WILLIAM MARSH RICE UNIVERSITY

The Entropy and Related Thermodynamic
Properties of Dimethoxymethane

by

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To my mother and father, whose wisdom and understanding have always been a source of joy and inspiration.

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I

INTRODUCTION

The goal of this research was to measure by means of isothermal calorimetric techniques the heat capacities and heats of isothermal transitions of dimethoxymethane and to determine the heat of vaporization of acetonitrile, in order to find the experimental ideal gas entropy of these substances. In general, the reasons for carrying out such an investigation are two. First, there is the intrinsic value of determining the thermal properties of any pure substance in order to characterize it. Second, these properties can be used in calculations employing the third law of thermodynamics to find the absolute entropy of the substance. This entropy can also be made available by other paths which involve the configuration of the molecule and its spectroscopic properties. Together, these two sources of the entropy serve as checks upon one another and offer a confirmation of the configuration.

Experimental determinations of the entropy of dimethoxymethane or the heat of vaporization of acetonitrile have not previously appeared. By using the freezing curves of binary mixtures which behaved as ideal solutions, Timmermans (1) obtained a value for the heat of fusion of dimethoxymethane. Earlier determinations of this quantity have also been reported (2,3). The melting point and

normal boiling point have appeared in the literature (4). Vapor pressure and vapor density measurements and boiling point determinations have been obtained and used to calculate the heat of vaporization of dimethoxymethane (5,6,7). Spectroscopic data for dimethoxymethane is available from Raman, ultra-violet, infra-red, and electron diffraction techniques (8,9,10,11). Additional physical constants for this compound have been reported (4,12,13,14,15,16). The heat of vaporization of acetonitrile has been calculated and reported from several sources by Putnam (17).

II

APPARATUS

A. Cryostats

The cryostat used to obtain the heat capacities and heat of fusion in this research was originally built by Johnson (18) and was later modified extensively by Taylor (19). Its laboratory designation is calorimeter "B". It was found during this research that the temperature stability necessary in the apparatus for reproducing thermometric fixed points could only be produced by careful and continuous control of the sample tube and outer can heaters. Provision is not made for controlling these heaters simultaneously from the power panel. The block heater, the upper tube heater, and the lower tube heaters operate from a single variac which precludes simultaneous heating. The can heater is powered directly by 110 volt a. c. house current. It was decided to use auxiliary variacs to control these heaters. In the event that either the upper sample tube, lower sample tube, or block heaters are grounded, a 1:1 isolation transformer prevents them from being shorted to ground. The can heater, not connected to this transformer, is protected from damage by being fused. The use of auxiliary variacs to control any of these heaters raises the danger that if a short to ground occurs, 110 volts may

be thrown across them. However, since the 110 volt a. c. available is grounded on one side, this can be prevented. The variable and fixed outlets on the variac are polarized with respect to the inlets. If care is exercised to connect the fixed outlet of the variac to the grounded inlet, then accidental grounding of one of the heaters can produce a voltage across it of only the value of the setting of the variac. Otherwise, 110 volts is placed across it. For this reason, all of the 110 volt wall plugs and the variacs used were marked for polarization orientation, and were connected in the manner described above. Connections for controlling the heaters with these variacs were made through the appropriate heater switches behind the power panel.

The sample container used for the heat capacity measurements was sample container "V" (19). The addition of a sample-block thermocouple made temperature adjustment prior to each heat capacity measurement easier and offered the means by which radiation corrections to the heat of fusion and heats of vaporization were determined.

For the heats of vaporization laboratory designated calorimeter "C" was used. It was built by Putnam (17) and modified by Weber (20). The sample container and thermometer were that of reference (20).

B. Measurements

The procedure for heat capacity measurements has been described previously (19). A change has been made in the quadratic extrapolation of sample container drifts from that used previously, which adds a small correction to this procedure, and which changes the method of extrapolation using first and second differences from one involving an approximation to one which is mathematically exact. This change has the effect of making the radiation correction for heat loss during a heat capacity measurement more accurate if quadratic drifts are encountered. If one assumes that the voltage drop, E , across the platinum resistance thermometer is given as a quadratic function of time, t , and that E is read at minute intervals up to the beginning of the heat input, then the following is true:

$$E^0 = E_0 + t_1 (D/S) \quad (1)$$

with:

$$D = R_{t_0} - R_{t_0-1} + \frac{1}{2} \Delta^2 (t_1 + 1) \quad (2)$$

where E^0 is the voltage drop at time t_1 , in μv

E_0 is the voltage drop at time t_0 , in μv

t_1 is the time from the beginning of the heating interval to its mid-point, in minutes

S is the sensitivity of the galvanometer, in div./ μv

D is the extrapolation drift, in div.

R_{t_0} is the reading of the galvanometer at t_0 ,
in div.

R_{t_0-1} is the reading of the galvanometer at t_0-1 ,
in div.

Δ^2 is the second difference in E versus t, in div.

The indicated change involves the addition of the $(t_1 + 1)$ factor in place of the factor t_1 into equation (2) for the extrapolation drift. Assuming a ten minute heating interval and values of $\Delta^2 = 0.04$ div., $S = 6$ div./ μ v, $D = 3$ div./min., and using temperature values around that of room temperature, a change of $\pm 0.0005^\circ$ K is produced in the temperature of the mid-point of the heating interval. In most cases the value of Δ^2 is so small that the introduction of $(t_1 + 1)$ instead of t_1 produces a negligible correction.

C. Thermometer

Upon beginning to calibrate laboratory designated platinum resistance thermometer 100-3, a large parasitic voltage of approximately 50 microvolts was noted when there was no current flowing through the thermometer. Tests conducted when the thermometer was at a temperature slightly in excess of 100° C and when it was at liquid nitrogen temperatures showed that this effect disappeared under these conditions, thus leading to a suspicion of the presence of moisture inside the thermometer being the cause of this effect. A circuit was set up using a 300

volt power supply in series with the thermometer leads and the case, with a 1 megohm safety resistor, in order to test the lead-to-case resistance of the thermometer by measuring with a potentiometer any current flow in this circuit. Because of either faulty wire insulation used for setting up the circuit or actual dielectric breakdown in the thermometer itself, 100-3 was shorted and ruined. Thus, construction was begun on a new platinum resistance thermometer, which was to be designated thermometer 4.

Construction details for platinum resistance thermometers have been outlined by Meyers (21). One of the more difficult portions of the work in accomplishing such a project is the building of the mica support cross. The cross used to build thermometer 4 was made from 0.007 inch thick mica sheet. Since clear, high-quality mica which will withstand annealing temperatures of approximately 600 ° C is difficult to obtain and is quite expensive, a method of pre-cutting strips of mica for insertion in the notching and teeth-cutting jigs was developed, which offered the most conservation of the mica. The difficulty experienced in this procedure involved cutting a strip of mica of width slightly larger than the first jig used without causing the edges to delaminate appreciably. Poor technique can cause delamination of about 1/8 inch into the mica. This splitting is very wasteful. The final

strips are, themselves, only about $1/4$ inch wide when completed. With care and technique a separation of less than $1/32$ inch can be obtained. The best method found was to use a surgical scalpel with size 20 scimitar-shaped blades and to clamp the mica tightly between a thick metal plate and a steel ruler, using the latter as a guide. Moderate pressure, requiring about five strokes with the blade, was found to be most suitable. It is interesting to note that the commercially available mica was cut in a manner at the factory which produced no separation whatsoever.

The most useful tool for producing the teeth in the previously shaped and slotted mica strip was not a roughened wire, as suggested by Meyers (21), but 0.020 inch wide steel files, constructed by grinding down swiss pattern files whose edges had been honed down to provide strengthening filets at the base of the teeth.

In dissolving the steel mandrels from beneath the close-wound helices, preparatory to winding the platinum coil around the mica cross, concentrated and dilute hydrochloric acid were used as suggested (21). This produced bits of adhering oxide which were difficult to clean away from the coil. Dissolving the mandrel in alum solutions obviated this difficulty, but was very slow. Finally the procedure of dissolving the mandrel in concentrated hydrochloric acid, followed by soaking in a concentrated alum

solution to clean away the oxide, followed by more hydrochloric acid to dissolve the calcium sulfate formed, was found to work best.

The completed thermometer was then annealed. According to Coruccini (22), optimum annealing conditions for platinum used in precision resistance thermometry should be attained by heating in a furnace for from one to two hours in air, at 400 to 500 °C, followed by slow cooling over a period of approximately one-half hour. This should suffice for platinum of the highest purity. Meyers (21) describes a preliminary annealing in air of the mica cross and platinum helix in a furnace for two to three hours at 600-650 °C, followed by a final period of heating, after a final adjustment of the resistance of the coil. Excessive heating, either in time or temperature, can cause weakness in the platinum from crystal growth. It was finally decided to anneal thermometer 4 for longer periods of time at a temperature of 450 °C, the lower temperature being chosen in order to furnish a margin of safety for the mica cross and the glass head. The criterion chosen for complete annealing was the stability of the triple point of water resistance. Table I presents a summary of the annealing periods for thermometer 4 in an electric furnace. It is to be noted that the practice of annealing a platinum resistance thermometer by passing a current through the coil

TABLE I

SUMMARY OF ANNEALING PERIODS AND WATER TRIPLE POINT RESISTANCE CHANGES----THERMOMETER 4

No.	Annealing Period at 450 °C	Subsequent Resistance	Change in Resistance
	hours	ohms	ohms
I	16(in air)	78.2500	0.0465
II	8(sealed) 16 cooled slowly	78.2965	
III	0.5(sealed)	78.2977	0.0012
IV	0.75(sealed)	78.2976	-0.0001

has the advantage, over the electric furnace method, that the mica cross and the encapsulation are not subjected to the full annealing temperature.

Thermometer 4 was calibrated for the International Temperature Scale by measuring its resistance at the benzoic acid melting point, the triple point of water, the triple point of nitrous oxide, and the normal boiling point of oxygen. The resistance measurements of the benzoic acid melting point and the water triple point were carried out in specially constructed cells which were set up outside of the cryostat. The benzoic acid cell has been described elsewhere (27). The triple point of water cell was that described by Weber (20).

The measurements of the resistance of thermometer 4 at the nitrous oxide triple point and at the normal oxygen boiling point were done inside the cryostat using the calibrating sample container constructed by Weber (20). Since calorimeter B contains a sample tube which does not enter the vacuum space axially, there is a soldered bend in it just below the spool which permits the lower end of the sample tube to be brought through the center of the top of the block. This bend makes it structurally unsound to support the sample container from the sample tube. For this reason three holes were drilled and tapped 120 degrees apart in the top of the sample container to accomodate

2x56,3/16 inch long screws, on the heads of which small wire loops were soldered so that thread could be passed through them. The sample container was thus supported entirely by nylon thread from the top of the block.

The calibrating sample container has wells for the thermometer to be calibrated and for a standard Leeds and Northrup platinum resistance thermometer whose nominal ice point resistance is 25 ohms. This thermometer serves the dual purposes of checking the fixed point temperatures and furnishing a calibration scale in the temperature range from 20 to 64° K.

Due to the small temperature difference between the normal boiling point and the triple point of nitrous oxide, difficulty was experienced in distilling the gas from the sample collection bulb into the calorimeter. The geometry of the sample tube makes it very easy for solid nitrous oxide to condense at the point where it enters the outer can or along the 2 ½ inches of exposed portion between the top of the block and the sample container. This latter section cannot be heater wound because the sample container-sample tube solder joint is near the center of it. A sample tube-block difference thermocouple was installed with one junction near the solder joint in order to better control the temperature of this critical section, while condensing nitrous oxide. Out of a large number of conditions

which were tried, those under which optimum distillation was realized occurred when the insulating vacuum pressure was approximately 25 microns and the liquid nitrogen level was below the bottom of the can, so that its temperature could be regulated to about 40°C below the nitrous oxide freezing point. The block temperature was kept as close above the freezing point as possible and the condensation was done at two atmospheres. Distillation into the sample container was carried on from a specially constructed sample bulb 13 m.m. in diameter which was calibrated for the purpose of monitoring the rate of condensation. The nitrous oxide used for this calibration was clinical grade bottled gas, with which great care was taken to prevent contamination by air or water vapor before introduction into the cryostat.

Oxygen was generated for the boiling point determinations by the method outlined by Scott (28). Although reagent grade potassium permanganate was used and care was taken so that all glassware used was clean, the problem of small traces of carbon dioxide condensing as solid crystals in the liquid oxygen collected became evident. Fractional distillation did not solve this problem because some of the solid carbon dioxide would adhere to the sides of the containing vessel above the meniscus while some of it would be trapped in the liquid oxygen itself, thus distilling continuously with the sample. Finally, a powerful carbon

dioxide absorbant, under the trade name of "Ascarite", was resorted to. The active agent in this material is sodium hydroxide. A trap filled with "Ascarite" was put between the oxygen generator and a liquid nitrogen-cooled trap, the purpose of which was to condense any water formed by the carbon dioxide absorption.

The temperatures corresponding to the measured oxygen vapor pressures were taken from Hoge's $1/T$ versus $\log P$ tables (29). As has been mentioned, the Leeds and Northrup thermometer calibrated by the National Bureau of Standards was used as a check and agreed to within 0.02 per cent of the certified calibration and to within 0.002 per cent of a previous determination (20) carried on in this laboratory at the normal boiling point of oxygen.

A summary of the resistances of thermometer 4 at the calibration points used to establish the International Temperature Scale is contained in Table II. The Callender-Van Dusen constants for this thermometer are presented in Table III. Thermometer 4 fulfilled all of the necessary restrictions set for these constants (30,31).

Below 90°K thermometer 4 was calibrated by the method described by Hoge and Brickwedde (32), in the manner outlined by Weber (20).

TABLE II

SUMMARY OF CALIBRATION POINTS OF THERMOMETER 4 FOR THE INTERNATIONAL TEMPERATURE SCALE

Point	Temperature °C	Thermometer Resistance abs. ohms
Benzoic Acid Melting Point	122.359	115.7528
Water Triple Point	0.0100	78.2973
Nitrous Oxide Triple Point	-90.809	49.5522
Oxygen Normal Boiling Point	-182.963	19.1037

TABLE III

CALLENDAR-VAN DUSEN EQUATION CONSTANTS OF THERMOMETER 4

R	78.2942
α	0.00392325
β	0.113722
δ	1.50028

III

EXPERIMENTAL

A. Dimethoxymethane

1. Sample

The dimethoxymethane used in this research was manufactured by the Matheson, Coleman, and Bell Company, a division of the Matheson Company, Inc., Norwood, Ohio, and was designated lot numbers 374222 and 314233, whose stated boiling points were 42-44 °C. Purification of the sample was accomplished by fractional distillation in a glass helix-packed column of length four feet. The reflux ratio was controlled with an electromagnetic reflux head and was set at 15 to 1. Monitoring the purity of the product was done with a Perkin-Elmer model 154 vapor fractometer using columns D and DX manufactured by the same company. The final sample was determined to have a mole percent purity of greater than 99.9.

Several drying agents, including phosphorus pentoxide, calcium chloride anhydrous salt, sodium, potassium hydroxide, and magnesium sulfate, were tested for suitability with dimethoxymethane. Sodium proved to be unreactive with the sample and was considered the most efficient drying agent available. After storage over sodium for four weeks, the sample was distilled from the drying agent without fractionation and placed in a dessicator charged with phosphorus pentoxide.

A portion of this sample was used for tests to determine if dimethoxymethane reacted with copper, the material from which the sample container is constructed. Polished copper strips tarnished faster in the sample than in air, but this was expected because of the enhanced reactivity of dissolved oxygen. Pre-tarnished copper showed no change in appearance after soaking in dimethoxymethane for several days. The interior of the sample container consists of tarnished copper. In order to be sure that the sample did not produce further rapid oxidation of copper, two strips were soaked in the sample for ten days. Both strips were first cleaned and polished. One strip was allowed to tarnish in air. The other strip was allowed to tarnish in dimethoxymethane. The strips were then carefully weighed and put into the sample. After soaking, there was no detectable weight change, so that it was decided that dimethoxymethane would have no reactive effect on the sample container. The possibility of cuprous and cupric oxides dissolving in the sample was investigated, also. Granulated, partially tarnished copper was put into dimethoxymethane and allowed to react for several days. The liquid was then decanted and extracted with aqueous ammonia solution. The absence of any blue cupric ammonia complex in the aqueous layer proved that copper oxide did not dissolve in the sample to any appreciable extent.

Because of an error in the initial weight of the sample container, which involved not weighing a small sample tube extension which was soldered on to the container for filling and removed afterward, the weight of sample used in the heat capacity measurements was gotten from one source--the difference in weight of the sample container before and after removal of the sample. The weight of sample in vacuum was 53.3614 grams and the molecular weight was taken to be 76.094. This is equivalent to 0.701256 moles of sample.

2. Heat capacities

No solid-solid transitions were observed for dimethoxymethane. The heat capacities as actually measured were carried out with a small amount of helium in the sample container to offer thermal conductivity to the sample in the solid phase. Without this helium, temperature equilibrium after a heating interval would be slow because the solid is made up of small crystals in poor thermal contact. The correction to the heat capacities due to this gas was small, since only 0.0017 grams was introduced into the sample container, and amounted to 0.002 cal./deg.-mole. Although the heat capacities are quoted to the nearest 0.01 cal./deg.-mole, this correction was applied before the final rounding off occurred and was used in the large scale graph constructed of heat

capacity versus temperature. The contribution of this amount of helium to the molar entropy of the sample at 298.15 °K is small and amounts to about 0.02 e.u./mole.

The heat capacity points taken are presented in Table IV in the order in which they were determined. Figure 1 gives these data graphically. Each series, designated by a capital letter, represents consecutive readings determined in the indicated temperature range, during which no phase transition of the sample took place. The heats and temperatures of fusion measurements are indicated as they occurred and are identified by lower case letters.

On the basis of data taken in the past, heat capacity precision should be better than 0.3 per cent above 250 °K and precise to better than 1 per cent at very low temperatures. In the intermediate temperature range it should be precise to about 0.03 per cent. Above 90 °K temperature can be measured to a precision of about 0.002 degree, which decreases until at 20 °K it is about 0.01 degree.

The heat capacity precision quoted above is not usually found near a transition because there is reason to believe that heat capacities in the region of premelting are generally subject to hysteresis. In the case of dimethoxymethane the heat capacities in the premelting

Figure 1

TABLE IV

MOLAR HEAT CAPACITY OF DIMETHOXYMETHANE

Temp. °K	Heat Capacity cal/deg.-mole	Temp. °K	Heat Capacity cal/deg.-mole
Series A (solid)		Series D (continued)	
89.19	16.42	94.40	17.00
106.26	18.37	104.11	18.07
136.35	21.05	113.25	18.99
149.85	21.94	121.93	19.78
		130.28	20.48
Series B (solid)		138.36	21.12
121.66	19.73	148.25	21.81
137.98	21.05	158.77	22.46
148.04	21.77		
162.29	22.24	Series E (solid)	
Temp. of fusion a		70.41	13.60
Series C (liquid)		82.29	15.45
173.28	34.49	89.20	16.41
183.01	34.66	95.75	17.18
171.08	34.47	101.99	17.88
176.96	34.62	108.49	18.53
184.79	34.69	115.36	19.19
192.57	34.81	123.57	19.92
200.15	34.94	138.61	21.13
207.63	35.10	146.37	21.71
215.15	35.27	154.15	22.25
222.40	35.45	160.00	22.30
229.83	35.69	164.53	22.59
235.50	35.87	63.22	12.35
243.34	36.16	Series F (solid)	
250.73	36.44	137.47	21.05
265.25	37.03	140.34	21.30
271.95	37.35	143.19	21.45
278.99	37.66	146.11	21.60
286.00	38.00	149.03	21.84
288.70	38.05	152.04	21.94
291.76	38.18	154.76	22.08
Series D (solid)		157.47	22.23
69.56	13.46	160.56	22.30
77.57	14.74	163.41	22.39
84.91	15.84	166.37	22.44

Temp. °K	Heat Capacity cal/deg.-mole

Series G (solid)

146.00	21.67
148.63	21.91
151.24	22.04

Heat of fusion a

Series H (solid)

154.30	22.09
155.76	22.09
157.35	22.07
158.85	22.17
160.43	22.20
162.09	22.36
163.72	22.36
165.16	22.26
166.57	22.51

Heat of fusion b

Heat of fusion c

Series J (liquid)

174.24	34.48
180.29	34.62
186.32	34.67

Heat of fusion d

Series K (solid)

16.06	1.369
18.92	1.959
20.40	2.289
23.08	2.933
26.25	3.746
30.09	4.745
33.88	5.752

Temp. °K	Heat Capacity cal/deg.-mole

Series K (continued)

37.66	6.732
41.70	7.719
46.00	8.754
50.93	9.879
56.80	11.11
63.48	12.41

Series L (liquid)

172.26	34.56
179.86	34.65
185.30	34.74

Temp. of fusion b

Series M (liquid)

193.57	34.85
199.84	34.94
284.72	37.95
292.13	38.28
300.15	38.68
307.77	39.05

region, that is, above 135° K to the melting point, exhibit a root mean square precision of 0.3 per cent with respect to the smooth curve. From this curve, which was drawn to the scale of 10 centimeters equivalent to 1 cal./deg.-mole and 2 centimeters equivalent to 1 Kelvin degree, the information contained in Table V was taken.

In the measured premelting region the assumption has been made that the curve of sample heat capacity approaches the melting temperature without sharp change of curvature, and that this behavior continues up to the temperature of fusion of the pure substance. The actual curvature observed has been considered an artifact due to sample impurity, and the premelting heat capacity has been subtraced from that observed according to the usual formula:

$$\bar{C} = NRT_{*}^2 / [(R_{*} - R'')(R_{*} - R'' + \Delta R)(dT/dR)_{\bar{R}}] \quad (3)$$

where $\bar{C}$ is the integral premelting heat capacity in cal./deg.-mole

N is the impurity concentration in moles/mole sample

T_{*} is the fusion temperature of the pure substance in °K

R'' is the thermometer resistance at the heating interval mid-point from final drift, in ohms

ΔR is the mid-point extrapolated thermometer resistance change, in ohms

$$\bar{R} = R'' - \frac{1}{2} \Delta R$$

TABLE V

THE MOLAR HEAT CAPACITIES OF DIMETHOXYMETHANE AT ROUNDED TEMPERATURES

T (° K)	C cal/deg.-mole	T (° K)	C cal/deg.-mole
15	1.148	170	34.46
20	2.19	175	34.54
25	3.42	180	34.62
30	4.72	185	34.69
35	6.04	190	34.77
40	7.31	195	34.86
45	8.52	200	34.95
50	9.67	205	35.04
55	10.74	210	35.15
60	11.74	215	35.26
65	12.68	220	35.39
70	13.54	225	35.53
75	14.35	230	35.69
80	15.12	235	35.86
85	15.84	240	36.04
90	16.50	245	36.22
95	17.10	250	36.41
100	17.66	255	36.60
105	18.18	260	36.81
110	18.68	265	37.02
115	19.14	270	37.25
120	19.60	275	37.48
125	20.04	280	37.72
130	20.47	285	37.95
135	20.87	290	38.18
140	21.27	295	38.42
145	21.63	300	38.67
150	21.92		
155	22.13		
160	22.29		
165	22.42		
Melting Point			

The corrected points above 165 °K are very sensitive to the concentration of impurity, N , chosen. A change of 0.001 mole per cent impurity produces a readily discernible change in the heat capacity curve two Kelvin degrees below the temperature of fusion. These last few points, then, essentially determine the impurity concentration in equation (3); and this concentration is used to consistently modify the lower temperature points. The value of N which offered the proper correction for the sample of dimethoxymethane used assumed the value of 3.0×10^{-4} moles/mole sample. From the temperature of fusion data plotted as a function of fraction of the sample melted, an estimate was obtained for the maximum value of $N = N_6^{\circ} \text{ max.}$, assuming the presence of solid soluble impurities. This estimating procedure is due to Putnam (17). It gave the value $N_6^{\circ} \text{ max.} = 3 \times 10^{-4}$ moles/mole sample.

A numerical investigation was undertaken on the data from the premelting region in order to see what impurity concentrations would result from the assumption that both solid soluble and solid insoluble impurities were present. The equation used for this analysis has been derived by Weber (20) and has the form:

$$C_{p.m.} = \frac{(\Delta H)^2}{RT^2} \left\{ \frac{(1-K)N_6^{\circ}}{X^{2-K}} \left(1 - K \frac{\beta'}{\alpha'} \right) + \frac{N_6^{\circ}}{X^2} \right\}^{-1} \beta' \quad (4)$$

where $\alpha' = 1 - \frac{K N_a^0}{X^{1-K}}$; $\beta' = 1 - \frac{N_a^0}{X^{1-K}} - \frac{N_b^0}{X}$

with $C_{p.m.}$: premelting heat capacity, cal./mole

ΔH : heat of fusion of pure substance, cal.

K : equilibrium constant for solid soluble impurity, a , for $a(\text{liquid}) \rightleftharpoons a(\text{solid})$

N_a^0 : total concentration of solid soluble impurity, moles/mole sample

N_b^0 : total concentration of solid soluble impurity, moles/mole sample

X : fraction of sample melted

As x approaches zero terms containing N_a^0 become very small with respect to terms containing N_b^0 , and the calculated value of N_b^0 approaches its true value if an erroneous K is used in the equation. Further, the correct K will be found by seeking that value for which the slope of calculated N_b^0 versus x approaches zero. Using these ideas, equation (4) was solved at closely spaced values of x , assuming different values of K . The results obtained were as follows: $N_b^0 = 8.7 \times 10^{-5}$, $N_a^0 = 9 \times 10^{-5}$, $K = 0.8$. These results are discussed in the next section.

At low temperatures, usually below 30°K , plots of $\Delta H/\Delta R$ show a minimum, and begin to increase rapidly as lower temperatures are reached. This is caused by dR/dT for the platinum resistance thermometer in this region being a rapidly increasing function of temperature. Because of the rapidly changing curvature in $\Delta H/\Delta R$, it is diffi-

cult to plot this quantity versus temperature and determine its relation to resistance with any degree of accuracy. A method by which points on this curve could be checked for smoothness and the curve defined accurately between them was needed. This can be done in the following manner. Heat capacities in this region vary as T^3 :

$$C = kT^3$$

The heat absorbed, ΔH , in a given temperature interval, ΔT , is given by

$$\Delta H = \int_{T-\frac{1}{2}\Delta T}^{T+\frac{1}{2}\Delta T} C dT = k \left[T^3 \Delta T + \frac{1}{4} T (\Delta T)^3 \right] \quad (5)$$

The mean heat capacity, $\bar{C}$, of the interval is, therefore

$$\bar{C} = k \left[T^3 + \frac{1}{4} T (\Delta T)^2 \right] \quad (6)$$

and

$$\bar{C} - C = \frac{1}{4} k T (\Delta T)^2 = \left(\frac{1}{4} C / T^2 \right) (\Delta T)^2 \quad (7)$$

Now

$$\bar{C} = (\Delta H / \Delta R) (dR / dT) \quad (8)$$

Substituting (8) into (7) gives

$$C = \frac{(\Delta H / \Delta R) (dR / dT)}{1 + (\Delta T / 2T)^2} \quad (9)$$

Using the experimentally determined $\Delta H / \Delta R$ values, a plot of calculated C versus T^3 can be made. The curve thus

found is straight for small T (less than about 20°K) and has small curvature above this temperature, being concave downward. The low temperature data in this investigation was treated in this manner.

3. Temperature of Fusion

The results of the temperature of fusion determinations a and b are given in Table VI. As stated previously, the upper limit of the solid insoluble impurity was found to be 0.03 mole per cent. Points lying below $(1/\text{fraction melted})$ equals seven were reasonably straight and were fitted to the usual equation of variation of freezing point with fraction melted, assuming solid insoluble impurity present only:

$$T = T_{*} - \frac{N RT}{\Delta H} \frac{1}{x} \quad (10)$$

The value obtained was $N = (6.7 \pm 0.8) \times 10^{-4}$ moles/mole sample. The freezing point found on this basis was $168.003 \pm 0.007^{\circ}\text{K}$.

The premelting heat capacity analysis of the previous section has indicated that the solid insoluble impurity concentration is 8.7×10^{-5} moles/mole sample. Using this value, and assuming, as before, that both solid soluble and solid insoluble impurities are present, treatment of the temperature of fusion data by the technique developed by Putnam (17) was carried out. The relation between

TABLE VI

THE TEMPERATURE OF FUSION OF DIMETHOXYMETHANE VERSUS THE
FRACTION MELTED-1

Determination a

Temp. of fusion ° K	1/Fraction Melted
167.880	7.30
167.938	3.22
167.959	2.07
167.971	1.52
167.981	1.20

Determination b

167.844	13.20
167.890	7.60
167.922	4.73
167.948	3.02
167.981	1.17

fusion temperature and the fraction melted is the following:

$$T = T_* - \frac{RT_*^2}{\Delta H} \left[\frac{N_a^0}{x+D} + \frac{N_c^0}{x} \right] \quad (11)$$

with

$$D = K/1-K$$

Rearrangement of the equation to the form

$$T' = \left[T + \frac{RT_*^2}{\Delta H} \frac{N_c^0}{x} \right] = T_* - \frac{RT_*^2}{\Delta H} \left[\frac{N_a^0}{x+D} + \frac{N_c^0 - N_c^0}{x} \right] \quad (12)$$

in which N_c^0 is an approximate value for N_c^0 , makes it convenient to apply to the data. N_c^0 is chosen and a value of D is found so that T' versus $1/(x+D)$ is a straight line. T_* is relatively insensitive to N_c^0 , so that a well chosen N_c^0 should lead to a better value for the melting point of the pure compound than the previous analysis of the straight portion of the temperature of fusion curve. The result of these calculations was $T_* = 168.009 \pm 0.003^\circ\text{K}$, so that the value finally assigned to the temperature of fusion of pure dimethoxymethane is 168.01°K with a deviation of $\pm 0.01\text{ K}$ degree. A previous published value of the temperature fusion, gotten without precise impurity correction, from a binary mixture analysis is -105.0°C or 168.2°K (4).

The distribution constant, K, for the solid soluble impurity was found to be 0.09 and the solid soluble impurity

concentration to be $6.0 \pm 0.1 \times 10^{-4}$ moles/mole sample.

It was hoped that the premelting heat capacity data and the temperature of fusion information could be used in conjunction in order to lead to unambiguous determinations of N_a° , N_g° , and K . Apparently, the impurities in the sample of dimethoxymethane used, although small in concentration, did not behave according to the assumptions implicit in the mathematical analysis. These assumptions are the following: (1) The temperature of fusion system behaves as an infinitely dilute solution, and the solid phase is homogeneous. (2) The premelting heat capacity system behaves as an ideal solution with an inhomogeneous solid phase. (3) The distribution coefficients of all solid soluble impurities are approximately the same size and do not vary with temperature for approximately thirty degrees below the fusion temperature. Assumption (1) would seem to be the most easily fulfilled in the real system. The ideality of the concentrated solution found in the premelting system, or the distribution coefficient assumption not being fulfilled can be more readily invoked to explain discrepancies in the values of N_a° and K . As has been mentioned, the value of N_a° found from premelting heat capacity data was 9×10^{-5} moles/mole sample, and from temperature of fusion data 6.10^{-4} moles per mole sample. For any N_g° used in equations (4) and (12), a departure from solution

ideality in which the activity coefficients are less than one, would be expected to lead to a lowered calculated value for N_2^0 in the concentrated solution since the activity would be less than the actual concentration. This is seen to be the actual case and is to be generally expected.

4. Heat of Fusion

Four determinations of the heat of fusion of dimethoxymethane were carried out. These are summarized in Table VII. In each case the heat required to bring the sample to the fusion temperature and raise it beyond this temperature was calculated from the final averaged heat capacity in this region. The premelting heat capacity corrections were all on the same basis, and are represented by a solid insoluble impurity concentration of 5.1×10^{-4} moles/mole sample. A previous published value for the heat of fusion of dimethoxymethane is due to Timmermans (1) and has the value 1900 cal./mole. The method by which it was determined, from a study of the freezing curves of binary mixtures, is accurate to approximately 10 per cent.

5. Heat of Vaporization

The sample of dimethoxymethane used for the heat of vaporization determinations was prepared in the same manner as that described under the heat capacity sample prepara-

TABLE VII

THE HEAT OF FUSION OF DIMETHOXYMETHANE

No.	Temp. Interval °K	Heat Input cal.	$\int C_d T$ cal.	Premelting cal./sample	ΔH <u>cal.</u> sample
a	162.970-170.874	1597.83	202.87	3.88	1396.4
b	166.337-169.890	1482.68	96.31	12.03	1396.5
c	166.410-170.562	1499.55	115.53	12.59	1395.7
d	152.668-167.724	1828.39	430.64	1.17	1397.0

Average value 1396.4 ± 0.4 cal./sample

Equivalent to 1991.3 ± 0.6 cal./mole

C is total heat capacity of sample and container

tion section, III.A.1.

The apparatus built for these measurements has already been described (20). During a determination, the temperature of the vaporization was followed by means of a combination of sample container surface thermometer readings and pressure readings. The vapor pressure readings were taken by a second observer at times independent of the surface thermometer readings. These vapor pressure readings were then used to monitor the surface thermometer during the times when electrical measurements for the power input and the block temperature were in progress. Once vaporization was begun, the throttling valves were left set at openings which had been found to produce the most stable temperature conditions for given power inputs in trial runs.

The method outlined by Weber (20) was used to calculate the vaporization heats. Table VIII gives the results for two determinations for dimethoxymethane. The precision uncertainty, calculated from its major source, the radiation heat correction, is approximately ± 8 cal./mole. This calculated uncertainty resulted from an analysis of the scatter in the initial and final drift data.

Static vapor pressures given in Table IX for dimethoxymethane were measured in the temperature range 280-300°K. The following Antoine equation was fitted to this data:

TABLE VIII

HEAT OF VAPORIZATION OF DIMETHOXYMETHANE AT 298.15 °K

No.	Amount distilled moles	Heat Input cal.	T' °K	T'' °K	Heat capacity (total) cal./deg.	ΔH <u>cal.</u> mole
a	0.103927	728.4	298.011	298.268	32.39	6910
b	0.103408	726.1	298.444	298.925	28.62	6897
Average						6904

TABLE IX

MEASURED VAPOR PRESSURES OF DIMETHOXYMETHANE AND RESULTING
HEAT OF VAPORIZATION.

No.	Temperature °K	Pressure m.m.
1	281.666	196.39
2	283.894	217.40
3	286.235	241.42
4	288.769	269.54
5	293.869	334.63
6	296.795	377.44
7	299.626	422.71

Antoine Equation: $\log \text{Pressure} = 7.10401 - 1162.58/\text{Temp.} - 40$ Heat of Vaporization: $6934 \text{ cal./mole} \pm 70 \text{ cal./mole}$

$$\log P_{m.m.} = 7.10401 - 1162.58/(T-40). \quad (13)$$

In the measured range the curve deviates from the actual points with a root mean square deviation of ± 0.07 m.m. The cathetometer used for the pressure readings can be read to the nearest 0.05m.m., so that the Antoine equation pressure deviation is within the expected range.

Equation (13) was used to solve the Clapeyron equation for the heat of vaporization as a function of the temperature variation of the vapor pressure. Compressibility data was taken from source (23). The results of these calculations are given in Table IX. An analysis of the scatter in the vapor pressure points resulted in the quoted deviation in the heat of vaporization being assigned a certainty of 95 per cent. The previously published heat of vaporization for dimethoxymethane (5,6) of 6890 ± 60 cal./mole was determined from vapor pressure data.

6. The Entropy

The heat capacities below the experimentally determined range of temperature were found by extrapolation of the lowest temperature data taken, by assuming that in this region the heat capacity varies as T^3 . A Debye function of four degrees of freedom gave the best fit to the experimental curve in the range 16-20° K, and was chosen as best for extrapolation purposes, not out of any theoretical considera-

tions. The values of θ calculated in this region and the average value are given in Table X. The θ chosen to calculate the entropy and heat capacities below 16°K has been assigned the value 117.91°K . Table XI presents the heat capacities of dimethoxymethane in the Debye extrapolated region at rounded temperatures.

The entropy from 16°K to 298.15°K was calculated from the heat capacities by numerical integration employing Weddle's rule. These heat capacities were read at closely spaced intervals from the graph described in section 3. In this manner it was determined that the entropy of the solid has the value

$$S_{168.01^\circ\text{K}}(\text{solid}) = 25.90 \pm 0.02 \text{ e.u./mole}$$

To this value was added the entropy of fusion and the liquid entropy contribution in the region from the fusion point to 298.15°K which produced the value

$$S_{298.15^\circ\text{K}}(\text{liquid}) = 58.32 \pm 0.05 \text{ e.u./mole}$$

The standard entropy of dimethoxymethane in the ideal gas state at 25°C can now be calculated using the additional information of the heat of vaporization and the entropy due to gas imperfection. The heat of vaporization has already been discussed and its entropy contribution is summarized in Table XII.

From the Berthelot equation of state the gas imper-

TABLE X

THE APPARENT DEBYE θ FOR FOUR DEGREES OF FREEDOM FOR DIMETHOXYMETHANE AS DETERMINED FROM EXPERIMENTAL HEAT CAPACITIES

$T(^{\circ}\text{K})$	$\theta(^{\circ}\text{K})$
16	117.44
17	117.98
18	118.26
19	118.18
20	117.68
Average	117.91

TABLE XI

THE HEAT CAPACITIES OF DIMETHOXYMETHANE IN THE DEBYE EXTRAPOLATED REGION FOR FOUR DEGREES OF FREEDOM AT ROUNDED TEMPERATURES

$T(^{\circ}\text{K})$	C $\frac{\text{cal.}}{\text{mole-deg.}}$
3	0.010
5	0.047
7	0.130
9	0.275
11	0.494
13	0.790
15	1.148
17	1.547

TABLE XII

MOLAR ENTROPY OF DIMETHOXYMETHANE AT 25 °C

	S e.u./mole
0-16°K, Debye ($\theta=117.91$, four degrees of freedom)	0.500
16-168.01°K, $\int C d(\ln T)$	25.398
Fusion, 168.01°K	11.852
168.01-298.15°K, $\int C d(\ln T)$	<u>20.569</u>
S at 298.15°K (liquid)	58.319
Vaporization a (Experimental, 298.15°K)	23.156
Vaporization b (Vapor Pressures, 298.15°K)	23.257
Gas imperfection	0.050
Compression	-1.283
S_a° (ideal gas) at 298.15°K	80.24
S_g° (ideal gas) at 298.15°K	80.34

fection is given by

$$S_{\text{ideal}} - S_{\text{real}} = 27RT_c^3 P / 32T^3 P_c$$

where T_c and P_c are the critical temperature and pressure. These constants were taken from reference (5) and have the values $T_c = 515.2^\circ\text{K}$ and $P_c = 33,570$ m.m. An earlier value for T_c reported is 497°K (25). This gives $S_{\text{ideal}} - S_{\text{real}} = 0.103$ e.u./mole. From reference (23) the value $S_{\text{ideal}} - S_{\text{real}}$ at 298.15 K and the saturated vapor pressure of the compound is given as 0.050 e.u./mole using generalized compressibility factors. Considering that the values for T_c and P_c are only approximate and that the Berthelot equation is not highly accurate, the gas imperfection entropy was assigned the value 0.050 e.u./mole from the more reliable source.

The entropy of dimethoxymethane in the ideal gas state at one atmosphere pressure and 25°C is given in Table XII. There have been no values for the entropy reported in the literature calculated from spectroscopic data for this molecule.

B. Acetonitrile

1. Sample

The acetonitrile sample used for the heat of vaporization determinations consisted of about 50 milliliters of

sample purified by Putnam (17) and 250 milliliters of spectroscopic grade material obtained from the Eastman Chemical Company. The purification procedure was the same as that outlined by Putnam; and the sample was dried over phosphorus pentoxide.

2. Heat of Vaporization

The apparatus used for these measurements has already been described (20). The methods by which data were taken appear in section III.A.6. The method outlined by Weber (20) was used to calculate the vaporization heats. Table XIII gives the results for two determinations for acetonitrile. The precision uncertainty arises primarily from the radiation heat correction and is ± 8 cal./mole. It was calculated from the initial and final temperature drift data of the sample container.

In the temperature range from 280-300°K the vapor pressures of acetonitrile were measured by the static method. These results are presented in Table XIV. The following Antoine equation was fitted to this data:

$$\log P_{\text{m.m.}} = 7.89511 - 1773.06/T$$

In the measured range the curve deviates from the actual points with a root mean square deviation of ± 0.06 m.m. This is within the expected range of pressure deviation considering the precision to which the cathetometer can be read.

TABLE XIII

HEAT OF VAPORIZATION OF ACETONITRILE AT 298.15°K

No.	Amount distilled moles	Heat Input cal.	T' ° K	T'' ° K	Heat capacity (total) cal./deg.	ΔH <u>cal.</u> mole
a	0.155393	1236.3	297.912	297.952	25.67	7944
b	0.141438	1127.2	299.696	300.026	22.39	7938
Average						7941

TABLE XIV

MEASURED VAPOR PRESSURES OF ACETONITRILE AND RESULTING HEAT OF VAPORIZATION

No.	Temperature ° K	Pressure m.m.
1	280.409	37.48
2	283.620	43.96
3	286.941	51.86
4	291.851	66.07
5	295.055	76.84
6	296.631	82.74
7	298.713	91.18
8	300.530	98.91

Antoine Equation: $\log \text{Pressure} = 7.89511 - 1773.06/\text{Temp.}$

Heat of Vaporization: 7865 ± 40 cal./mole

The Antoine equation derived from the vapor pressure measurements was used to solve the Clapeyron equation for the heat of vaporization as a function of the temperature variation of the vapor pressure. The results of this calculation are presented in Table XIV. The second virial coefficient used came from source (26) and had the value $-6355 \frac{\text{ml.}}{\text{mole}}$. An analysis of the scatter in the vapor pressure points resulted in the quoted deviation in the heat of vaporization being assigned a certainty of 95 per cent.

3. The Entropy

As found by Putnam (17), the gas imperfection for acetonitrile is 0.55 ± 0.01 e.u./mole and the liquid entropy has the value

$$S_{298.15^\circ\text{K}}(\text{liquid}) = 35.76 \pm 0.20 \text{ e.u./mole}$$

These values, together with the heats of vaporization were used to calculate the results given in Table XV.

TABLE XV

COMPARISON OF HEATS OF VAPORIZATION AND IDEAL GAS ENTROPIES
OF ACETONITRILE AT 25 °C

Reference	ΔH cal./mole	S e.u./mole	Method
This research	7865 $\pm$ 40	58.42 $\pm$ .25	Vapor Pressure
This research	7941	58.67	Experimental
Putnam	7843 $\pm$ 45	58.36 $\pm$ .25	Vapor Pressure
(24)		58.01	Spectroscopic

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