

Methanol: Heat Capacity, Enthalpies of Transition and Melting, and Thermodynamic Properties from 5–300°K

H. G. CARLSON AND EDGAR F. WESTRUM, JR.

Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48104

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Thermal properties of methanol were studied by adiabatic calorimetry. The first-order nature of the phase transition at 157.4°K with an entropy increment of 0.97 cal mole⁻¹·°K⁻¹ was confirmed. The heat capacity of the crystalline phase stable just below the triple point was defined and shown to be extremely sensitive to impurity. No evidence for a second previously-reported phase transition could be detected. The standard entropy (S°) and Gibbs energy function ($-[G^\circ - H^\circ_0]/T$) for the liquid at 298.15°K are 30.40 and 15.18 cal mole⁻¹·°K⁻¹, respectively. The proposed classification of methanol as a plastic crystal on the basis of its small entropy of melting (4.38 cal mole⁻¹·°K⁻¹) is considered with respect to hydrogen bonding in the liquid phase.

INTRODUCTION

The numerous studies of the physicochemical properties of methanol include an early heat capacity study over a limited range by Parks,¹ who in 1925 reported the existence of a transition at 161°K. In a later calorimetric study, extending from 14°K into the liquid phase, Kelley² interpreted the transformation with a maximum at 157.4°K as lambda-type. More recently a semimicrocalorimetric study was made by Staveley and Gupta³ from 100°K through the melting point. However, their use of a very small sample gave low precision. Lower-temperature heat capacity measurements were made by Ahlberg, Blanchard, and Lundberg⁴ over the range 3–28°K.

An x-ray structural determination on methanol at 113°K (Crystal II) and 163°K (Crystal I) by Tauer and Lipscomb⁵ established the crystals as monoclinic and orthorhombic, respectively. More compact packing in Crystal II was attributed to a slight displacement of members of the infinite, hydrogen-bonded methanol chains in planes normal to the direction of the chains. Preparation of singly crystalline Crystal II was found to be difficult, and faint superlattice lines were noted in Crystal II as studied. Dreyfus-Alain and Viallard⁶ used an x-ray powder diffraction technique and found a hexagonal structure for Crystal I. A monoclinic structure for Crystal II at 93°K has also been reported in a recent study by Murti.⁷ In none of the Crystal II structure studies is any mention made of a thermal conditioning process to ensure complete phase transformation on cooling to low temperatures. Because of the finding by Staveley and Gupta that methanol tends to shatter glass bulbs on warming through the transition region, a dilatometric investigation was made by Staveley and Hogg.⁸ With isopentane as the dilatometric fluid an abrupt volume increment of 0.49 cc mol⁻¹ at 159°K and a smaller gradual change of only 0.14 cc mol⁻¹ at 156°K were found (rather than the single increment, ΔHt , found in the calorimetric investigations¹⁻³) in addition to the 2.75 cc mol⁻¹ volume change attendant on melting. However, the interaction between isopentane and methanol (solubility of isopentane is 1.3 mol% in the liquid at 175°K)

results in a depression of the freezing point of the alcohol by about 1°K. Davidson⁹ also found a second transition in methanol-*d* of 0.04 cc mol⁻¹ at 158°K in addition to the "known" calorimetric transition, which he found to have a volume change of 0.43 cc mol⁻¹. However, if the additional transition is energetically small (as expected), the precision of the previous calorimetric work may have been too low for discrimination.

In addition to the aforementioned studies, several measurements have been made of the variation in dielectric constant in the solid state. Smyth and McNeight¹⁰ demonstrated the presence of a hysteresis loop in the dielectric constant vs temperature similar in appearance to that for phenol containing a trace of water.¹¹ The dielectric constant associated with Crystal I was observed as low as 133°K in this study. A more recent investigation of the dielectric constant of crystalline methanol by Davidson¹² involved a thermal conditioning process (cooling to 120°K, heating to 153°K, and equilibrating the sample there for several hours to remove any undercooled Crystal I) prior to making measurements on Crystal II. Dielectric constant measurements made without this thermal conditioning showed a decrease near 150°K, presumably associated with conversion from the undercooled Crystal I to the stable Crystal II form. Several static measurements made of the dielectric constant at various temperatures after equilibration periods of at least 3 h revealed a gradual rise in the dielectric constant at 155°K. This was associated by Davidson with the gradual rise in molal volume reported by Staveley and Hogg at 156°K. At 159.6°K a sharp rise in dielectric constant occurred which was taken to represent the calorimetric transition. Above this temperature the dielectric constant was continuous through the Crystal I phase. Davidson further noted an electrical conductivity maximum near 130°K, which he assumed to be occasioned by the formation of a small amount of liquid phase at the temperature of the water-methanol eutectic.¹³ A similar phenomenon at 123°K in samples which had not been thermally conditioned was taken to represent a eutectic in the undercooled Crystal I-water system.

Since recent experiments¹² indicated the necessity for adequate thermal conditioning to ensure a pure Crystal II phase, and dilatometric as well as dielectric constant studies showed the presence of two solid phase transformations where only one had been found by heat capacity measurements, a new calorimetric investigation was initiated in this laboratory to clarify the phase behavior of methanol and to provide a complete, accurate table of the thermodynamic functions. In addition, because of the present interest in globular molecules,¹⁴ a re-evaluation of the plastically crystalline nature of methanol provided a further incentive.

EXPERIMENTAL

Samples

A sample of Belle refined methanol produced by the Polychemicals Department of E. I. du Pont de Nemours and Company was generously provided to this laboratory by Perkins. The alcohol was an extremely pure batch having the reported analysis (in ppm): 0.3 acetone, 10 ethanol, 0.3 water, 99.92%–100% methanol, boiling range=0.035°C (ASTM). Sample I was distilled into Calorimeter W-14 and weighed 53.551 g in vacuum. Sample II, removed from the bottle two years later and transferred to Calorimeter W-24, weighed 61.428 g in vacuum. Final purity of the samples was evaluated from the fractional melting data below.

Calorimeters

Calorimeter W-14, fabricated from fine silver rod, had a wall thickness of 0.50 mm and was gold plated on all surfaces. Its geometry resembled that of another previously described¹⁵ except that eight 0.40-mm-thick radial (circular) vanes and the bottom were machined integrally with the thermometer-heater well, and that a demountable valve designed for sealing fluids within the calorimeter was added. The length of the cylindrical portion containing the sample was 7.6 cm and the diameter was 3.9 cm.

Since experience indicated that transitions in condensed phases with significant volume increments tend to fracture a soldered joint of the type with which the cylindrical portion of Calorimeter W-14 was soldered to the bottom, a new calorimeter, W-24, was constructed to eliminate this source of failure. The cylindrical shell and the bottom of this calorimeter were turned from a single rod of OFHC copper and were gold plated. A well with 10 equispaced, 0.25-mm-thick, integral circular vanes was inserted as a press fit from the inside of the calorimeter into a machined aperture in the bottom. With the soldered seam made on the outside of the press fit, expansion of the calorimeter's contents put the seam under compression rather than tension. Both calorimeters had internal volumes of about 80 cc. A pressure of 10 cm Hg of helium gas was used for conduction within the calorimeters.

Cryostats

Sample I was measured in the Mark I cryostat,¹⁶ with manual shield control to maintain adiabatic conditions about the calorimeter. The heat capacity of Sample II was determined in the Mark III Cryostat¹⁷ which is designed to utilize automatic adiabatic shield control during normal heat capacity measurement and throughout the long periods frequently required for thermal equilibration during phase transitions. Departures of adiabaticity were in general not greater than 0.03°K at the time of a thermal upset in the system, lasted not more than a minute, and were compensated for by damped sinusoidal regulation in both the manual and automatic shield control systems. All measurements of temperature, time, potential, resistance, and mass were referred to devices calibrated by the National Bureau of Standards.

Calculations

The defined thermochemical calorie equal to 4.184 abs J, an ice point of 273.15°K, and one mole=32.043 g are assumed in the calculations. Temperatures measured with the platinum resistance thermometer (laboratory designation A-3) are considered to correspond within 0.04° to the international temperature scale from 90–350°K and within 0.03°K from 10–90°K. From 4–10°K a provisional scale was constructed from an equation given by Hoge and Brickwedde¹⁸ fit to the resistance, the slope of the resistance vs temperature, and the measured value of the resistance at the boiling point of helium. The heat capacity was adjusted for the slightly different amounts of Apiezon-T conduction grease and helium gas present with the empty and filled calorimeters. Correction (amounting to 0.1% of the heat capacity at 325°K) in the liquid region of the sample was made for the vaporization of methanol into the space above the sample. Appropriate adjustment was also applied to the data for curvature (i.e., the difference of the measured $\Delta H/\Delta T$ from $dH/dT=C_p$). All calculations including curve fitting and integration were developed by an IBM-704 computer program¹⁹ which first fit a least-squares polynomial in temperature to the heat capacity data and then performed the necessary operations upon this polynomial to obtain the final values of the functions.

Heat Capacity Measurements

Molal heat capacity data on both samples are presented in chronological sequence in Table I. Determinations of enthalpy increments and heat capacities in transition regions are summarized in Table II and may be integrated into the thermal history by reference to Table I. Comparison of directly measured enthalpy increments with those obtained by numerical quadrature beneath the smoothed C_p vs T curve is given in Table III and provides a test both of the data and of the integration procedure. Table IV summarizes

TABLE I. Heat capacity of methanol. Units are degrees Kelvin and calories per mole-degree Kelvin.

T	C_p	T	C_p	T	C_p	T	C_p
Sample I, Mark I Cryostat							
Series 1		6.32	0.031	153.84	14.43	Series 14	
ΔH_f Detns A		7.12	0.047	154.66	14.09		
		7.93	0.069	155.19	14.13	153.68	14.14
Series 2		8.48	0.098	155.63	14.23	155.10	14.29
		8.98	0.118	156.06	14.53	156.22	14.26
56.08	6.440	9.40	0.135	156.48	14.37	157.40	14.40
59.42	6.832	10.45	0.199	156.91	14.28		
65.32	7.482	11.83	0.284	ΔH_f Detn F		Series 15	
71.26	8.067	12.88	0.374				
77.01	8.607	13.94	0.471	Series 10			
83.09	9.161	15.15	0.600			153.81	14.00
89.69	9.731	16.70	0.776	154.76	11.06	155.02	14.20
97.04	10.26	18.48	1.009	156.17	11.14	156.25	14.22
105.4	10.84	20.52	1.299	157.02	11.12	157.45	14.26
113.18	11.49	22.76	1.631	157.36	11.36		
121.32	12.01	25.19	2.010	157.78	11.18	Series 16	
		27.86	2.444	158.26	12.31		
Series 3		30.66	2.881	158.69	11.42	129.81	12.48
		33.85	3.392	159.19	11.18	135.43	12.88
Enthalpy Detn B		37.51	3.995	160.52	11.24	142.30	13.36
		41.61	4.504	165.77	11.66	149.01	13.83
Series 4		46.15	5.204	Melting Detns G		152.59	13.88
		50.64	5.780			153.82	14.18
128.09	12.42	55.20	6.362	Series 11		155.02	14.23
136.69	13.03			Melting Detns H		156.21	14.26
145.54	13.20	Series 7				157.39	14.25
				Series 12			
ΔH_f Detn C		5.09	0.014			Series 17	
		5.98	0.025	180.38	16.94		
Series 5		6.95	0.043	188.28	16.93		
		7.84	0.068	196.86	16.95	156.82	14.12
		8.52	0.090	205.86	16.99	157.95	14.29
161.65	11.32	9.33	0.136	215.17	17.08		
162.44	11.37	10.43	0.199	224.59	17.20	Series 18	
163.00	11.36	11.71	0.279	233.92	17.34		
163.44	11.45	13.08	0.392	243.12	17.53	Series 19	
163.96	11.47	14.48	0.528	252.17	17.75		
164.64	11.48	15.97	0.697	261.05	17.97	Trans. Detns K	
165.40	11.53			269.87	18.26		
166.25	11.61	Series 8		278.78	18.59	Series 20	
167.56	11.72			287.97	18.95		
169.49	12.02	Enthalpy Detn D		297.41	19.37	158.33	12.87
		Enthalpy Detn E		306.81	19.83		
Series 6		Series 9		316.10	20.33		
				325.17	20.83		
4.86	0.014			Series 13		159.32	11.05
5.68	0.022	152.81	13.16	Melting Detns J		160.19	11.27
						Melting Detns L	
Sample II, Mark III Cryostat							
Series 21		Series 22		Series 23		Series 24	
Trans. Detns M		Melting Detns N		68.45	7.788	Enthalpy Detns P	
				76.04	8.503		
				82.86	9.128		

the evaluation of fractional melting data. In these tables, T_i and T_f refer to the initial and final temperatures of the determination, T to the mean temperature, and ΔT to the temperature increment involved.

Since thermal conditioning is a prerequisite to formation of pure Crystal II,¹² a procedure was adopted in which the methanol was cooled slowly (i.e., several degrees per hour) through the transition region to about 100°K, then heated to 150–155°K, and the sample kept in this region for 8 h or more after completion of the energy liberation before measurements

TABLE II. Transition region of methanol.^a Units are degrees Kelvin and calories per mole.

T_i	T_f	ΔH or $\Sigma\Delta H$	ΔH_t
Sample I, Mark I Cryostat			
Series 1, Detns A (6 detns)			
151.25	167.94	358.36	152.5
Series 2, Detn C			
150.04	167.10	364.20	151.5
Series 9, Detn F			
157.12	167.16	266.47	151.9
Sample II, Mark III Cryostat			
Series 21, Detns M (6 detns only)			
151.25	157.91	202.27	152.3
T	ΔT	C_p	
Sample I, Mark I Cryostat			
Series 18, Detns K (3 detns)			
157.42	0.02	43.72	
157.44	0.01	90.35	
157.45	0.01	60.61	
Sample II, Mark III Cryostat			
Series 21, Detns M			
129.44	8.041	12.45	
148.40	2.383	13.74	
150.76	2.358	13.89	
153.10	2.328	14.09	
155.34	2.180	15.33	
156.86	0.887	44.42	
157.32	0.021	1330	
157.34	0.014	1900	
157.38	0.076	679	
157.64	0.437	549	
159.12	2.574	12.20	
161.71	2.635	11.77	

^a T_i and T_f are the initial and final temperatures; T , the mean temperature; and ΔT the temperature increment involved. ΔH or $\Sigma\Delta H$ refers to directly determined enthalpy increments over the range T_f-T_i ; ΔH_t is the enthalpy increment associated with the transition after deletion of the normal background vibrational or lattice enthalpy.

TABLE III. Comparison of directly measured enthalpy increments of methanol with the integral under the smoothed C_p curve.^a Units are degrees Kelvin and calories per mole. Sample I, Mark I cryostat.

T_i	T_f	ΔH	ΔH_{calc}
Series 3, Detn B			
53.49	126.59	698.7	698.4
Series 8, Detn D			
4.21	52.58	127.7	127.7
Series 8, Detn E			
52.58	153.03	1052.7	1050.5

^a T_i and T_f are the initial and final temperatures of the determinations; $\Delta H = H_{T_f} - H_{T_i}$; ΔH_{calc} = digital computer evaluated enthalpy with reference to the smoothed C_p curve.

were made on Crystal II. The rate of energy liberation, and hence of phase conversion, was increased by reheating the sample to temperatures nearer the transition. The heat capacities of undercooled Crystal I and of superheated Crystal II were also measured in Series 10 and are shown in Fig. 1. Sample I invariably superheated 1 or 2° above the heat capacity maximum before it would finally begin to transit and absorb energy. It was not convenient to follow this absorption of energy quantitatively with manual shield control; however, three enthalpy-type determinations were made over the entire transition region to determine the enthalpy of the transition and the completeness of the conversion of the sample to Crystal II. As a further check of the data on Crystal II, enthalpy-type runs B, D, and F were made and compared with the integral under a smooth polynomial curve constructed with the IBM-704 computer (results shown in Table III). While the data presented do not permit a detailed picture of the minutiae of the thermal history of the samples, they do indicate that it is possible under suitable precautions to make reliable measurements of the heat capacity of pure methanol except in the transition region.

The fractional melting technique was applied to both samples to permit calculation of their purities and of their melting points. Since Sample I showed (cf. Fig. 1) comparatively little premelting, the Crystal I heat capacity of Sample I was extended smoothly through the melting point and used to represent the background heat capacity contribution (i.e., lattice C_p) to measurements for both samples in this region. The magnitude of this contribution may be seen from the data assembled in Table IV. From this treatment the excess enthalpy was calculated and used in the calculation of reciprocal fraction melted vs temperature. A plot of these data was fit well by a straight line and extrapolated to the melting point of the calorimetric samples and that of pure methanol. It was also used to deter-

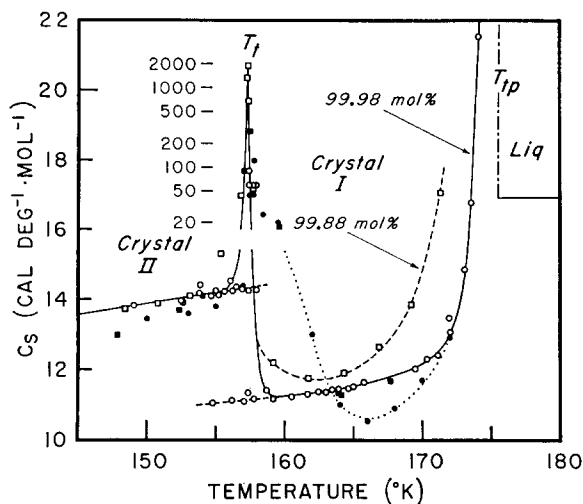


FIG. 1. Heat capacity of methyl alcohol over the transition and fusion regions. Sample I and II data are represented by \circ and \square , those of Kelley² by \blacksquare , and those of Staveley and Gupta³ by \bullet .

mine the mole fraction (N_2) of solid-insoluble liquid-soluble impurity. Since the amount of impurity is small, use of the equation²⁰

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

(which assumes the solution to be perfect) yields values of N_2 for Samples I and II of 0.00025 and 0.0012, respectively, with $T_0 = 175.587^\circ\text{K}$, $T_1 = 175.569^\circ\text{K}$, and $\Delta Hm = 768.5 \text{ cal mol}^{-1}$ for Sample I and $T_0 = 175.53^\circ\text{K}$, $T_1 = 175.41^\circ\text{K}$, and $\Delta Hm = 761 \text{ cal mol}^{-1}$ for Sample II. T_0 is the triple point of pure methanol, and T_1 is that of the particular sample.

These data reveal that an appreciable fraction of the premelting energy is missing for Sample II. However, from examination of Fig. 1, premelting is evident immediately after the solid phase Crystal I is formed. No evidence, however, for any appreciable pretransitional effect on the heat capacity due to impurity is seen in the approach to the transition in Crystal II. The series of equilibrium measurements (cf. Series 21, Table II; each point requiring 5–15 h of thermal equilibrium time) shows a sharp rise to a very high heat capacity maximum and a similarly sharp drop to the heat capacity of Crystal I. Enthalpy-type measurements on Sample I also indicated the transition to be quite sharp since Run F had an initial temperature only 0.3°K below the transition maximum.

The measurements of Sample I, coupled with identification of the transition temperature for Sample II, permitted compilation of the thermodynamic functions at selected temperatures in Table V. These functions are considered to have a probable error less than 0.1% above 70°K . An extra digit has frequently been retained for internal consistency and to permit interpolation and differentiation within the table. Omission of nuclear spin and isotope mixing contributions to the enthalpy and Gibbs energy give practical values for

chemical thermodynamic purposes. A comparison is made of the vital facets of the thermal data of this investigation with previously reported results in Table VI.

DISCUSSION

Zero-Point Entropy of Crystalline and Glassy Methanol

The probability of the existence of a significant zero point entropy was largely dispelled by the structural

TABLE IV. Melting region of methanol.^a Units are calories, moles, and degrees Kelvin.

T	ΔT	C_p	ΔH_{excess}	$1/F$	T_f
Sample I, Mark I Cryostat					
Series 10, Detns G					
170.353	0.786	12.29	0.3		170.746
171.147	0.809	12.41	0.6		171.147
172.059	1.024	13.06	9.6		172.571
173.108	1.085	14.87	4.6		173.651
174.112	0.934	21.54	13.3		174.579
175.028	0.73	98.38	79.2	9.705	175.410
Series 11, Detns H					
171.994	1.949	13.48	3.3		172.969
173.567	1.214	16.77	8.8		174.174
174.776	1.208	77.53	87.9	8.743	175.380
175.434	0.122	787.6	182.8	4.205	175.495
175.530	0.084	1 140	278.2	2.762	175.529
175.539	0.020	4 720	374.6	2.051	175.549
175.874	0.657	612.8	767.9		176.202
Series 13, Detns J					
174.796	1.429	136.5	185.1	4.151	175.510
175.525	0.049	4 070	385.3	1.995	175.550
175.550	0.020	10 500	593.3	1.295	175.566
176.900	2.676	823	769.1		178.238
Series 20, Detns L					
173.416	1.890	16.18	10.0		174.361
174.664	0.663	34.50	23.2	33.2	174.980
175.239	0.535	301.3	178.4	4.308	175.506
175.524	0.052	3 860	379.3	2.026	175.550
175.556	0.011	20 200	602.4	1.276	175.561
Sample II, Mark III Cryostat					
Series 22, Detns N					
164.29	2.612	11.92	2.42		
166.83	2.491	12.66	4.91		
169.21	2.327	13.85	9.54		
171.34	1.980	17.08	19.48		
173.00	1.364	26.96	39.58	19.22	173.684
174.35	1.357	103.4	163.07	4.665	175.031
175.13	0.248	593.4	307.05	2.478	175.251
175.30	0.092	1 606	453.62	1.677	175.343
175.37	0.048	3 063	600.98	1.266	175.391
175.76	0.769	217.6	760.79	(1.000)	(175.391)

^a ΔH_{excess} is the enthalpy increment associated with melting after deletion of the extrapolated normal background vibrational or lattice enthalpy; T_f is the final temperature of a given enthalpy input; and $1/F$, the reciprocal fraction melted, equals $[\Sigma \Delta H_{\text{excess}}(\text{at } T_f)/\Delta Hm]^{-1}$.

studies of Tauer and Lipscomb.⁵ The entropy of the liquid at 298.15°K found in this present investigation agrees within 0.01 cal mol⁻¹·°K⁻¹ with that calculated by Pitzer and Weltner.²¹ Failure to correct for dimers and tetramers in the gaseous state accounts for the earlier apparent discrepancy^{22,23} between the third law and spectroscopic determinations of the entropy.

Sugisaki, Suga, and Seki^{24,25} have studied the thermal properties of an amorphous "glassy" state of methanol obtained by slow condensation from the vapor phase at about 70°K. Their adjustment of data from 20–104°K for the presence of some crystalline phase, inclusion of a glass-type transition at 105°K, and extrapolation of the liquid-phase data from 175–105°K corresponds to an apparent zero-point entropy for the "glass" of 6.6 cal/(mol °K). Their crystalline heat capacity data from 21–112°K accord with the present data within the relatively low precision (1.4%–0.5%) of their measurements.

Mechanism of Transition and Melting

From the heat capacity data presented in this paper it is seen that no evidence was found for the existence of the reported second transition slightly below the observed transition. However, the finding of other investigators¹² that reliable measurements can be made of the properties of Crystal II only after an adequate thermal conditioning procedure is confirmed. The marked effect of small traces of impurity on the thermal behavior in the transition region of Crystal I is also notable.

In view of the ease of both superheating and undercooling the transition in pure Sample I and the sharpness of the transition revealed both by the enthalpy-type measurements with Sample I and the equilibrium measurements with Sample II, the transition should be regarded as of first order, rather than of lambda type. Although numerous reports have been made of such phenomena associated with first-order transformations, none are known for second-order phase transformations. Treatment of the methanol transition as first order has also been suggested by authors of dilatometric and dielectric constant studies.¹²

The temperatures deduced from dilatometric data⁸ for the maximum rate of volume increase (156 and 159°K) differ significantly from that of the calorimetric heat capacity peak (157.4°K). The dielectric constant studies were more suggestive than conclusive in establishing the existence of a "second transition." Since thermal and phase equilibria in the transition region were not attained for several hours in this calorimetric study, it is suggested that some of the other reported physical measurements in this region may be representative of *transitive*, rather than *pertinent* properties of the solid phase.

Nature of the Fusion Transition

Dielectric constant¹² and proton magnetic resonance^{26,27} studies have indicated that a more marked

TABLE V. Thermodynamic properties of methanol. Units are calories, moles, and degrees Kelvin.

T	C_p	S°	$H^\circ - H_0^\circ$	$-(G^\circ - H_0^\circ)/T$
Crystal II				
5	0.015	0.005	0.02	0.001
10	0.168	0.047	0.37	0.011
15	0.584	0.186	2.14	0.043
20	1.219	0.436	6.57	0.108
25	1.983	0.789	14.54	0.207
30	2.776	1.221	26.46	0.339
35	3.566	1.708	42.32	0.499
40	4.330	2.235	62.08	0.683
45	5.050	2.787	85.54	0.886
50	5.719	3.354	112.5	1.104
60	6.905	4.505	175.8	1.575
70	7.921	5.647	250.0	2.075
80	8.825	6.765	333.8	2.592
90	9.668	7.853	426.3	3.116
100	10.47	8.914	527.1	3.643
110	11.24	9.949	635.7	4.170
120	11.93	10.957	751.6	4.694
130	12.54	11.937	874.0	5.213
140	13.10	12.886	1002.3	5.728
150	13.73	13.811	1136.2	6.236
Crystal I				
160	11.25	15.635	1421.1	6.753
165	11.51	15.985	1477.9	7.028
170	11.93	16.334	1536.4	7.296
175	12.43	16.687	1597.3	7.539
Liquid				
180	16.91	21.523	2447.4	7.926
190	16.92	22.438	2616.6	8.666
200	16.96	23.307	2786.0	9.377
210	17.03	24.136	2955.9	10.060
220	17.14	24.931	3126.8	10.718
230	17.29	25.696	3298.9	11.353
240	17.47	26.435	3472.7	11.966
250	17.70	27.153	3648.5	12.559
260	17.96	27.850	3826.8	13.134
270	18.27	28.536	4007.9	13.692
280	18.63	29.207	4192.4	14.234
290	19.03	29.867	4380.6	14.762
300	19.48	30.520	4573.2	15.276
310	19.98	31.167	4770.4	15.778
320	20.54	31.810	4973.0	16.269
273.15	18.38	28.75	4066	13.86
298.15	19.39	30.40	4537	15.18

TABLE VI. Comparison of thermal measurements on methanol.^a Units are degrees Kelvin, calories, and moles.

Investigator	T_t	ΔHt	ΔSt°	T_{tp}	ΔHm°	ΔSm°	$S^\circ_{298.15}$
Parks	161.1	140	0.87	175.3	759	4.33	32.6
Kelley	157.4	154.3	0.98	175.22	757.0	4.32	30.3±0.2
Staveley and Gupta	157.8	170±2	1.08	175.37	755.1±3	4.31	...
This research	157.34	152.0±0.5	0.966	175.59	768.5±1	4.377	30.40±0.03

^a T_t , transition temperature; T_{tp} , triple point; $S^\circ_{298.15}$ values are for the liquid phase.

change in properties occurs at the transition than at fusion. Furthermore, in this study the effect of a small amount of impurity on Crystal I of Sample II was noted, whereas no such effect was found for Crystal II. Extensive hydrogen bonding exists in the liquid²⁰ as well as in the solid; however, in the former bonding is limited to chains of fewer members than in the solid state. The transition mechanism of Tauer and Lipscomb postulates that the methanol molecules are hydrogen bonded into relatively stable, discrete chains. Premelting phenomena and the melting process itself could involve rupture of the chains into smaller units, or at least a more rapid interchange of members among the chains. However, Luck²⁸ has deduced the percentage of non-H-bonded CH₃OH in liquid methanol from infrared spectral data and concludes that less than 1% is dissociated below 250°K. They have evaluated the trend of the heat capacity of the liquid from 250–400°K on the basis of their model. Wertz and Kruh²⁹ have further established that the hydrogen-bonded oxygen–oxygen contacts occur in methanol at about the same distance in both crystalline and liquid states.

Plastic Nature of Crystal I

Timmermans¹⁴ empirical definition of a plastic crystal as a substance which has an entropy of melting less than 5 cal mol⁻¹·°K⁻¹ would occasion classification of methanol as a plastic crystal. Other characteristic macroscopic properties of typical plastic crystals (plasticity, high vapor pressure, relatively entropic transition into the plastically crystalline state, and more marked change in physical properties on transition than on melting) occur as a consequence of globularity of the molecule. However (as noted previously), persistence of hydrogen bonding in the liquid and gaseous phases²¹ causes methanol to have unusual properties for a molecule of its small mass, e.g., a relatively low vapor pressure and an extended liquid range (163°K). In this respect it resembles succinonitrile³⁰ more than a characteristic plastic crystal.

The considerable similarity between the Crystal I and liquid states is noted in the section on melting and discussed subsequently in connection with proton magnetic resonance experiments. (Timmermans¹⁴ error in asserting that there is a continuity in the heat capacity across the melting transition apparently arises from a

plotting error.) However, the abnormally small entropy of the liquid phase—a consequence of the ordering resulting from hydrogen bonding—is the prime cause for the small entropy of melting rather than the supposed plastically crystalline nature of Crystal I. This is confirmed by examination of the data in Table VII comparing the behavior of methanol with that of other small molecules. Hence, the small entropy of melting ($\Delta Sm = 4.377$ cal mol⁻¹·°K⁻¹) is a consequence of intermolecular structures (ordering in the liquid) rather than of independent molecular behavior (reorientational–rotation) in the Crystal I phase.

The small entropy of transition ($\Delta St = 0.966$ cal mol⁻¹·°K⁻¹) and the decrease in heat capacity across the Crystal II→Crystal I transition (similar to that in dimethyl acetylene³¹) is atypical for plastic crystals.

This argument against the plastically crystalline nature of phase I finds support in the proton magnetic resonance (PMR) measurements of Cooke and Drain,²⁶ which showed that the spin–lattice relaxation time changes discontinuously across the transition but continuously through the melting point. This had been taken as an indication that the molecular reorientation is of the same order in the Crystal I phase as in the liquid. Das³² concluded that the spin–lattice relaxation times in the Crystal I phase are less likely a consequence of rolling motion of the entire molecule or a correlated motion of the methyl and hydroxyl groups than of uncorrelated motion of the methyl group above the transition. On the other hand, Krynicky and Powles,²⁷ who also used the PMR technique, found a gradual increase in relative intensity of the narrow line together with the simultaneous persistence of the broad line to the melting point. However, they asserted that only 3% of the molecules are rotating even at 163°K in the Crystal I phase and also confirmed that the bulk of the Crystal I phase should not be considered to be a “rotator” phase. A further linewidth narrowing through two orders of magnitude was found on melting.

In conclusion, we note that although the thermodynamics of the methyl alcohol system have now been well defined under saturation pressure, the striking 3-cal mol⁻¹·°K⁻¹ drop in heat capacity at the transition has not proven accountable in terms of molecular freedom. Hence, data on the isothermal compressibility and the thermal expansion for conversion of the heat capacity to constant volume are clearly desiderata.

TABLE VII. Thermodynamic properties of selected monosubstituted methanes. Units are degrees Kelvin, grams, calories per mole, and calories per mole-degree Kelvin.

Compound	Mole wt.	T_i	ΔS_i	T_m	ΔS_m	$S_{298.16^\circ K}^\circ$		T_b^a
						(liq.)	(ideal gas)	
Methylamine ^b	31.06	101.5	0.230	179.70	8.157	35.90	57.73	266.5
Methanol	32.04	157.3	0.966	175.59	4.377	30.40	57.24	337.65
Methanethiol ^c	48.10	137.6	0.350	150.16	9.399	...	60.86	280.6
Chloromethane ^d	50.49			175.44	8.760	36.74	55.94	248.78
Nitromethane ^e	61.01			244.73	9.476	41.05	65.73	374
Bromomethane ^f	94.95	173.8	0.653	179.44	7.964	...	58.61	276.56

^a J. Timmermans, *Physico-Chemical Constants of Pure Organic Compounds* (Elsevier, New York, 1950).

^b J. G. Aston, C. W. Siller, and G. H. Messerly, *J. Am. Chem. Soc.* **59**, 1743 (1937).

^c H. Russell, Jr., D. W. Osborne, and D. M. Yost, *J. Am. Chem. Soc.* **64**, 165 (1942).

^d G. H. Messerly and J. G. Aston, *J. Am. Chem. Soc.* **62**, 886 (1940).

^e W. M. Jones and W. F. Giaque, *J. Am. Chem. Soc.* **69**, 983 (1947).

^f C. J. Egan and J. D. Kemp, *J. Am. Chem. Soc.* **60**, 2097 (1938).

^g Reference 21.

^h References 22 and 23.

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¹ G. S. Parks, *J. Am. Chem. Soc.* **47**, 338 (1925).

² K. K. Kelley, *J. Am. Chem. Soc.* **51**, 180 (1929).

³ L. A. K. Staveley and A. K. Gupta, *Trans. Faraday Soc.* **45**, 50 (1959).

⁴ J. E. Ahlberg, E. R. Blanchard, and W. O. Lundberg, *J. Chem. Phys.* **5**, 539 (1937).

⁵ K. J. Tauer and W. N. Lipscomb, *Acta Cryst.* **5**, 606 (1952).

⁶ B. Dreyfus-Alain and R. Viallard, *Compt. Rend.* **234**, 536 (1952).

⁷ G. S. R. K. Murti, *Indian J. Phys.* **33**, 458 (1959).

⁸ L. A. K. Staveley and M. A. P. Hogg, *J. Chem. Soc.* **1954**, 1013.

⁹ D. W. Davidson, *Can. J. Chem.* **34**, 1243 (1956).

¹⁰ C. P. Smyth and S. A. McNeight, *J. Am. Chem. Soc.* **58**, 1597 (1936).

¹¹ C. P. Smyth and C. S. Hitchcock, *J. Am. Chem. Soc.* **54**, 4631 (1932).

¹² D. W. Davidson, *Can. J. Chem.* **35**, 458 (1957).

¹³ G. Baume and W. Borowski, *J. Chim. Phys.* **12**, 276 (1914).

¹⁴ J. Timmermans, *J. Phys. Chem. Solids* **18**, 1 (1961).

¹⁵ D. W. Osborne and E. F. Westrum, Jr., *J. Chem. Phys.* **21**, 1884 (1953).

¹⁶ E. F. Westrum, Jr., G. T. Furukawa, and J. P. McCullough, "Adiabatic Low-Temperature Calorimetry," in *Experimental*

Thermodynamics, edited by J. P. McCullough and D. W. Scott (Butterworths, London, 1968), p. 133.

¹⁷ H. G. Carlson, "Thermodynamic Properties of Methyl Alcohol, 2-Methyl- and 2,5-Dimethylthiophene, and 2-Methylfuran," Ph.D. dissertation, University of Michigan, 1962.

¹⁸ H. J. Hoge and F. G. Brickwedde, *J. Res. Natl. Bur. Std.* **22**, 351 (1939).

¹⁹ B. H. Justice, "Calculation of Heat Capacities and Derived Thermodynamic Functions from Thermal Data with a Digital Computer," Appendix I to Ph.D. dissertation, University of Michigan, 1961; also see TID-12722, Office of Technical Services, Oak Ridge, Tenn., 1961.

²⁰ D. D. Tunnicliff and H. Stone, *Anal. Chem.* **27**, 73 (1955).
²¹ J. H. Badley, *J. Phys. Chem.* **63**, 1991 (1959).
²² S. V. R. Mastrangelo and R. W. Dornte, *J. Am. Chem. Soc.* **77**, 6200 (1955); S. S. Todd, G. D. Oliver, and H. M. Huffman, *ibid.* **69**, 1519 (1947).

²³ K. S. Pitzer and W. Weltner, Jr., *J. Am. Chem. Soc.* **71**, 2842 (1949).

²⁴ J. O. Halford, *J. Chem. Phys.* **18**, 361 (1950).

²⁵ J. O. Halford and G. A. Miller, *J. Chem. Phys.* **61**, 1536 (1957).

²⁶ M. Sugisaki, H. Suga, and S. Seki, *Bull. Chem. Soc. Japan* **40**, 2984 (1967).

²⁷ M. Sugisaki, H. Suga, and S. Seki, *Bull. Chem. Soc. Japan* **41**, 2586 (1968).

²⁸ A. H. Cooke and L. E. Drain, *Proc. Phys. Soc. (London)* **65**, 894 (1952).

²⁹ K. Krynicki and J. G. Powles, *Proc. Phys. Soc. (London)* **1964**, 983.

³⁰ W. A. P. Luck, *Discussions Faraday Soc.* **43**, 115 (1967).

³¹ D. L. Wertz and R. K. Kruh, *J. Chem. Phys.* **47**, 388 (1969).

³² C. A. Wulff and E. F. Westrum, Jr., *J. Phys. Chem.* **67**, 2376 (1963).

³³ D. M. Yost, D. W. Osborne, and C. S. Garner, *J. Am. Chem. Soc.* **63**, 3492 (1941).

³⁴ T. P. Das, *J. Chem. Phys.* **27**, 763 (1957).