(T) − H(298.15))/T (J K^{-1} mol^{-1})	−(G(T) − H(0))/T (J K^{-1} mol^{-1})
760	72.12	27904	54.61	34819	96.07	59.356	50.257
780	73.47	29359	56.50	36274	97.96	60.322	51.455
800	75.60	30848	58.39	37763	99.85	61.287	52.642
820	78.30	32385	60.28	39301	101.74	62.250	53.816
840	88.0	34031	62.26	40947	103.72	63.207	54.974
860	68.22	35988	64.57	42904	106.03	64.184	56.142
900	68.40	38720	67.68	45636	109.14	66.113	58.429
950	68.79	42149	71.38	49065	112.84	68.476	61.196
1000	69.25	45600	74.92	52516	116.38	70.783	63.867
1050	69.71	49074	78.31	55990	119.77	73.036	66.449
1100	70.12	52571	81.57	59486	123.03	75.235	68.948
1150	70.46	56085	84.69	63001	126.15	77.381	71.367
1200	70.72	59615	87.70	66531	129.16	79.476	73.713
1250	70.91	63156	90.59	70072	132.05	81.521	75.989
1300	71.07	66706	93.37	73622	134.83	83.519	78.199
1350	71.23	70263	96.06	77179	137.52	85.469	80.346
1400	71.43	73829	98.65	80745	140.11	87.374	82.435
1450	71.75	77408	101.16	84324	142.62	89.236	84.467
1500	72.24	81007	103.60	87923	145.06	91.057	86.446
1550	72.98	84636	105.98	91552	147.44	92.837	88.376
1600	74.05	88310	108.31	95226	149.77	94.580	90.258
1650	75.55	92048	110.61	98964	152.07	96.288	92.096
1700	77.58	95874	112.90	102790	154.36	97.962	93.894

Hemingway [9] up to 1000 K and by Richet et al. [8] from 1001.9 to 1676.3 K. Results by other investigators scattered so badly that equal weighting led to acceptance of all results with a standard deviation of about 1400 J mol^{-1}. The assignment of weight 2 to the first-mentioned results made little change in the acceptance limit, while with weight 3 the acceptance limit dropped to 12 J mol^{-1}. Instead, therefore, results deviating more than 200 J mol^{-1} from the combined results by Richet et al. [8] and the present authors were rejected, see Table 5. A least-squares fit of the remaining enthalpies gave the additional results presented in Table 6. Here a 4-term polynomial was used with the restrictions that $C_{p,m}(860\ \text{K}) = 68.22\ \text{J K}^{-1}\ \text{mol}^{-1}$ and $[H_m^\ominus(860\ \text{K}) - H_m^\ominus(298.15\ \text{K})] = 35988\ \text{J mol}^{-1}$.

Below 1000 K, these revaluated enthalpies of quartz differ from those obtained experimentally in this study by 40 J mol^{-1} at most, cf. deviation from base line in Fig. 1. Above 1000 K, the least-squares-fitted enthalpies differ insignificantly from the results reported by Richet et al. [8].

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