Thermodynamic Properties and Third-Law Cycle for Malononitrile

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The heat capacity of malononitrile, $CH_2(CN)_2$, has been determined by adiabatic calorimetry from 5° to 320° K. A gradual transition occurs in the stable form at 260.3° K. with an entropy increment of 1.15 cal. per mole ° K. The compound melts at 304.9° K. with an entropy of melting of 8.46 cal. per mole ° K. Low-temperature heat capacities were also made on the metastable crystal obtained by quenching the stable form through the 260.3° K. anomaly. This phase has a gradual transformation which takes place over the 137° to 151° K. with an excess entropy of 0.05$_5$ cal. per mole ° K. The heat capacity (C_p), entropy ($S°$), and Gibbs energy function $[-(G° - H_0^\circ)/T]$ at 298.15° K. are 26.36, 31.30, and 15.34 cal. per mole ° K., respectively. The approximate accord of the experimental entropy of gaseous malononitrile at 298.15° K. (68.5 ± 0.4 cal. per mole ° K.) with the value (69.02) calculated from spectroscopic data indicates the absence of disorder in the crystal at 0° K.

THE characteristic features of plastic crystals as defined by Timmermans (*7*) are typical in systems composed of molecules of high symmetry. The extent to which these properties pertain to systems of less symmetrical molecules is also of considerable interest. Of the first three dinitriles in the series $NC(CH_2)_nCN$, only succinonitrile (n = 2) has been shown to possess a plastic crystalline phase (*12*); glutaronitrile (n = 3) shows a normal entropy of melting (*2*). The first member of the series—i.e., malononitrile—is solid at room temperature, and its entropy of melting was determined by freezing-point depression as 7.9 cal. per mole ° K. (*8*). Since such values are often not reliable, a deeper insight into the phase behavior and molecular freedom of malononitrile was sought by direct calorimetric measurements.

EXPERIMENTAL

The commercial malononitrile sample was purified by 56 passes in an automatic multiple-zone apparatus. The 76.350 grams (in vacuo), degassed, completely colorless, transparent molten sample was transferred into the calorimeter under a helium atmosphere. Helium gas (81.5 torr) was added to facilitate thermal equilibration in the sample space. The purity of the sample as determined by fractional melting will be discussed later; a density of 1.045 grams per cc. was employed. Measurements were made in the gold-plated calorimeter (laboratory designation W-24A, fabricated from oxygen-free, high-conductivity copper) within the Mark III cryostat (*9*). The quasi-adiabatic technique was used (*10*) with manual shield control below 80° K. and with three channels of automatic electronic shield control to maintain adiabaticity to within a millidegree above that temperature. All measurements of time, temperature, potential, resistance, and mass were referred to standardizations or calibrations of the National Bureau of Standards. Between 70 and 80% of the total heat capacity was provided by the sample.

RESULTS AND DISCUSSION

Thermal Behavior. Experimental heat capacities plotted in Figure 1 are also presented in chronological order in Table I so that the temperature increments employed can usually be deduced by differences in the mean temperature of adjacent determinations. The data are given in terms of the defined thermochemical calorie equal to 4.1840 joules and an ice point of 273.15° K. The probable error in the heat capacity data is considered to be about 2% up to 10° K., 0.3% at 30° K., and less than 0.2% above 100° K. Of six series of runs made through the transition region, only three corresponded to complete conversion. Three sets of heat capacity measurements were made below 90° K. The close agreement between the data of the first set (series II through V) with those on undercooled crystal I of the third set indicated that the former measurements were also made on the metastable (undercooled crystal I) form. The second set (series XIV through XVI) was preceded by complete transformation of crystal I to crystal II and therefore represents values for the stable form. The third set (series XVIII through XX) was on the undercooled form of crystal I obtained by quenching—i.e., reducing the calorimeter temperature to 140° K. within an hour. This was achieved by the expedient of temporarily breaking the vacuum in the cryostat with 1 torr helium gas.

Because the conversion of crystal I to crystal II (T_t = 260.3° K.) is very slow under ordinary conditions, rapid cooling (>14° K. per hour) of crystal I from 300° to 140° K. permits undercooling to still lower temperatures and consequently allows heat capacity determinations on the undercooled (metastable) crystal I phase to be made. Even upon relatively slow cooling of the sample (5° K. per hour) to 140° K. and holding it at this temperature for 2 days, crystal II does not appear. However, the conversion is initiated upon heating the sample to 190° K.; holding it at this temperature nearly 4 days provides complete conversion. The heat evolved during the first 3 hours of the transformation of undercooled crystal I to crystal II (about 95%

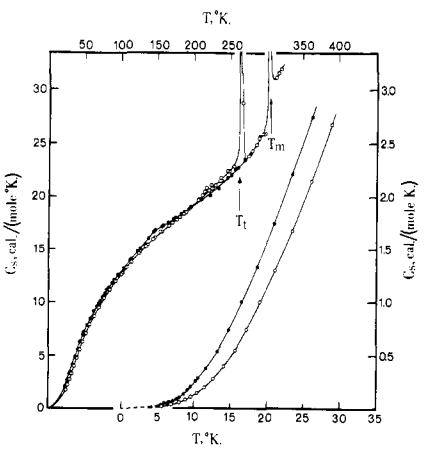

Figure 1. The heat capacity of malononitrile

○ Heat capacities of equilibrium phases

● Heat capacities on quenched sample—i.e., below the transition temperature they represent values for the metastable crystal I

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Table I. Heat Capacity of Malononitrile[a]

T	C_s	T	C_s	T	C_s	T	C_s	T	C_s	T	C_s
Series I		Series III[b]		Series VII		Series XIII		Series XVI		Series XVIII[b]	
259.27[b]	22.70	58.73	8.557	244.65	22.40	108.76	13.33	76.41	10.26	57.49	8.428
		64.58	9.334	254.48	23.27	123.96	14.56	83.97	11.10	62.57	9.105
268.71	23.41	70.72	10.05	262.90	33.61	133.24	15.24	91.77	11.86	68.28	9.796
278.54	24.28	77.47	10.79	268.45	54.69	143.28	15.95	99.92	12.56	73.91	10.42
287.77	25.41			274.96	25.19	153.67	16.68	107.61	13.26	79.77	11.06
296.77	25.81	Series IV[b]		284.27	24.82	163.66	17.31				
302.60	104.8			293.46	25.84	173.28	17.89	Series XVII		Series XIX[b]	
304.24	487.0	75.35	10.56			182.83	18.49				
304.78	4270	82.40	11.32	Series VIII		192.41	19.05	210.60	20.11	86.29	11.73
304.78	4260	88.96	11.98			201.82	19.61	219.61	20.59	94.40	12.46
304.83	7930	95.16	12.51	249.86	22.02	210.99	20.13	228.45	21.02	102.92	13.16
304.87	10900	102.47	13.12	ΔHt Run A				237.10	21.48	111.86	13.89
304.89	17700	113.15	13.94	274.45	24.02	Series XIV		245.56	22.16	121.32	14.64
304.90	119000	125.51	15.00							132.07	15.48
306.28	99.58	137.05	16.02	Series IX		5.63	0.018	ΔHt Run D		144.06	16.69
311.58	31.04					6.87	0.035			157.31	17.26
319.24	31.84	Series V[b]		169.88	17.51	8.00	0.054	282.81	24.65	170.87	17.86
				180.00	18.05	8.84	0.081	291.00	25.88	184.01	18.50
Series II[b]		146.53	16.83	188.48	18.51	9.58	0.103			196.75	19.14
		155.21	17.14			10.42	0.143	ΔHm Run A		209.09	19.68
5.92	0.047	163.72	17.50	Series X		11.41	0.194			221.14	20.11
6.62	0.056	172.48	17.93			12.70	0.277	Series XVIII[b]		232.93	20.71
7.64	0.085	181.45	18.37	197.00	19.09	14.14	0.393			244.35	21.71
8.60	0.136	190.20	18.81	206.66	19.78	15.61	0.541	5.40	0.027	255.41	22.52
9.55	0.204			216.22	20.77	17.29	0.738	6.35	0.041	266.05	23.75
10.52	0.282	Series VI		225.82	21.06	19.05	0.980	7.15	0.068	277.16	24.15
11.55	0.358			235.64	21.72	21.07	1.293	8.10	0.103	289.56	25.60
12.64	0.469	100.45	12.69	247.61	22.36	23.47	1.707	9.14	0.169		
14.05	0.634	113.37	13.74	253.46	22.80	26.01	2.175	10.19	0.253	ΔHm Run B	
15.86	0.879	124.95	14.67	257.87	52.92	28.75	2.706	11.59	0.370		
17.99	1.204	135.44	15.40	260.16	85.85			13.14	0.533	Series XX	
20.28	1.592	145.47	16.06	262.15	52.94			14.73	0.735		
22.72	2.043	155.10	16.67	265.24	28.75	Series XV		16.48	0.986	Melting runs	
25.50	2.593	165.03	17.22	269.42	23.34			18.60	1.328	310.63	31.16
28.68	3.238	175.29	17.80	273.91	23.76	28.85	2.727	20.96	1.739	315.13	31.48
32.17	3.961	185.24	18.36	278.27	24.24	31.25	3.209	23.39	2.205	319.14	31.86
36.01	4.748	194.91	18.98			34.76	3.916	26.08	2.741		
40.13	5.768	204.31	19.62	Series XI		38.80	4.713	29.08	3.354	Series XXI	
43.77	6.216	213.39	20.44			42.88	5.475	32.32	4.026		
				ΔHt Run B		47.15	6.227	35.89	4.760	ΔHm Run C	
Series III[b]		Series VII				52.02	7.040	39.79	5.511		
				Series XII		57.25	7.836	44.01	6.286	Series XXII	
47.80	6.898	223.91	20.73			62.87	8.622	48.59	7.058		
53.05	7.737	234.48	21.46	ΔHt Run C		69.13	9.425	53.07	7.767	ΔHt Run E	

[a] Units: cal., mole, °K. [b] Metastable phase.

of $-\Delta Ht$) was sufficient to heat the calorimeter by approximately 6° K. When transformation ceased, crystal II was cooled to 5° K., and heat capacity measurements of series XVIII were begun.

A reproducible, small hump was observed in the temperature dependence of the heat capacity of undercooled crystal I in the temperature range 137° to 151° K. It was associated with larger than normal negative drifts, but thermal equilibration was achieved without noticeable hysteresis. No corresponding detectable anomaly appears near this temperature in the heat capacity of the crystal II phase. The excess enthalpy and entropy are $8._0$ cal. per mole and 0.05_5 cal. per mole °K., respectively. So small an entropy increment may be due to the lattice (liberalization) expansion of the undercooled (metastable) form of crystal I, but no definite conclusion can be drawn without crystal structure data. However, Zussman and Alexander (*13*) find four resonance lines in malononitrile (on unidentified phase) below 140° K. by pure N^{14} nuclear quadrupole resonance, which apparently change continuously and without hysteresis (hence presumably as a second order transition) at 140° K. to eight resonance lines. Since N^{14} has unit nuclear spin, this transformation appears to involve a change from two to four distinct nitrogen sites with increasing temperature.

Naveau (*5*) studied malononitrile crystals with a polarizing microscope and reported formation of a metastable solid phase (melting about 303° K.) obtained from the supercooled liquid at 293° K. (without stirring), but this phase converted rapidly to the stable form. The present authors were unable to detect such anomalous behavior near the melting region. Possibly the nuclear quadrupole line width transition, without effect on the first moment, detected by Zussman and Alexander (*13*) at 294.7° K. is related to this metastable phase. The present measurements show no detectable deviation in heat capacity from the smooth curve in this region.

The enthalpies of the 260.3° K. transition (ΔHt) and of melting (ΔHm) are summarized in Table II. The average values of ΔHt and ΔHm are 302 ± 1 and 2580 ± 2 cal. per mole. The corresponding values of the entropy increments, ΔSt and ΔSm, are 1.16 ± 0.01 and 8.46 ± 0.01 cal. per mole °K.

Purity of the Sample. The fractional melting data for series I are recorded in Table III where $\bar{T}$ and $1/F$ are the mean temperature and reciprocal fraction melted for each run. The triple point of the calorimetric sample (at $1/F = 1$) and that of the pure sample (corresponding to $1/F = 0$) are 304.91° and 304.99° K., respectively. The melting point has been reported previously as 304.80° (*6*,

Table II. Enthalpy of Phase Changes for Malononitrile[a]

Designation	Number of Runs	$H_{280} - H_{240}$	Designation	Number of Runs	$H_{315} - H_{295}$
	TRANSITION			MELTING	
Series VII	6	(1204)[b]	Run *A*	1	3156
Series X	9	1218	Run *B*	1	3157
Run *C*	2	1216	Run *C*	4	(3109)[c]
Run *D*	3	1220			
Run *E*	3	(1165)[c]			
Av.		1218[d]	Av.		3156[d]
Lattice $H_{240} - H_{280}$		916.5	Lattice $H_{295} - H_{315}$		576
ΔHt		302	ΔHm		2580

[a] Units: cal., mole, °K. [b] Incomplete conversion. [c] Runs taken after partial decomposition of the sample. [d] Runs in parentheses are excluded from the average.

Table III. Fractional Melting Data for Malononitrile[a]

$\bar{T}$	ΔT	$\Sigma\Delta H_i$	T_{final}	$1/F$
304.65	0.186	937	304.74	3.144
304.78	0.073	1293	304.82	2:279
304.83	0.039	1650	304.85	1.785
304.87	0.029	2007	304.88	1.468
304.89	0.017	2364	304.90	1.246
304.90	0.003	2721	304.90	1.083
	Triple point of sample =			304.911
	Triple point of pure compound =			304.987
	Mole fraction of impurity =		0.001	

[a] Data from series I. Units: cal., mole, °K.

8) and 304.65°K. (5). The mole fraction of the liquid-soluble, solid-insoluble impurity was estimated with the expression:

$$N_2 = \Delta Hm(T_0 - T_1)/RT_0^2$$

The premelting enthalpy has been included in ΔHm in the evaluation of impurity.

An initial set of fractional melting runs (series I, Table I; in which true thermal equilibration was not waited for) indicated 99.9$^+$ mole % purity. During the course of the study, enthalpies of transition and melting were investigated a number of times, and all these values are in agreement within experimental error. Observation of larger than normal positive drifts in the liquid region suggested the onset of thermal decomposition at these temperatures. For this reason, the time that the sample was in the liquid state was carefully minimized and only after completion of all other measurements was the sample subjected to customary fractional melting procedures. However, true constancy of temperature was not attained even after a week of equilibration. The gradual but continuous decrease in the apparent melting temperature presumably was a consequence of impurities formed by decomposition or polymerization of the sample. The triple point of the sample and the purity computed from this data set (series XX) were 303.26°K. and about 99.5 mole %, respectively. Enthalpy runs through transition and melting subsequently made for this partially decomposed sample gave values significantly smaller than previously determined values. Hence, the measurements prior to those of series XX reported here pertain to a sample of 99.9$^-$% purity.

Thermodynamic Functions. Smoothed values of the heat capacity at selected temperatures obtained by a digital computer fit of the experimental data and carefully compared with large scale plots are presented in Table IV. Molal values of the entropy, enthalpy increment, and Gibbs energy function are also listed in Table IV at selected temperatures. These have been integrated by a high-speed digital computer using a least-squares polynomial fit through the data points. Anomalous regions were analyzed by numerical quadrature. Below 5°K., the heat capacity data were extrapolated using the Debye T^3 limiting law. Nuclear spin and isotopic mixing contributions have not been included in the entropy and Gibbs energy function.

Mechanism of Transition and Fusion. The high value of ΔSm, 8.46 cal. per mole °K., indicates that malononitrile is not a plastic crystal. This value is in reasonable accord with van de Vloed's (8) reported value of ΔSm determined from cryoscopic data. Since no plastic crystalline state occurs, the interpretation and mechanism of the apparently λ-type transformation with a maximum at 260.3°K. remain uncertain. Although the entropy of transition is 1.15 cal. per mole °K. and approximates R ln 2—i.e., 1.38 cal. per mole °K.—the suggestion that the transition involves an order-disorder type of reorientation into indistinguishable configurations is unwarranted in the absence of crystal structure data. Some evidence for a phase transition in the range 233° to 265°K. was also detected by nuclear quadrupole resonance techniques (13). This transition may be accompanied by a considerable volume change, as the calorimeter was distended by about 5% upon completion of the measurements. Borosilicate glass tubes containing sample shatter on cooling through the transition.

Third-Law Comparison. Figure 1 shows that the heat capacity curve of undercooled crystal I merges with that of crystal II at 268°K. The entropy increments, $S_{270} - S_{0°K.}$, via undercooled crystal I and via the stable forms (crystals I and II) were calculated as 23.84 and 23.85 cal. per mole °K., respectively. The excellent agreement between these two entropy increments indicates a lack of (or the same extent of) residual disorder at 0°K. in both malononitrile crystalline phases.

Comparison with Spectroscopic Entropy. The entropy of gaseous malononitrile has been calculated from spectral data (4). This has been recalculated from new data and recently revised assignments for structural parameters of Fujiyama and Shimanouchi (3) to determine the vibrational, rotational, and translational entropy contributions. A total (spectroscopic) ideal gas entropy at 298.15°K. of 69.02 cal. per mole °K. was obtained. The entropy from calorimetric and vapor pressure data is summarized in Table V and discussed briefly here. Recently, Boyd (1) has made determinations of the vapor—i.e., sublimation—pressure of malononitrile by the Knudsen effusion technique above the transition temperature. The computed values of the sublimation pressure and the enthalpy of sublimation (ΔHs) at 298.15°K. are 0.09 torr and ~18 kcal. per mole. The total entropy of the gas at 298.15°K. would be ~74 cal. per mole °K. or about 5 cal. per mole °K. higher than the spectroscopic entropy if Boyd's values are employed. Alternatively, if the vapor pressures and ΔHv relations, $\log P = 0.222n + 11.936 - (173n + 2996)/T$ (P in microns) and $\Delta Hv_{298.15} = (0.79 \pm 0.02)n + 13.71 \pm 0.11$ (ΔHv in kcal. per mole), for the dinitriles [$NC(CH_2)_nCN$ for n = 2 to 8] determined by Woodman, Murbach, and Kaufman (11) are extrapolated to $n = 1$, values of 0.0338 torr and 14.5 ± 0.1 kcal. per mole would be obtained. Admittedly, extrapolation of the foregoing generalization back to the first member of a homologous series is a suspect procedure. However, the resultant entropy of the gas, 68.5 ± 0.4, accords better with the spectroscopic value and is within the limits of reliability of the data employed.

ACKNOWLEDGMENT

The authors appreciate the cooperation of Wen-Kuei Wong in the experimentation.

Table IV. Thermodynamic Functions of Malononitrile[a]

T	C_s	$S°$	$H° - H_0°$	$-(G° - H_0°)/T$
	Crystal II–Stable Form			
5	0.008	0.004	0.016	0.001
10	0.122	0.037	0.028	0.009
15	0.477	0.143	1.654	0.033
20	1.123	0.363	5.542	0.086
25	1.985	0.703	13.25	0.173
30	2.956	1.150	25.57	0.297
35	3.965	1.681	42.87	0.456
40	4.940	2.275	65.16	0.646
45	5.857	2.910	92.19	0.862
50	6.710	3.572	123.6	1.100
60	8.229	4.933	198.5	1.625
70	9.534	6.302	287.5	2.195
80	10.67	7.652	388.7	2.793
90	11.69	8.968	500.5	3.407
100	12.60	10.248	622.1	4.027
110	13.45	11.49	752.4	4.649
120	14.25	12.69	890.9	5.270
130	15.01	13.86	1037	5.886
140	15.73	15.00	1190	6.497
150	16.41	16.11	1352	7.101
160	17.07	17.19	1519	7.698
170	17.70	18.25	1693	8.288
180	18.31	19.28	1873	8.870
190	18.91	20.28	2059	9.444
200	19.50	21.27	2251	9.728
210	20.07	22.23	2449	10.57
220	20.61	23.18	2652	11.12
230	21.09	24.10	2861	11.67
240	21.68	25.01	3075	12.20
250	22.28	25.91	3295	12.73
	Crystals I + II (Stable Form)–Transition Region			
255	23.50	26.36	3409	12.99
260	85.90	27.40	3677	13.26
260.3 (max.)	90.30	27.50	3704	13.27
265	25.45	28.40	3939	13.53
270	23.52	28.84	40.57	13.81
	Crystal I–Stable Form			
273.15	23.78	29.11	4131	13.99
280	24.43	29.71	4297	14.36
290	25.49	30.58	4547	14.90
298.15	26.36	31.30	4758	15.34
300	31.50	31.49	4816	15.44
304.91	27.09[b]	31.91	4939	15.71
	Liquid			
304.91	30.48[b]	40.37	7519	15.71
310	30.95	40.87	7676	16.11
320	31.90	41.97	7991	17.00
	Crystal I–Metastable Form (Undercooled)			
5	0.025	0.007	0.026	0.002
10	0.229	0.065	0.503	0.015
15	0.771	0.251	2.882	0.059
20	1.569	0.577	8.646	0.145
25	2.523	1.028	18.83	0.274
30	3.546	1.578	33.99	0.445
35	4.578	2.202	54.30	0.650
40	5.553	2.878	79.66	0.886
45	6.458	3.584	109.7	1.146
50	7.291	4.309	144.1	1.426
60	8.762	5.772	224.6	2.029
70	10.01	7.219	318.6	2.667
80	11.10	8.628	424.3	3.325
90	12.06	9.992	540.2	3.990
100	12.93	11.31	665.2	4.656
110	13.74	12.58	798.6	5.319
120	14.53	13.81	939.8	5.976
130	15.33	15.00	1089	6.620
140	16.38	16.21	1247	7.298
150	17.03	17.37	1416	7.928
160	17.34	18.47	1587	8.548
170	17.82	19.53	1764	9.160
180	18.31	20.57	1944	9.763
190	18.82	21.57	2130	10.36
200	19.30	22.54	2321	10.93
210	19.73	23.49	2517	11.51
220	20.06	24.42	2716	12.08
230	20.54	25.32	2919	12.63
240	21.27	26.21	3128	13.18
250	22.10	27.09	3345	13.71
260	22.78	27.97	3570	14.24
270	23.52	28.85	3802	14.77

[a] Units: cal., mole, ° K. [b] Assuming melting to be truly isothermal.

Table V. Entropy of Malononitrile (Ideal Gas) at 298.15° K.[a]

Temp., ° K.		ΔS	ΔS
0–298.15	Crystal I	31.30	31.30
298.15–304.91	Crystal I	0.61	...
304.91	$\Delta Hm/T_m$ melting	...	8.46
304.91–298.15	Liquid	−0.68	...
	ΔHv/298.15 vaporization	...	48.63 ± 0.44[c]
	ΔHs/298.15 sublimation	~60[b]	...
298.15	R ln P compression to 1 atm.	~−17.3[b]	−19.8[d]
	Ideal gas correction[d]	0	0.0
	Entropy (ideal gas)	~74	68.5$_0$ ± 0.4
298.15	Spectroscopic Entropy		69.02

[a] Units: cal., mole, ° K. [b] Using Boyd (*1*) data for enthalpy of sublimation and vapor pressure. [c] Enthalpy of vaporization and vapor pressure computed from an empirical relationship (*11*). [d] Assumed negligible for vapor pressure of malononitrile ($<10^{-1}$ torr at 298.15° K.).

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