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The Entropy and Related Thermodynamic
Properties of Propionitrile

by

Lloyd Adolph Weber, Jr.

A THESIS

SUBMITTED TO THE FACULTY
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF
Doctor of Philosophy

Houston, Texas

May, 1960

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INTRODUCTION

The purpose of this investigation was the calorimetric determination of the saturated heat capacity and the heats and temperatures of all phase transitions of propionitrile (ethyl cyanide) from about 15°K to room temperature. From this data, and gas imperfection data available in the literature, the entropy of this compound was calculated in the ideal gas state. This value was then compared with the entropy calculated from Raman and infrared spectroscopic data. Agreement between the two methods may be used as a check on the molecular model used and on the accuracy of the calorimetric data.

No experimental value for the entropy of propionitrile has been reported. Janz and Duncan (1) have calculated a value from spectroscopic data. There is some room to doubt the validity of their calculations, however, as will be shown in the section on the entropy. The Raman and infrared spectra have been measured by several authors, (2,3,4,5,6,7). Lerner and Dailey (8) and Laurie (9) have reported the microwave spectrum with values for the principal moments of inertia and the torsional frequency.

The sample used in this research was found to contain an appreciable amount of solid soluble impurity. Putnam (10)

-2-

investigated the effects of this type of impurity on sharpness of melting data. However, his results were not completely satisfactory, and this analysis was extended to include premelting heat capacity data.

II

EXPERIMENTAL

A. APPARATUS

The major portion of the apparatus used in the research has been described elsewhere (11, 12).

1. Cryostat

The calorimeter used has the laboratory designation 'calorimeter C' and was built by Putnam (10). Three modifications were made in it. The glass tubing connecting the calorimeter to the pumping manifold had a tendency to crack due to warpage of the vacuum bench. This tubing was replaced with an all-metal system which joins to the manifold by means of an O ring seal. The connecting tube contains a series of two flexible phosphor bronze bellows which allow the cryostat to move slightly with respect to the vacuum manifold. The electrical leads emerge from the vacuum system through a wax trap, as before. It was felt that the spool, which acts as a thermal sink for wires entering the calorimeter, was not in good enough thermal contact with the vacuum can. Accordingly, copper jackets were soldered around the three brass pins connecting the spool to the can. The third modification was the addition of a copper constantan difference thermocouple between the sample container and the block. This was made from #40 wire, and it is estimated that

the heat leak to the sample container was increased by not more than ten percent. This thermocouple was very useful for adjusting the block temperature and for making radiation corrections to the heats of fusion and vaporization measurements. The sample container was the same as that used in reference (10) except for a one-quarter inch length of #24 copper wire soldered to the top to serve as a mount for the sample-block thermocouple.

2. Electrical Measurements

In the electrical measurement apparatus the sensitive galvanometer was removed and the output of the White Double Potentiometer was fed into a Model 14 Liston-Becker D. C. breaker amplifier and then into a Leeds and Northrup Type G Speedomax Recorder. This arrangement has a number of advantages not the least of which is the ease of reading the data during long periods of operation. Voltage measurements can be made to ± 0.1 microvolt, and the variable gain allows a constant sensitivity regardless of the resistance across which the measurements are made. A quicker response time of about 8 seconds, compared to 30 seconds for the galvanometer, is a convenience in some situations. Also, the recorder is a great help in watching temperature drifts, cooling curves, and in making radiation corrections.

3. Thermometer

In conjunction with this research the platinum resistance thermometer, bearing the laboratory designation '100-1', was recalibrated. This thermometer has been described by Johnson (13). Above 90°K it was calibrated on the International Temperature Scale.

The four calibration points used were the freezing point of a calibrated benzoic acid cell (122.358°C), the triple point of water, the triple point of nitrous oxide, and the boiling point of oxygen. The benzoic acid cell was described by Johnson (13). The triple point of water cell was similar to that described by Johnson with the exception that the glass vessel connected to the cell was omitted. The cell was filled with doubly distilled water, the air removed, and sealed off under the vapor pressure of the water. The same procedure was used to freeze the ice mantle.

The other calibration points were carried out in the cryostat in a specially designed sample container. This was made from a round brass rod, 1 3/4" dia. by 3 1/8" long. The first 1/4" was turned down to 9/16" dia. and a 1/2" center well was drilled, thus leaving a thin walled neck at the top. A brass cap, drilled to take a piece of 0.100" inconel tubing was silver soldered on this neck. Three wells, 3/8" dia. by 2 3/4" deep, were filled with lead to provide additional low temperature heat capacity. Three other wells

were drilled for the thermometer, heater, and the 25 ohm Leeds and Northrup thermometer. The center well has a volume of about 9.6 milliliters. One to two grams of Chrome Alumina Catalyst in pellet form, from Harshaw Chemical Company, were placed in the well to facilitate ortho to para hydrogen conversion.

Even with the modified sample tube described by Putnam (10), considerable difficulty was encountered in distilling the nitrous oxide into the sample container. Since only about 2.3 degrees separate the triple point and normal boiling point, solid plugs invariably formed in the sample tube. This trouble was finally cured by distilling at about two atmospheres pressure, adjusting the block temperature to about ten degrees below the triple point, and applying 20 to 30 volts to the sample tube heater. A thermocouple was installed on the sample tube at the point where it passes through the block to facilitate temperature control. Commercial, clinical nitrous oxide was fractionally distilled several times before use.

The thermometer was calibrated at the boiling point of oxygen at eleven pressures ranging from 14 to 900 mm. Hg. The oxygen was generated by heating potassium permanganate, which had been thoroughly degassed under vacuum. It was then purified by several fractional distillations.

The absolute temperature scale used in this research is that proposed by Giauque (14) and adopted by the Comité Consultatif de Thermométrie in 1954 (15) as the International Kelvin Temperature. This scale defines the triple point of water as 273.16°K . Of the four calibration points used only the centigrade temperature of the oxygen boiling point is changed appreciably from its old value, and it was taken as -182.963°C .

TABLE 1

CALIBRATION POINTS AND RESISTANCE OF THERMOMETER 100-1

Calibration Point	Temperature $^{\circ}\text{C}$	Resistance abs. ohms
Benzoic Acid	122.358	138.0510
Triple point of H_2O	0.0100	93.4095
Triple point of N_2	-90.809	59.1431
Boiling Point of O_2	-182.963	22.8374

These four points were used to calculate the constants of the Callendar-Van Dusen equation.

TABLE 2

CALIBRATION CONSTANTS FOR THERMOMETER 100-1

R_0	93.4058
α	0.00391954
δ	1.5086
β	0.1142

Below 90°K the method suggested by Hoge and Brickwedde (16) was used. The vapor pressure of oxygen was taken as the standard down to 64°K . The vapor pressure and triple point equilibrium hydrogen were used below 20°K . In the region between these temperatures the Leeds and Northrup resistance thermometer was used for comparison. This thermometer was calibrated by the National Bureau of Standards on the International Temperature Scale in 1950 and again in 1953. The two calibrations agree quite closely. From 10°K to 90°K it was calibrated by comparison with a standard resistance thermometer kept at the National Bureau of Standards.

This calibration differed appreciably from the original one by Johnson only at the Benzoic acid point. Here there was a discrepancy of 8 milliohms. Because of this, a study was made of the effects of an error in the Benzoic acid point on the calibration. The results of this study are given in Appendix 1.

B. MEASUREMENTS

Above 90°K temperature could be measured with a precision of about 0.001 degree, which increased to about 0.004 degree at 20°K . The fact that the accuracy was probably not this great is relatively unimportant since the primary interest was in measuring temperature differences.

Past experience indicates that the heat capacity data should be more precise than 0.3 per cent. above 250° and

better than one per cent. at very low temperatures. In the region between, a precision of better than 0.03 per cent. should be realized.

The experimental procedure used in taking the data was described by Taylor (12).

C. PROPIONITRILE

1. Sample

The sample of propionitrile used in this research was purchased from Eastman Chemical Products, Inc., and was purified by drying over magnesium sulfate followed by distillation from freshly added phosphorous pentoxide. The distillation was carried out at one atmosphere through a glass helix packed column approximately ninety centimeters long at a reflux ratio of about twelve-to-one. This process was carried out twice, the center cut, consisting of approximately two thirds, being kept each time. The third time the sample was distilled into a glass ampule and sealed. After the first distillation the index of refraction was measured at 25°C and found to be 1.3638 compared to values in the literature of 1.3633 and 1.36353 (1, 17).

As in the case of acetonitrile reported by Putnam (10) the propionitrile slightly attacked the copper sample container. A very small amount of dull grey powder was found in the empty sample container. There was also a small amount of another type impurity, a white crystalline substance, which was left when the sample distilled out. This substance was readily soluble in organic solvents and yielded an infrared spectrum which showed very little C≡N stretching but exhibited large peaks in the region of C=N- and >N-H

stretching frequencies. Hence it was concluded that a small amount of the sample polymerized. A small contamination of this type should not cause any serious errors in the data. The amount of sample was taken from the difference in weights on filling the sample container and is estimated to be accurate to better than 0.02 per cent. Taking 55.078 as the molecular weight, the weight in vacuum of the sample used was equivalent to 0.79138 mole.

2. Phases

One fusion and one solid transition were observed for propionitrile. The system used by Putnam for acetonitrile will be used here to describe the phases: (in order of decreasing temperature) liquid, fusion, solid I, transition, solid II.

3. Heat Capacities

The data taken in the calorimeter do not correspond to the saturated heat capacity exactly because of the presence of an inert atmosphere of helium. However, the difference is smaller than the uncertainty in the measurements, and the data are quoted as being for the sample under its own vapor pressure. These data are presented in chronological order in Table 3. Each series is designated by a capital letter. Determinations of the heats and temperatures of fusion and transition are listed as they occurred, and each measurement of each type is designated by a lower case letter

for identification.

The data is accurate to within the limits described previously except for the short temperature interval between the transition and fusion. This data on solid I shows somewhat more scatter for several reasons. The temperature interval of each point was much smaller than usual, thus increasing the relative uncertainty. Also, solid I exists entirely in the region of premelting, and such heat capacities are generally subject to hysteresis effects.

A premelting correction was applied to the data on solid I. Due to the proximity of the transition and melting points no reasonable extrapolation of the true heat capacity at lower temperatures could be made, and this correction is somewhat arbitrary. The usual expression for premelting heat capacity (26) was used and a solid insoluble impurity concentration of 0.042 mole per cent. corrected the heat capacity curve to a straight line. From the sharpness of melting data it was found that the maximum amount of solid insoluble impurity was 0.020 mole per cent. This discrepancy can be explained, however, by the fact that the major impurity seems to be solid soluble, and this also affects the premelting heat capacity as discussed in the theoretical section. At any rate, it was felt that making this correction to the heat of fusion gives a value closer to that of the pure substance.

TABLE 3

MOLAR HEAT CAPACITY OF PROPIONITRILE

Temp. °K	Heat Capacity cal/mole deg.	Temp. °K	Heat Capacity cal/mole deg.
Temp. of fusion a			
Temp. of fusion b			
Series A		Series D	
177.69	25.68	155.30	18.12
177.87	26.18	159.81	18.55
178.04	27.31	164.05	18.94
178.66	31.89	168.26	19.70
179.30	47.20	172.30	20.20
Series B		Series E	
177.47	25.10	202.81	26.58
178.23	28.60	212.91	26.69
178.93	38.03	225.39	26.88
Heat of fusion a		Series F	
Heat of fusion b		81.65	12.15
Heat of fusion c		89.28	12.94
Temp. of transition a		146.60	17.47
Series C		151.03	17.86
99.02	13.75	157.05	18.31
106.75	14.38	162.96	18.81
135.29	16.60	168.31	19.80
143.67	17.26	Series G	
150.83	17.81	186.58	26.46
154.43	18.06	195.18	26.49
161.77	18.72	204.75	26.65
168.55	19.80		
172.29	20.04		
175.18	21.25		

Temp. °K	Heat Capacity cal/mole deg.

Series H

185.42	26.35
193.76	26.44
206.03	26.59
216.04	26.69
226.03	26.85
235.87	27.02
245.99	27.21
257.01	27.45

Series I

70.69	10.91
78.72	11.83
86.57	12.68
94.21	13.36
101.79	13.98
109.34	14.59
117.18	15.22
125.03	15.83
135.76	16.74
144.39	17.33
153.82	18.05
160.74	18.62
165.95	19.17
170.64	20.19
174.88	21.22

Heat of trans. a

Series J

177.64	26.22
178.48	30.62
179.23	47.99

Heat of fusion d

Series K

58.32	9.349
66.91	10.49
74.81	11.40
125.75	15.91
133.64	16.52
157.90	18.37
164.66	19.01
170.23	20.08
174.59	20.97

Temp. °K	Heat Capacity cal/mole deg.

Temp. of trans. a
Heat of trans. b
Temp. of trans. b
Heat of trans. & fusion a

Series L

189.09	26.37
196.85	26.47
206.37	26.57
216.24	26.67
226.25	26.78
253.57	27.36
263.85	27.63
275.89	27.92
286.11	28.24
297.04	28.54

Series M

15.24	0.987
16.77	1.293
18.34	1.598
20.20	1.994
22.54	2.509
25.46	3.167
28.53	3.872
31.58	4.568
34.74	5.257
38.24	5.973
42.12	6.714
47.30	7.632
53.14	8.587
59.52	9.475

Heat of trans. & fusion b

Heat of trans. c
Heat of fusion e
Heat of vap. a
Heat of vap. b

The heat capacities at rounded temperatures are given in Table 4.

4. Temperature of Fusion and Transition

Two experimental determinations of the temperature of fusion of propionitrile were made in the usual way. The data are presented in Table 5. The plots of temperature versus the reciprocal of the fraction melted are not straight lines, but are concave upward, indicating the presence of solid soluble impurities as discussed by Putnam (10) and the theoretical section of this thesis. The data were treated in the manner described by Putnam. However, the solid soluble, solid insoluble impurity analysis from sharpness of melting data is not unique and unfortunately the premelting heat capacity does not yield sufficient additional information in this case. The upper limit on the amount of solid insoluble impurity was established at 0.020 mole per cent. Several values below this limit were assumed, and the other parameters of melting were calculated for each case. The results are displayed in Table 6. From the table, it may be seen that as long as the assumed values for the solid insoluble impurity do not approach too closely to the calculated upper limit, the calculated melting temperature changes by only a small amount.

On the basis of this table the melting point was taken as $180.37 \pm 0.03^{\circ}\text{K}$. These measurements were made on the sample

TABLE 4

THE MOLAR HEAT CAPACITY AT ROUNDED TEMPERATURES
OF PROPIONITRILE

Temp. °K	Cp cal/mole deg.	Temp. °K	Cp cal/mole deg.
15	0.947	160	18.54
20	1.948	165	19.06
25	3.060	170	19.92
30	4.213	175	21.17
35	5.309		
40	6.314	177	23.55
45	7.231	180	26.49
50	8.088		
55	8.868	185	26.34
60	9.586	190	26.39
65	10.25	195	26.44
70	10.84	200	26.49
75	11.41	205	26.55
80	11.97	210	26.61
85	12.51	215	26.68
90	13.00	220	26.75
95	13.43	225	26.82
100	13.83	230	26.91
105	14.24	235	27.00
110	14.64	240	27.10
115	15.04	245	27.19
120	15.45	250	27.29
125	15.84	255	27.40
130	16.23	260	27.52
135	16.62	265	27.65
140	17.00	270	27.79
145	17.38	275	27.92
150	17.76	280	28.06
155	18.14	285	28.20
		290	28.34
		295	28.48
		300	28.61

Figure 1

TABLE 5
 TEMPERATURE OF FUSION
 VARIATION OF TEMPERATURE WITH FRACTION MELTED

Determination a	
T(°K)	X
180.113	0.0876
180.183	0.1774
180.214	0.2658
180.231	0.3545
180.251	0.4872
180.262	0.5667

Determination b	
T (°K)	X
180.104	0.0849
180.221	0.3126
180.256	0.5884
180.281	0.8193

Best value (zero impurity) $180.37 \pm 0.03^{\circ}\text{K}$

in an inert atmosphere of helium at approximately 51 centimeters pressure but should yield the triple joint temperature within the accuracy quoted.

The solid I - solid II transition was quite sharp and little difficulty was encountered in determining its temperature. The heat capacity bowed upward somewhat in the region below the transition but no corrections were made since it was felt that this effect was probably not due to impurities. Apparent heat capacities were measured through the transition, and the equilibrium temperature was measured as a function of the fraction of the sample in the high temperature phase. Table 7 gives the results.

5. Heat of Fusion and Transition

The difficulties encountered in determining the heat of fusion seem to stem from the complicated nature of the premelting curve. Five measurements were made on the heat of fusion and the average of these is 1206.13 ± 1.6 cal/mole. The data on the sample are given in Table 8. The uncertainty is precision uncertainty. Three determinations, shown in Table 9, were made on the heat of transition, and an average value of 407.92 ± 1.0 cal/mole. was obtained. The same premelting heat capacity curve was assumed to hold in all these determinations. The integral of the corrected heat capacities between the transition and the fusion plus the sum of the heat of fusion and the heat of transition should add

TABLE 6

SUMMARY OF TEMPERATURE OF FUSION CALCULATIONS
FOR PROPIONITRILE

	Solid Insoluble Concentration assumed mole per cent.	Solid Soluble Concentration calculated mole per cent.	Distribution Coefficient calculated	Triple Point calc. °K
Detn. a	0.00	0.09	0.12	180.331
Detn. b	0.00	0.11	0.14	180.339
Detn. a	0.010	0.11	0.20	180.342
Detn. b	0.010	0.13	0.23	180.350
Detn. a	0.015	0.16	0.32	180.360
Detn. b	0.015	0.20	0.35	180.368
Detn. a	0.017	0.25	0.41	180.381
Detn. b	0.017	0.29	0.44	180.388
Detn. a	0.019	0.68	0.60	180.454
Detn. b	0.019	0.65	0.59	180.443

Calculated maximum solid insoluble impurity 0.020 mole per ct.

Best values

Temperature of fusion under
approximately 51 cm helium pressure $180.37 \pm 0.03^{\circ}\text{K}$

Solid soluble impurity concentration 0.23 ± 0.12 mole per ct.

Solid insoluble impurity concentration 0.016 ± 0.008 mole per ct.

TABLE 7

TEMPERATURE OF THE SOLID TRANSITION

Equilibrium Temperature °K	Percent in high temper- ature phase

Determination a	

176.959	50.0

Determination b	

176.963	24.3

176.964	52.1

176.968	81.0

Best value $176.964 \pm 0.005^{\circ}\text{K}$

Little weight was given to determination a because of difficulty in adjusting the block temperature. The temperature of the transition was taken to be $176.964 \pm 0.005^{\circ}\text{K}$.

up to the total of the heat absorbed between the transition and the melting points. Accordingly, two experimental determinations were made on this quantity, and the results are given in Table 10. It may be seen that the total heat absorbed is 3.12 cal./sample less than the sum of the average values of the components. This discrepancy is too large to be explained by the uncertainty in any of the measurements. The discussion in the theoretical section offers perhaps the best explanation. The sample was always frozen very slowly in an effort to insure an equilibrium distribution of impurity. It would seem to be impossible, however, to freeze the last few per cent. slowly enough for this distribution to hold. It is this small amount of the sample with which we are concerned in the premelting region, and the heat capacities measured would be for a system which has essentially a nonequilibrium composition. No definite statement can be made about how long it would take for equilibrium to be reached, but in all except one of the heat of fusion determinations the sample was allowed to sit overnight or longer in the premelting region. It is shown in the theoretical section that for a given sample at a given temperature the nonequilibrium distribution of impurity leads to a higher premelting heat capacity curve than does the equilibrium distribution. If, during the night, the sample achieved even a partial redis-

TABLE 8
THE HEAT OF FUSION AT 180.37°K OF
PROPIONITRILE

No.	Temp. interval °K	Heat input calories	$\int C_d T$ * calories	Premelt cal.per sample	ΔH cal.per sample
a	177.586-187.038	1216.12	260.16	0.27	956.23
b	178.629-187.513	1198.26	246.06	3.08	955.28
c	178.323-186.731	1188.25	232.32	1.75	957.68
d	177.308-181.672	1072.36	117.68	0.05	954.73
e	177.555-181.897	1070.40	117.59	0.24	953.05

Average value   955.39 ± 1.25 cal/sample

Equivalent to   1206.13 ± 1.60 cal/mole

* Sample plus sample container

TABLE 9
HEAT OF TRANSITION AT 176.964°K OF
PROPIONITRILE

No.	Temp. interval °K	Heat input calories	$\int C_d T^*$ calories	ΔH cal/sample
a	176.743-177.780	350.66	26.99	323.67
b	176.441-177.940	361.90	38.76	323.14
c	176.493-177.534	348.03	26.37	321.66

Average value   322.82 ± 0.78 cal/sample

Equivalent to   407.92 ± 1.0 cal/mole

* Sample container plus sample

TABLE 10

TOTAL HEAT ABSORBED BETWEEN 176.964°K
AND 180.37°K

No.	Temp. Interval $^{\circ}\text{K}$	Heat Input calories	$\int C_d T$ calories	Net Heat cal./sample
a	176.726-182.151	1420.86	57.53	1363.33
b	176.755-181.767	1409.47	46.03	1363.44
Average value				1363.39 ± 0.06
Heat of fusion plus heat of transition plus $\int C_d T^*$				1366.51 ± 2.60
Discrepancy				3.12

* This integral refers to the heat capacity of the sample between the transition and fusion.

tribution of impurity, the premelting correction to the data might lead to an apparent heat of fusion which is greater than the true heat by as much as several calories.

Some credence is given to this theory by heat of fusion determination e which was run immediately upon the completion of heat of transition c, thereby allowing little time for redistribution. It may be noticed that this determination gave a result which is significantly lower than the average heat of fusion.

It is felt that the total heat absorbed, given in Table 10, less that amount due to heat capacity and the heat of transition, leads to a more accurate heat of fusion than the value measured directly. This is due to the uncertainty in the actual state of the sample when the latter measurements were taken. Accordingly, the discrepancy of 3.12 calories shown in Table 10 was assigned wholly to the heat of fusion and was subtracted from the values shown in Table 8. Therefore, the heat of fusion used for the purpose of the entropy calculation is 1202.19 cal./mole.

6. Heat of vaporization

Since no reliable data existed for the heat of vaporization of propionitrile at room temperature, it was necessary to measure this quantity. Heats of vaporization had not been measured in this laboratory previously, and some additions to the equipment were made for the purpose. The sample con-

tainer was connected to the sample tube which joined onto an external manifold of 8 mm. pyrex tubing. Into this manifold was built a throttling system which consisted of three parallel capillary tubes, each with a notched stopcock. The capillary tubes were about 20 cm. long and had nominal diameters of 1, 1/2, and 1/4 millimeters. Next there was a two-way stopcock which connected the system to either of two condensing bulbs. The large bore manometer was connected to the manifold through a stopcock and a gold foil trap.

In practice, the measurements were similar to heat of fusion determinations with several exceptions. A practice run was made first in order to establish the proper settings for the stopcocks in the throttling system. These were set to maintain the temperature as nearly constant as possible for a given rate of energy input. Between power measurements a tracing of the voltage drop across the resistance thermometer was made. This was used to calculate the temperature of the vaporization as a function of time and also to make radiation corrections. It is felt that this method of finding the temperature leaves something to be desired. The thermometer probably reads more of an average temperature for the whole sample rather than the surface temperature where the vaporization really takes place. The results obtained from reading the vapor pressure during the run should lead to a more realistic value. This data was taken, but because of the

relatively high scatter of the vapor pressure data and because of the low vapor pressure of propionitrile in this region, the method was considered to have neither the accuracy nor the sensitivity required. Also there is an appreciable pressure drop between the sample container and the manometer which must be corrected for.

Due to an accident, the sample-block difference thermocouple was not operative during these measurements and it was found necessary to calibrate the block thermocouple in this narrow temperature interval to obtain the radiation correction. The proper use of the thermometer, difference thermocouple, and sample container surface thermometer should yield a more accurate correction. It should be pointed out that, due to the small amount of sample vaporized, the radiation correction becomes much more important here than for the heat of fusion.

The sample vaporized was condensed in a bulb with liquid nitrogen and weighed. The heat of vaporization was then calculated by the iterative method described in Appendix 2, at 296°K. The results of the two determinations are shown in Table 11. The uncertainty is precision uncertainty and probably bears little relation to the accuracy, which is estimated at about ± 10 cal./mole. For the purpose of comparison and for the calculation of the entropy, the heat of vaporization was corrected to 25°C. An extrapolation of the

TABLE 11

HEAT OF VAPORIZATION OF PROPIONITRILE
AT 296°K

No.	Amount distilled	Heat input	T'	T''	Heat [*] capacity	ΔH_o
	moles	calories	°K	°K	cal/deg.	cal./mole
a	0.079380	689.51	296.002	296.044	26.78	8659.7
b	0.083614	728.84	295.951	296.086	27.00	8661.9
Average value						8660.8

* Sample container plus amount of sample present at beginning of run (see Appendix 2).

equation of Iwanciw (18) showed the temperature coefficient to be about 13.6 cal./mole deg. at this temperature. Thus, the heat of vaporization at 298.15°K is 8631.6 cal./mole.

In conjunction with the heat of vaporization the vapor pressure of propionitrile was measured at five points between 9° and 25°C. The data, given in Table 12, established the vapor pressure equation as,

$$\log P_{\text{mm}} = 8.0298 - 1895 (1/T)$$

in this temperature interval. The heat of vaporization calculated from this equation is 8671 cal./mole and serves as a check on the experimental determination.

TABLE 12
VAPOR PRESSURE OF PROPIONITRILE

P(mm)	T(°K)
21.76	283.174
28.65	288.337
30.16	289.280
33.92	291.536
44.49	296.960

7. Analysis of Results.

Neither the experimental heat capacities nor the solid transition have been previously reported in the literature. The difficulties involved in deciding the best value for the heat and temperature of fusion have already been discussed. Several authors have reported the heat and temperature of melting, and their results are compared with those of this

research in Table 13. Timmerman's value results from cooling curve data of quite impure samples of known compositions, assuming ideal solutions. Therefore, his values may be considered somewhat uncertain. Dreisbach and Martin used the method of precise heating and cooling curves of Mair (24) on nearly pure samples. However, vapor pressures measured on their sample differed by as much as 1 mm. at room temperature from those of Heim (21) and Milazzo (22), indicating the possible presence of more impurity than was quoted. The presence of solid soluble impurities would very likely go unnoticed in melting point measurements of that sort and could easily lead to an error of as much as 0.1 degree. Rossini (27) pointed out that these impurities are quite likely to be present in substances such as propionitrile, which have a large solid transition very near the melting point.

The heat of vaporization and vapor pressure have been measured and calculated by several persons. Heim, Milazzo, and Martin all used vapor pressure equations of the Antoine form, adjusted to fit data from about room temperature to the normal boiling point. The value of the heat of vaporization calculated from these equations varied from 8561 to 8780 cal./mole (see Table 14). It is felt that these agree as well as can be expected with this research. Iwanciw

TABLE 13

COMPARISON WITH OTHER INVESTIGATIONS OF THE
HEATS AND TEMPERATURE OF FUSION OF PROPIONITRILE

Reference	ΔH	Temp. °K	Impurity mole per cent.
Timmermans (19)	1450	181.2	
Timmermans & Delcourt (20)		181.2	
Dreisbach & Martin (17)		180.26	0.16
This research	1202.19	180.37 ± 0.03^a	0.24 ± 0.13

a. Under approximately 51 cm. pressure of helium, zero impurity.

TABLE 14

COMPARISON WITH OTHER INVESTIGATIONS OF THE
HEAT OF VAPORIZATION OF PROPIONITRILE AT 25° C

Reference	ΔH cal./mole	Method
Heim (21)	8561	Vapor pressure data
Milazzo (22)	8780	Vapor pressure data
Dreisbach & Martin (17)	8746	Vapor pressure data
Iwanciw (18)	8583	Experimental 60°-100° C
This research	8631.6	Experimental
This research	8671	Vapor pressure

measured the heat experimentally from 60° to 96° C. He fitted the data to an equation, quadratic in temperature, and the value calculated from this equation at 25° C agrees reasonably well with this research, considering the long extrapolation.

8. The Entropy

The heat capacity below 25° K was represented best by a Debye function of five degrees of freedom. The values of θ calculated from the six lowest experimental heat capacities are listed in Table 15. The value of 138.4° K was used to find the entropy below 16° K.

A smooth curve, passed through the heat capacity data from 16° K to 298.15° K, was integrated numerically to calculate this portion of the entropy. This was added to the entropy of the fusion and of the solid transition as shown in Table 16, to produce the calorimetric entropy in the liquid phase with the value,

$$S_{298.15^{\circ}\text{K}} (\text{liquid}) = 45.24 \pm 0.08 \text{ cal./mole deg.}$$

Also given in Table 16 are data on the heat of vaporization, vapor pressure, and equation of state, which are combined with the liquid entropy. The result is the entropy in the ideal gas state at one atmosphere pressure with a value of,

$$S_{298.15^{\circ}\text{K}} (\text{ideal gas}) = 68.73 \pm 0.15 \text{ cal./mole deg.}$$

TABLE 15
THE APPARENT DEBYE θ FOR FIVE DEGREES OF
FREEDOM COMPUTED FROM EXPERIMENTAL
HEAT CAPACITIES

$T(K^{\circ})$	θ
15.24	138.2
16.77	137.3*
18.34	138.0
20.20	138.3
22.54	138.7
25.46	138.7
Best value	138.4

* Not averaged

TABLE 16

THE MOLAR ENTROPY OF PROPIONITRILE AT 25°C
IN THE IDEAL GAS STATE AT ONE ATMOSPHERE

	Cal./mole deg.
0-16°K, Debye ($\theta = 138.4^\circ\text{K}$, five deg. of freedom)	0.391
16-176.964°K, $\int C_p d\ln T$	21.784
Transition 407.92/176.964	2.305
176.964-180.37°K, $\int C_p d\ln T$	0.478
Fusion, 1202.19/180.37	6.665
180.37-298.15°K, $\int C_p d\ln T$	13.627
Vaporization, 8631.6/298.15	28.949
Gas imperfection	0.050
Compression	<u>-5.521</u>
$S_{298.15}$ (ideal Gas)	68.73

The entropy of gas imperfection was calculated in two ways, using the Berthelot equation and using virial coefficient data. In using the Berthelot equation, the critical temperature and pressure were taken as 564.4°K and 41.3 atm. respectively. The entropy was calculated to be $0.02\text{ cal./mole deg.}$ For the virial equation, values of the second virial coefficient were determined experimentally by Iwanciw (18), from 65° to 95°C. These values were extrapolated to 25°C. and an entropy correction of $0.08\text{ cal./mole deg.}$ was obtained. Since the correction is small and since both methods are subject to error, the average value of $0.05\text{ cal./mole deg.}$ was used.

Janz and Duncan (1) have reported the value of the entropy from a normal coordinate analysis of Raman and infrared spectroscopic data. Their calculated value is $67.812\text{ cal./mole deg.}$ It is felt, however, that their result involved some rather questionable assumptions. The torsional frequency which they used was taken from the difference of two observed lines, one with an anomalous depolarization factor, and had a value of 293 cm.^{-1} This is equivalent to a rotational barrier of 5200 cal. , which is much higher than would be expected on the basis of studies of hydrocarbons. Lerner and Dailey (8) using microwave studies found that their data could be explained by using a barrier of $3280 \pm 290\text{ cal./mole.}$ Laurie (9), also using microwave techniques, determined perhaps the most accurate value of 3050 cal./mole.

He also found the three principal moments of inertia. The product of these three moments is $1.095 \times 10^{-114} \text{ gm.cm}^2$ compared to the value $1.055 \times 10^{-114} \text{ gm.cm}^2$ used by Duncan and Janz. Lerner and Dailey reported the reduced moment for the torsion to be $5.050 \times 10^{-40} \text{ gm.cm}^2$. Using this value in addition to the data of Laurie, the spectroscopic entropy of propionitrile was recalculated and found to be 68.58 cal./mole deg. This leaves a discrepancy of 0.15 cal./mole deg. between the experimental and calculated entropy. This small discrepancy can easily be explained by the experimental uncertainty and possible uncertainty in the assignment of the spectroscopic data. It is felt that in a molecule as complex as propionitrile the experimental data is probably more reliable than the results obtained from statistical thermodynamics.

III

A THEORETICAL ANALYSIS OF THE EFFECT OF
SOLID SOLUBLE IMPURITIES ON THE MELTING
CHARACTERISTICS OF NEARLY PURE SUBSTANCES

A. TEMPERATURE OF FUSION

Precise calorimetry has long been used to obtain the melting point of pure substances by means of the study of the equilibrium temperature of nearly pure samples with various fractions melted (25,27,28). If the impurity present is soluble only in the liquid phase of the sample, a plot of the equilibrium temperature versus the reciprocal of the fraction melted yields a straight line. The intercept of this line on the ordinate is the melting point of the pure substance, and the slope of the line is proportional to the amount of impurity present. Often, however, this sharpness of melting plot produces not a straight line, but a curve, usually concave upward. This behavior is due to the presence of an impurity soluble in both the liquid and solid phase.

Putnam (10) made a study of this effect on the sharpness of melting. His work is summarized below. Unfortunately, however, the procedure does not determine the purity analysis unambiguously. Although the triple point temperature can be found to within 0.05 degrees, the latitude on the calculated mole fraction of impurity is quite large. Accordingly, a study was made on the premelting heat capacity. Since this quantity depends on the various parameters, such as purity,

in a somewhat different manner, it can be used to improve the accuracy of the calculations.

A three component, two phase system will be considered. The major component will be denoted by the letter s, and b will be used to denote an impurity which is soluble only in the liquid phase of the sample. The third component, designated a, is soluble in both phases, and has a distribution coefficient, K, defined as follows,

$$K = \frac{N_a''}{N_a'}$$

where the prime and double prime refer to the liquid and solid phases respectively. The overall composition of the system is denoted by the mole fractions N_s^0 , N_a^0 , N_b^0 . The true melting point of pure substance s will be called T^* .

Equating the free energy of the two phases assuming an ideal solution leads to the relationship,

$$\frac{\Delta H}{RT^2} dT = d \ln N_s' - d \ln N_s'' . \quad (1)$$

For sufficiently dilute solutions ΔH is the heat of fusion of the solvent, and it will be taken as such here.

At this point it is necessary to consider the distribution of component a in the solid phase. Putnam proposed two possibilities. One possibility is that component a is distributed uniformly throughout the solid phase and is in equi-

librium with component a in the liquid phase. This will be designated as the homogeneous case. It leads to the following relationship between the equilibrium temperature and the fraction melted, x , assuming an infinitely dilute solution,

$$T = T^* - \frac{RT^{*2}}{\Delta H} \left\{ \frac{N_a^0}{x+D} + \frac{N_b^0}{x} \right\} \quad (2)$$

where,

$$D = \frac{K}{1-K}$$

The other possible assumption is that the solid freezes out in layers. When each layer forms it has a composition which is in equilibrium with the liquid at that instant. However, once any solid is covered by a new layer its composition does not change. Thus, there is a concentration gradient throughout the solid. This assumption is called the inhomogeneous case and leads to the following relationship,

$$T = T^* - \frac{RT^{*2}}{\Delta H} \left\{ \frac{(1-K)N_a^0}{x^{1-K}} + \frac{N_b^0}{x} \right\} \quad (3)$$

Since diffusion through the solid phase is quite slow, the inhomogeneous case would seem very plausible. However, Putnam found that equation (2) could explain the experimental data whereas equation (3) did not. Therefore, he assumed that some mechanism, probably recrystallization, is available

for attaining homogeneity in the solid phase. Since the samples were frozen very slowly this would seem to be a reasonable assumption.

Equation (2) cannot be easily applied to the data to find the four unknown parameters, T^* , K , N_a^0 , and N_b^0 . However, for small values of x the curve approaches a straight line characterized by component b only. Therefore, as was shown by Putnam, the slope of the curve at the smallest value of x obtained experimentally may be used to calculate the maximum value for N_b^0 . For any assumed value of N_b^0 less than this maximum the other parameters can be calculated.

This method may be illustrated by rearranging equation (2) to the form,

$$T' = \left\{ T + \frac{RT^{*2}}{\Delta H} \frac{N_b^{\oplus}}{x} \right\} = T^* - \frac{RT^{*2}}{\Delta H} \left\{ \frac{N_a^0}{x+D} + \frac{N_b^0 - N_b^{\oplus}}{x} \right\} \quad (4)$$

where $N_b^{\oplus}$ represents an assumed value for N_b^0 . For a given $N_b^{\oplus}$, a value of D is found such that the plot of T' versus the reciprocal of $(x+D)$ is a straight line within experimental accuracy. The T^* calculated in this manner does not depend strongly on $N_b^{\oplus}$. Table 6 illustrates the application of this method on the sample of propionitrile used in this research.

B. PREMELTING HEAT CAPACITY

From Table 6 it may be seen that although the value of T^* may be determined with fairly good accuracy, there exist a large number of sets of N_a^0 , N_b^0 , and K all of which fit the data. Therefore, to find the correct set of parameters a study of the premelting heat capacity was made. This is the apparent heat capacity in the region just below the melting point, which arises from the fact that the sample is partially melting. It forms a very sensitive test for the presence of impurities.

A three component system will be considered as before. Now, however, it would be unreasonable to make the assumption of an infinitely dilute solution because of the small amount of sample in the liquid phase. Premelting heat capacities are generally useful only for values of x less than 0.05.

Without making the dilute solution assumption, but assuming ideal solutions in both phases, we may write two slightly more complex relationships, (5) and (6), corresponding to sharpness of melting equations (2) and (3) respectively. These have the following form,

$$T = T^* - \frac{RT^*T}{\Delta H} \left\{ \ln \left[1 - D \frac{N_a^0}{x+D} \right] - \ln \left[1 - \frac{D}{K} \frac{N_a^0}{x+D} - \frac{N_b^0}{x} \right] \right\} \quad (5)$$

and,

$$T = T^* - \frac{RT^*T}{\Delta H} \left\{ \ln \left[1 - \frac{KN_a^0}{x^{1-K}} \right] - \ln \left[1 - \frac{N_a^0}{x^{1-K}} - \frac{N_b^0}{x} \right] \right\} \quad (6)$$

These two equations may be differentiated to obtain $\Delta H \frac{dx}{dT}$, the premelting heat capacity, for the homogeneous and inhomogeneous cases respectively,

$$C_{pm} = \frac{\Delta H^2}{RT^2} \left\{ \frac{DN_a^0}{(x+D)^2} \left(\frac{1}{K} - \frac{\beta}{\alpha} \right) + \frac{N_b^0}{x^2} \right\}^{-1} \beta \quad (7)$$

where,

$$\alpha = \left[1 - \frac{DN_a^0}{x+D} \right] \quad \beta = \left[1 - \frac{D}{K} \frac{N_a^0}{x+D} - \frac{N_b^0}{x} \right]$$

and,

$$C_{pm} = \frac{\Delta H^2}{RT^2} \left\{ \frac{(1-K)N_a^0}{x^{2-K}} \left(1 - K \frac{\beta'}{\alpha'} \right) + \frac{N_b^0}{x^2} \right\}^{-1} \beta' \quad (8)$$

where,

$$\alpha' = \left[1 - \frac{KN_a^0}{x^{1-K}} \right] \quad \beta' = \left[1 - \frac{N_a^0}{x^{1-K}} - \frac{N_b^0}{x} \right]$$

Although it may be possible to freeze the bulk of the sample homogeneously, it would seem to be impossible to freeze the last few per cent. slowly enough to achieve complete homogeneity. There just would not be enough liquid present to allow quantitative recrystallization in a reasonable length of time. This part of the sample melts first, giving rise to a premelting heat capacity which would be for a

system not in complete thermodynamic equilibrium. In practice, C_{pm} is rather sensitive to the manner in which the sample is frozen (28). The best method of treating the sample under these circumstances would be a technique of rapid freezing. The heat capacity data should be taken immediately after freezing and would then be treated according to equation (8).

Figure 2 illustrates examples of assumed data fitting equations (7) and (8). The curve labeled "Solid insoluble only" is the usual premelting curve for an impurity of type b only, having a concentration of 0.05 per cent. The curves labeled "Homogeneous" and "Inhomogeneous" show the effects of an additional impurity of type a, having a concentration of 0.20 mole per cent. and a distribution coefficient $K=0.25$. It may be seen that the inhomogeneous distribution leads to a greater amount of premelting than does the homogeneous distribution, a fact noted by McCullough and Waddington (20) and Putnam (10). The nearly vertical line labeled "Homogeneous only" shows the results of equation (7) when only type a impurity is present.

In figure 3 the total amount of impurity is kept constant at 0.25 mole per cent. The curves show how the distribution of the impurity between type a and type b affects the premelting. Only the inhomogeneous case is considered. The

terms of equation (8) are of two types, having the forms $N_a^0 x^K$ and N_b^0 . Therefore, terms of the first type must become small compared to terms of the second type as x approaches zero. Also, K appears only in terms of the first type. This fact suggests a method for applying equation (8) to the data. If a reasonable value for K is assumed, the quantities N_a^0 and N_b^0 may be calculated. These calculated values will be designated $N_a^\oplus$ and $N_b^\oplus$ respectively. This may be done by solving two simultaneous equations at a pair of closely spaced values of x . If several pairs of x 's are used the calculated $N_a^\oplus$ and $N_b^\oplus$ may be plotted as functions of x . Since, as was shown above, the terms containing N_a^0 and K become less important as x decreases, the effect of an erroneous choice for K becomes vanishingly small as x approaches zero. Therefore, the function $N_b^\oplus(x)$ should approach the true N_b^0 as x approaches zero. This is illustrated in figure 4 for two assumed values (0.20 and 0.50) of K . If the correct K (0.25) had been used the curve would have been a horizontal line. In the usual case, when the plot of temperature against $1/x$ is concave upward, K should lie between zero and one.

The solution of equation (8) can be found more easily by the use of an iterative technique in which approximate values are substituted for the terms in the square brackets. The quantities in these brackets approach unity in the

limiting case of infinite dilution, and this would be a good first approximation.

Equation (8), when used with a technique of rapid freezing, leads to an accurate value for N_b^0 . This is the quantity needed in equations (2) and (4) in order that the method which Putnam devised might be used to calculate the other parameters accurately. However, equation (8) provides some additional information. From figure 4 it may be seen that when the assumed value of K is too large, $N_b^{\oplus}$ is a monotonically increasing function of x . When K is chosen too small $N_b^{\oplus}$ decreases with x . Therefore, by trial and error, K could also be found. This could be used in equation (4) to calculate D independently. Then the quantities on the left side and the right side of equation (4) may be found independently. If the assumptions of this discussion are correct, a plot of T' versus $1/(x + D)$ should produce a straight line. The slope and the intercept could then be used to find N_a^0 and T^* .

Mastrangelo and Dornte (29) also devised a relationship analogous to equation (2) for a simpler system consisting of only components s and a . McCullough and Waddington (28) applied that equation to data on many samples of various organic substances. They found that the method often gave excellent results but failed to represent the data in many other cases. They stated that this failure might be due to

the fact the measurements were made on a system in pseudo-equilibrium or because of the presence of several impurities. In either case equations (2) or (3) should give satisfactory results.

In some of the samples which they studied the amount of curvature in the melting point plots depended on the rate at which the sample was frozen. An extreme example of this behavior was 1-decene. The plot of temperature versus $1/x$ showed pronounced curvature when the sample was frozen slowly but was nearly linear when the sample was frozen rapidly. This behavior could be explained very well with equations (2) and (3). When the sample was frozen slowly it obeyed equation (2) but when it was frozen rapidly equation (3), corresponding to the inhomogeneous case, predominated. From equation (3) it may be seen that when K is small compared to 1 the melting point plot will be nearly linear.

Aston, Cines, and Fink (30) reported two experimental measurements of premelting heat capacities on samples known to contain large amounts of solid soluble impurity. They concluded that C_{pm} in such cases has a shape which differs greatly from that caused by solid insoluble impurities. Their heat capacity curves rise abruptly and are concave downward. This is in direct contradiction to the results of this research and of other workers. It is believed to be due to a misinterpretation of the experimental data. According to

equations (7) and (8) the heat capacity has the same characteristic shape in both cases, with the possible exception of the curve labeled "Homogeneous only" in figure 2. The experimental observation of this last case appears rather unlikely.

Any sample may contain several different impurities, but they may all be divided into two classes depending upon whether or not they are soluble in the solid phase of the sample. An analysis of premelting heat capacity data and of sharpness of melting data can lead to the accurate determination of the purity of the sample and the melting point of the pure substance provided certain requirements are met. The sample should be nearly pure, and the various impurities should form ideal solutions in both phases. If there are more than one solid soluble impurity present, the distribution coefficients should all be approximately the same size. The heat capacity of the sample must be accurately known for at least 10 degrees below the melting point, preferably more. This is necessary in order that the premelting heat capacity can be differentiated from the true heat capacity of the solid. If one or more of these conditions is not fulfilled the accuracy of the analysis suffers. Unfortunately, in the case of propionitrile the proximity of the solid transition and the fusion makes the analysis of the heat capacity impossible.

COMPARISON OF
HOMOGENEOUS AND
INHOMOGENEOUS
DISTRIBUTIONS
FOR THE CASE
 $N_A^0=0.20, N_B^0=0.05$
 $K=0.25$

Figure 2

Figure 3

Figure 4

APPENDIX

EFFECT OF AN ERROR IN THE BENZOIC ACID POINT ON THE CALIBRATION OF THE PLATINUM RESISTANCE THERMOMETER

It is desired to find the effect of an error in the Benzoic acid point on the calibration of a platinum resistance thermometer, as carried out in this laboratory.

Since the value of R_0 is usually found directly from the calibration point, we need only concern ourselves with the effect of an error on α , β , and δ . If points 1, 2, and 3 are the Benzoic acid point, the nitrous oxide triple point, and oxygen boiling point respectively, we may write the Callender-Van Dusen equation in the following form:

$$t_1 = \alpha (R_1 - R_0) + F(t_1, \delta) \quad (1)$$

$$t_2 = \alpha (R_2 - R_0) + F(t_2, \delta, \beta) \quad (2)$$

$$t_3 = \alpha (R_3 - R_0) + F(t_3, \delta, \beta). \quad (3)$$

We would like to find $\partial\alpha/\partial t_1$, $\partial\beta/\partial t_1$, and $\partial\delta/\partial t_1$. If we differentiate,

$$1 = \partial\alpha/\partial t_1 (R_1 - R_0) + \partial F/\partial t_1 + \partial F/\partial \delta \partial\delta/\partial t_1 \quad (1')$$

$$0 = \partial\alpha/\partial t_1 (R_2 - R_0) + \partial F/\partial \delta \partial\delta/\partial t_1 + \partial F/\partial \beta \partial\beta/\partial t_1 \quad (2')$$

$$0 = \partial\alpha/\partial t_1 (R_3 - R_0) + \partial F/\partial \delta \partial\delta/\partial t_1 + \partial F/\partial \beta \partial\beta/\partial t_1. \quad (3')$$

The quantities $\partial F/\partial \delta$, $\partial F/\partial \beta$, and $\partial F/\partial t_1$, may be found

easily from equations (1,2,3) and may then be substituted into equations (1',2',3'). Solving these last three equations for $\partial\alpha/\partial t_1$, $\partial\beta/\partial t_1$, and $\partial\delta/\partial t_1$, we find, in terms of the temperatures involved,

$$\frac{\partial\beta}{\partial t_1} \left\{ 1 + A \right\} \left\{ \frac{0.047584}{B} \right\} = -0.056450 \left(\frac{R_3 - R_0}{R_1 - R_0} \right) - A \left\{ \frac{0.032579 \left(\frac{R_2 - R_0}{R_1 - R_0} \right)}{B} \right\},$$

$$A = 0.27357 \left(\frac{R_3 - R_0}{R_1 - R_0} \right) - 5.1772, \quad B = 1 - 0.15789 \left(\frac{R_2 - R_0}{R_1 - R_0} \right),$$

$$\frac{\partial\delta}{\partial t_1} = - \frac{0.56462 \left(\frac{R_2 - R_0}{R_1 - R_0} \right) + 0.82467 \frac{\partial\beta}{\partial t_1}}{B},$$

$$\frac{\partial\alpha}{\partial t_1} = \frac{0.97832 - 0.27357 \frac{\partial\delta}{\partial t_1}}{R_1 - R_0}.$$

For a typical 100 ohm thermometer such as the one used in this research,

$$\partial\alpha/\partial t_1 = 0.01933$$

$$\partial\beta/\partial t_1 = -0.04706$$

$$\partial\delta/\partial t_1 = 0.4211 \quad \text{per degree.}$$

Now at any temperature, t , the error in the calibration is,

$$\Delta t = \frac{\partial \alpha}{\partial t_1} (R - R_0) + F(t, \delta + \frac{\partial \delta}{\partial t_1} + \frac{\partial \beta}{\partial t_1}) - F(t, \delta, \beta) \quad (4)$$

per degree error in t_1 .

Equation (4) is plotted as a function of temperature in Figure 5 and shows the effect caused by a one degree error in the Benzoic acid point.

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and,

$$q(t) = Q(t) + \int_0^t C(t) \frac{dT}{dt} dt$$

Using the definitions,

$$N\Delta H_0 = q(t) - b \int_0^t (T - T') \frac{dN}{dt} dt - c(T - T') - q \int_0^t n \frac{dT}{dt} dt$$

Integrating the last term by parts, we have,

$$N\Delta H_0 = q(t) - (c + qn')(T - T') + N(qT + bT') - (b + q) \int_0^t T \frac{dN}{dt} dt$$

This equation may be solved in two ways, integrating from $t = 0$ to $t = t''$, we have,

$$\Delta H_0 = \frac{1}{N''} \left\{ q'' - (c + qn')(T'' - T') + N''(qT'' + bT') - (b + q) \int_0^{t''} T \frac{dN}{dt} dt \right\} \quad (1)$$

Or solving for N and integrating from 0 to t,

$$N = \frac{1}{\Delta H_0} \left\{ q(t) - (c + qn')(T - T') + N(qT + bT') - (b + q) \int_0^t T \frac{dN}{dt} dt \right\} \quad (2)$$

Every term in equation (1) can be calculated except the integral. For that term N must be known as a function of time. For computation the integral may be replaced by a sum over a series of suitably short intervals of time which will be designated h . The integrand may be found by differentiating equation (2) with respect to time, using h as the differential element of time. Rearranging we have,

$$\frac{\Delta N}{h} = \frac{1}{\Delta H_0} \left\{ \frac{\Delta q}{h} - (c + qn') \frac{\Delta T}{h} + b(T^2 - T) \frac{\Delta N}{h} + Nq \frac{\Delta T}{h} \right\} \quad (2')$$

which gives the rate of distillation at any time. To calculate $\Delta N/h$ an iterative process is employed. First, an initial guess for $\Delta N/h$ is needed, and this guess can be summed to provide N as a function of time. A good approximation would be to let $\Delta N/h$ rise linearly, when the stopcock is opened to allow distillation, to a value, a , where it remains constant until the stopcock is closed, dropping linearly to zero. The value of a can be found from N'' and the length of the distillation. A first approximation for ΔH_0 may be calculated from the first two terms of equation (1). Using these, a value for $\Delta N/h$ may be calculated for each interval, h . These values, multiplied by the appropriate T , can be summed to provide the needed integral in equation (1), which then yields a better determination of ΔH_0 . If the experimental conditions are carefully set up, one iteration will give the calculated value of the heat of vaporization within 1 cal./mole.

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