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P. A.

HEAT CAPACITY FROM 80° TO 300° K., MELTING POINT
AND HEAT OF FUSION OF NITROETHANE

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HEAT CAPACITY FROM 80° TO 300° K., MELTING POINT
AND HEAT OF FUSION OF NITROETHANE

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TABLE OF CONTENTS

	Page
ACKNOWLEDGMENTS	ii
LIST OF TABLES	iv
LIST OF FIGURES	v
SUMMARY	vi
Chapter	
I. INTRODUCTION	1
II. APPARATUS AND PROCEDURE	3
III. PURIFICATION OF SAMPLE	8
IV. RESULTS AND DISCUSSION	10
APPENDICES	17
A. NUMERICAL CONSTANTS AND CONVERSION FACTORS	18
B. CALCULATION OF HEAT CAPACITY, HEAT OF FUSION, AND PURITY	20
C. HEAT CAPACITY DATA AND LEAST SQUARES FIT	31
D. VERIFICATION OF THE CONDITION OF THE CALORIMETER	38
E. LIQUID HEAT CAPACITY DATA OF BEARD	41
BIBLIOGRAPHY	42

LIST OF TABLES

	Page
Tables	
1. Smoothed Values of Heat Capacity of Nitroethane.	12
2. Equilibrium Temperature - Fraction Melted	15
3. Evaluation of the Heat of Fusion and Purity. Series A . .	26
4. Evaluation of the Heat of Fusion and Purity. Series B . .	27
5. Experimental Heat Capacity Data	31
6. Polynomial Fit for the Solid Range	35
7. Polynomial Fit for the Liquid Range	36
8. Heat Capacity of Ethanol-Methylcyclohexane (This Work: Run 1400)	38
9. Heat Capacity of Ethanol-Methylcyclohexane (Data of Hwa: ⁹ Table 11)	40
10. Heat Capacity of Nitroethane (Data of Beard ¹)	41

LIST OF FIGURES

		Page
Figure		
1.	Schematic Diagram of Calorimeter	4
2.	Smoothed Values of Heat Capacity of Nitroethane	14
3.	Equilibrium Temperature Versus 1/Fraction Melted	28
4.	Heat Capacity of Ethanol-Methylcyclohexane	39

SUMMARY

The objective of this work was to measure the heat capacity of nitroethane, $C_2H_5NO_2$, from room temperature to about 77° K., the normal boiling point of liquid nitrogen. At the same time the melting point, heat of fusion, and purity were to be determined.

The apparatus used was a precision adiabatic-shield high-vacuum calorimeter, which has been used and described by McGee,¹³ Hwa,⁹ and Ziegler.²⁷

The experimental heat capacity data have a reproducibility of about 0.03 cal./gm. mole $^{\circ}$ C., while the temperature has a reproducibility of one or two thousandths of a degree. The experimental heat capacity data has been fitted, by the least squares method, with two polynomials with temperature ($^{\circ}$ C.) as the independent variable. The solid-range polynomial represents the experimental data with a maximum deviation of 0.24 percent of the experimental value. The liquid-range polynomial represents the experimental data with a maximum deviation of 0.15 percent. The melting point was determined to be $-89.46 \pm 0.02^{\circ}$ C., and the heat of fusion to be 2355 ± 4 cal./gm. mole. The calorimetric and gas chromatographic purity were determined to be 99.9⁺ and 99.2⁺ mole percent nitroethane respectively.

One interesting feature of the heat capacity data for the liquid is that a minimum occurs near -45° C. The presence of this minimum has not been accounted for quantitatively. It is suggested that it may be

associated in part with the contribution to the heat capacity arising from internal rotation about the C-C and C-N bonds.

CHAPTER I

INTRODUCTION

Nitroparaffins, of which nitroethane is a member, are important solvents widely used in the coating and dye industries. The extent to which the physical chemistry of these compounds has been studied can be summarized thusly:

- a. Physical constants -- boiling and freezing points²³
- b. Physical properties -- liquid density,^{2,23} vapor density,¹⁷
surface tension,^{2,20} and vapor
pressure²³
- c. Thermodynamic properties -- heats of combustion, formation,
and vaporization,⁷ ionization
constants in water.^{15,16,25}

A problem of considerable interest is that of internal rotation in the nitroparaffins.^{6,17,21,22} However, in this respect only nitromethane has been studied experimentally. In fact, it is the only member of the nitroparaffins whose physical chemistry has been studied to any extent. Its internal rotation barrier has been calculated from vapor heat capacity data,¹⁷ and from microwave spectra.²² The former method gave a value of approximately 800 cal./gm. mole, a number of doubtful accuracy since the accuracy of the data was such that values of 0 to 1000 cal./gm. mole were possible.¹¹ The latter method yielded a value of 6.0 ± 0.03 cal./gm. mole. The heat capacity (from 15 to 300° K.),

melting point (-28.37°C.), and the heat of fusion ($2319\text{ cal./gm. mole}$) of nitromethane have been measured.¹¹ Toops²³ found the melting point of nitromethane to be -28.55°C. The heat capacity of nitroethane and 1-nitropropane has been measured over a narrow range (Appendix E) of temperature in the liquid state.¹ No other heat capacity data for the nitroparaffins appear to be available.

The presence of the polar nitro group in the nitroparaffins makes them interesting substances from the point of view of their solution chemistry. The vapor-liquid equilibrium at sub-atmospheric pressures of nitromethane-nitroethane has been studied.³ The vapor-liquid equilibria⁴ and liquid-liquid solubility¹⁰ of nitroparaffin-hydrocarbon systems have also been studied. The thermodynamics of solutions can be studied in terms of the excess thermodynamic properties, which can be derived from a knowledge of the properties of the solution and those of the pure components. A method of arriving at the excess properties is by way of the excess heat capacity.⁹

The objective of this experiment was to measure the heat capacity of nitroethane, $\text{C}_2\text{H}_5\text{NO}_2$, from room temperature to the normal boiling point of liquid nitrogen, at about 77°K. At the same time the melting point, the heat of fusion, and purity were to be determined.

CHAPTER II

APPARATUS AND PROCEDURE

Description of Apparatus

The apparatus used in this experiment was a precision adiabatic-shield high-vacuum calorimeter, which has been used and described by McGee,¹³ Hwa,⁹ and Ziegler.²⁷ A brief description of the apparatus will be presented here. Detailed descriptions are given by McGee,¹³ and Hwa.⁹

Figure 1 is a schematic diagram of the calorimeter. The gold-plated copper calorimeter can, C, (containing the liquid sample) is suspended by a fine wire (No. 32 Nichrome), W, within the light-weight copper shield, S. The shield itself is suspended from the ring, R, which is in turn suspended from the lid, L, of the vacuum jacket, J. The jacket is immersed in a constant temperature bath, B. The copper plug in the reentrant well of the can carries the calorimeter heater, H, and the platinum resistance thermometer, T (Leeds and Northrup No. 1048215), which has been calibrated by the National Bureau of Standards on the International Temperature Scale. Temperature differences between the can and shield are detected at the side, the bottom, and the top by three-junction (constantan-chromel-P) difference couples TD1, TD2, and TD3, respectively. Difference couple TD4 detects the temperature difference between the ring and the top of the shield. Corresponding to TD1, TD2, TD3, and TD4 are the heaters H1, H2, H3, and H4 respectively. All the electrical leads are wrapped around R

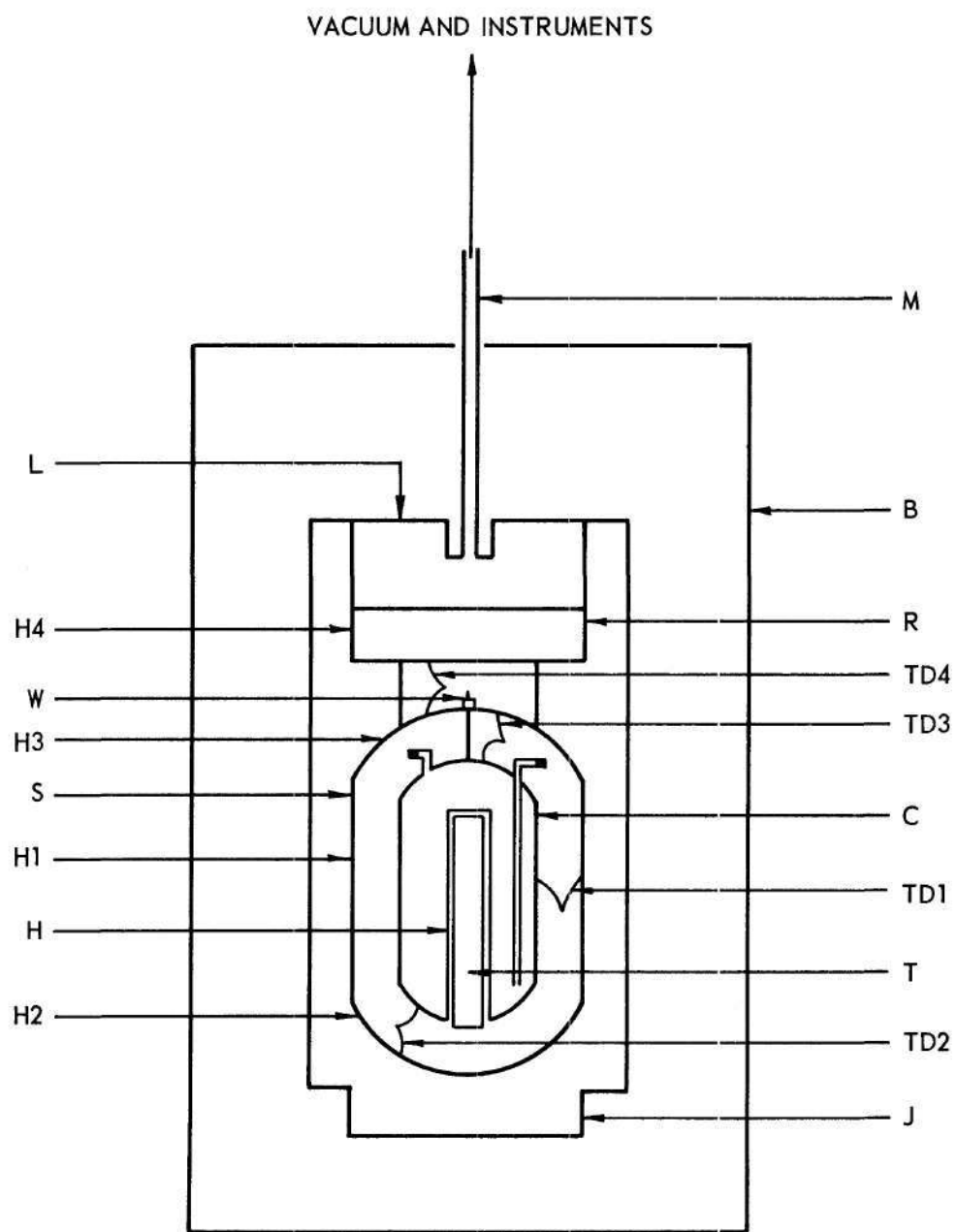


Figure 1. Schematic Diagram of Calorimeter.

before passing through the monel tube, M, to the appropriate connections. The monel tube also connects to the high-vacuum system, and to a supply of helium gas. The latter is used as an exchange gas to expedite heat transfer between the calorimeter can and the surrounding bath when rapid cooling of the can is required.

The energy to the calorimeter heater is supplied by an Edison battery, which has the characteristic of maintaining a steady discharge voltage over short periods of time. The resistance of the thermometer is measured with a Leeds and Northrup Mueller G-2 resistance bridge, which permits measurement of resistance to within 0.0001 ohm (about 0.001° C.). The potential across a one-ohm standard resistor and across the calorimeter heater is measured with a Leeds and Northrup 100,000 microvolt White Double Potentiometer. The heating period is measured with a 110-volt, 60-cycle type S-10 electric timer manufactured by the Standard Electric Timer Company, Springfield, Massachusetts. The accuracy of this timer has been determined to be ± 0.1 second.¹³ The shield and ring heaters are heated by a 110-volt A.C. source, the voltage of which is suitably reduced to supply a maximum of one-quarter ampere to each heater. All the standard cells and standard resistors that were used were calibrated by the National Bureau of Standards.

Experimental Procedure

A desired amount of nitroethane was transferred to a weighing bottle and weighed. The empty calorimeter can, which weighs about 193.5 gm. and has a volume of 160 ml., was filled to within about 10 ml. of capacity. All transfer of liquid was accomplished under dry nitrogen

gas. The can was then sealed with brass caps which were soldered with 50-50 lead-tin solder to the monel filling and withdrawal tubes. The can was weighed before and after soldering to determine the amount of solder used. The can was suspended from the top of the shield with a length of No. 32 Nichrome wire. The electrical leads were connected, and tested for electrical grounding and shorts. The shield was then replaced and the leads tested again. Next, the vacuum jacket was soldered and the system tested for vacuum tightness. The calorimeter is cooled to the temperature of the bath by admitting helium gas into the jacket. An ice bath was used for the range 0 to 30° C., a dry ice-ethanol bath for the range -78 to 0° C., and a liquid nitrogen bath for the range -196 to -78° C. The automatic device described, and used by Hwa⁹ for controlling the temperature of the bath was not used in this work. When the calorimeter has cooled to the temperature of the bath, the helium gas was pumped out and the system evacuated to better than 1×10^{-5} torr. The shield and ring were brought to the same temperature as the can, and the system was ready for measurement.

The initial resistance of the thermometer was recorded. The calorimeter heater was switched on, at which moment the timer was started. The shields were again brought to balance. The voltage across the one-ohm standard resistor and across the calorimeter heater (reduced through a volt box) was recorded at regular intervals. The heater was switched off, which also stopped the timer, and the heating interval recorded. The shields were brought to balance again. The final resistance of the thermometer was recorded until steady; usually ten to fifteen minutes after the heater was switched off. The next

interval was then ready to be measured. At all times, except in the short moments when the heater was switched on and off, the shield and ring, and the calorimeter can were maintained at a temperature difference of within 0.01°C . A heating interval varied from 700 to 1500 seconds depending on the temperature of the measurements. The measurements were carried out continuously, with the final temperature of one measurement as the starting temperature of the following one. The temperature increments were from three to five degrees centigrade, and each measurement took approximately thirty to forty minutes. A traverse of the melting region was divided into five to six intervals, each being treated as a heat capacity measurement. Such a traverse took about five hours.

CHAPTER III

PURIFICATION OF SAMPLE

A bottle which was labeled as containing 99.98⁺ percent pure nitroethane was available in the laboratory. Heat capacity measurements from 0 to 30° C. of this material were quite normal. However, the heat capacity measurements below -30° C. were irregular and unreproducible. A small amount of nitroethane was withdrawn from the same bottle and slowly cooled in a test tube. At about -47.5° C. a flocculent precipitate appeared, which on warming disappeared at -27° C. The addition of a desiccant (Drierite) did not eliminate this precipitate. Gas chromatographic analysis indicated the presence of about 1.9 percent of 2-nitropropane, 0.3 percent nitromethane, 0.1 percent water, and small amounts of unidentified substances. The sample had been stored in an amber bottle for about two and a half years, and it was not possible to determine the cause of the discrepancy between the labeled and actual contents of the bottle.

About one liter of stock redistilled nitroethane was charged into the pot of a Todd column with an automatic still head. The column was three feet long and one inch in diameter, packed with glass helices. Approximately 900 ml. of distillate were collected under a pressure of 100 mm. Hg and a reflux ratio of 10:1. The distillate was redistilled under 96 mm. Hg pressure and a reflux ratio of 50:1. Analysis showed the presence of still considerable quantity of 2-nitropropane. At a

pressure of 100 mm. Hg the boiling points of nitroethane and 2-nitropropane are 57.5°C . and 61.0°C . respectively.⁵

A longer column, with a manual still head, that was six feet long, half an inch in diameter, and packed with glass helices, was used to distill the distillate from the previous attempts. The pressure was 92 mm. Hg. A forerun of about 70 ml. was collected at a reflux ratio of 26:1. A first cut of about 200 ml. was collected at a reflux ratio of 30:1, and a second cut of another 200 ml. was collected at a reflux ratio of 40:1. Chromatographic analysis showed the first cut to be the purest. It contained 99.2^{+} mole percent* nitroethane, with the remainder consisting mainly of 2-nitropropane and water, and traces of unidentified substances. It was chosen to be the calorimetric sample.

The type of apparatus used and the conditions of analysis are presented below.

Chromatograph -- Perkin-Elmer model 154

Column -- Column A (supplied with the apparatus)

Column temperature -- 110.0°C .

Carrier gas -- helium, at a flow rate of 110 ml./minute at 70°F .

Detector voltage -- 8.0 volts.

The percentages were calculated directly from the area under the peaks. It should be noted that the chromatograph was not calibrated for quantitative analysis. It was used to obtain an indication of the relative quality of the distillation products.

* See Appendix B (p. 29) for the determination of calorimetric purity.

CHAPTER IV

RESULTS AND DISCUSSION

The experimental heat capacity data are presented in Appendix C. They have been fitted with polynomials obtained by the least squares method. Equations 1 and 2 represent the data in the solid and liquid regions respectively.

$$C_s(\text{solid}) = -28.2972 - 1.9882149xt - 0.029578408xt^2 - 0.2067204 \times 10^{-3}xt^3 - 0.70838749 \times 10^{-6}xt^4 - 0.95205115 \times 10^{-9}xt^5 \quad (1)$$

$$C_s(\text{liquid}) = 31.490681 + 0.018468551xt + 0.17348328 \times 10^{-3}xt^2 + 0.7310325 \times 10^{-6}xt^3 + 0.16627775 \times 10^{-7}xt^4 \quad (2)$$

$t = ^\circ\text{C}.$

C_s = Heat capacity of the saturated* solid, or liquid.

Tables 6 and 7 in Appendix C show the difference between the values calculated from Equations 1 and 2 and the observed values of the heat capacity. Table 1 presents the smoothed values calculated from Equations 1 and 2, at five degree intervals. The maximum deviation in the solid region between the calculated and observed values is 0.24 per-

* Hoge^{6a} has considered the heat capacity of pure two-phase systems. By assuming that the nitrogen is insoluble in the nitroethane, application of his treatment shows that the heat capacity measured in this work is, within the accuracy of the data, the same as the saturated heat capacity.

cent of the observed value. In the liquid region the maximum deviation is 0.15 percent. A less accurate, but more widely representation of the heat capacity data in the solid region is Equation 3.

$$C_s(\text{solid}) = 34.16413 + 0.20268662 \times t + 0.82405911 \times 10^{-3} t^2 + 0.19337333 \times 10^{-5} t^3 \quad (3)$$

Equation 3 has a maximum deviation of 0.28 percent of the observed value. Simpler representations of the heat capacity data for the liquid region could be obtained by truncating the higher powers of the temperature terms in Equation 2. Table 2 summarizes the results of the melting region traverses and the average values of the melting point, heat of fusion, and purity of the sample. The observed melting point of $-89.46 \pm 0.02^\circ \text{C}$. may be compared with the value of -89.52°C reported by Toops.²³ His reported purity of 99.9⁺ mole percent nitroethane was determined by cryoscopic and ebullioscopic methods.

The Mueller bridge permits measurement of the resistance to 0.0001 ohm. However, the scale is incremental and the last decimal place is usually obtained by linear interpolation. This is equivalent to some uncertainty in the third decimal place of the temperature values. The analysis in Appendix B leads to the conclusion that the neglected and unaccounted for effects in the calculation of the heat capacity amount to the order of 0.01 cal./ $^\circ \text{C}$., while the reproducibility of the experimental heat capacity is of the order of 0.03 cal./gm. mole $^\circ \text{C}$. Hence, the heat capacity values are certain to the first decimal place. The melting point is probably certain to the first decimal place. The difference in the heat of fusion values from the two melting region

Table 1. Smoothed Values of Heat Capacity of Nitroethane

Temperature °C	Heat Capacity, C cal./gm. mole °C ^s
-195.0	11.67
-190.0	12.14
-185.0	12.62
-180.0	13.09
-175.0	13.56
-170.0	14.03
-165.0	14.48
-160.0	14.92
-155.0	15.35
-150.0	15.78
-145.0	16.20
-140.0	16.63
-135.0	17.05
-130.0	17.49
-125.0	17.93
-120.0	18.37
-115.0	18.82
-110.0	19.27
-105.0	19.71
-100.0	20.14
-95.0	20.54
-90.0	20.90
-89.46	melting point
-85.0	31.59
-80.0	31.43
-75.0	31.30
-70.0	31.20
-65.0	31.12
-60.0	31.06
-55.0	31.03
-50.0	31.01
-45.0	31.01
-40.0	31.03
-35.0	31.05
-30.0	31.09
-25.0	31.13
-20.0	31.19

(continued)

Table 1. Smoothed Values of Heat Capacity of Nitroethane
(concluded)

Temperature °C	Heat Capacity: C_p cal./gm. mole °C ^s
-15.0	31.25
-10.0	31.32
-5.0	31.40
0.0	31.49
5.0	31.59
10.0	31.69
15.0	31.81
20.0	31.94
25.0	32.08
30.0	32.23

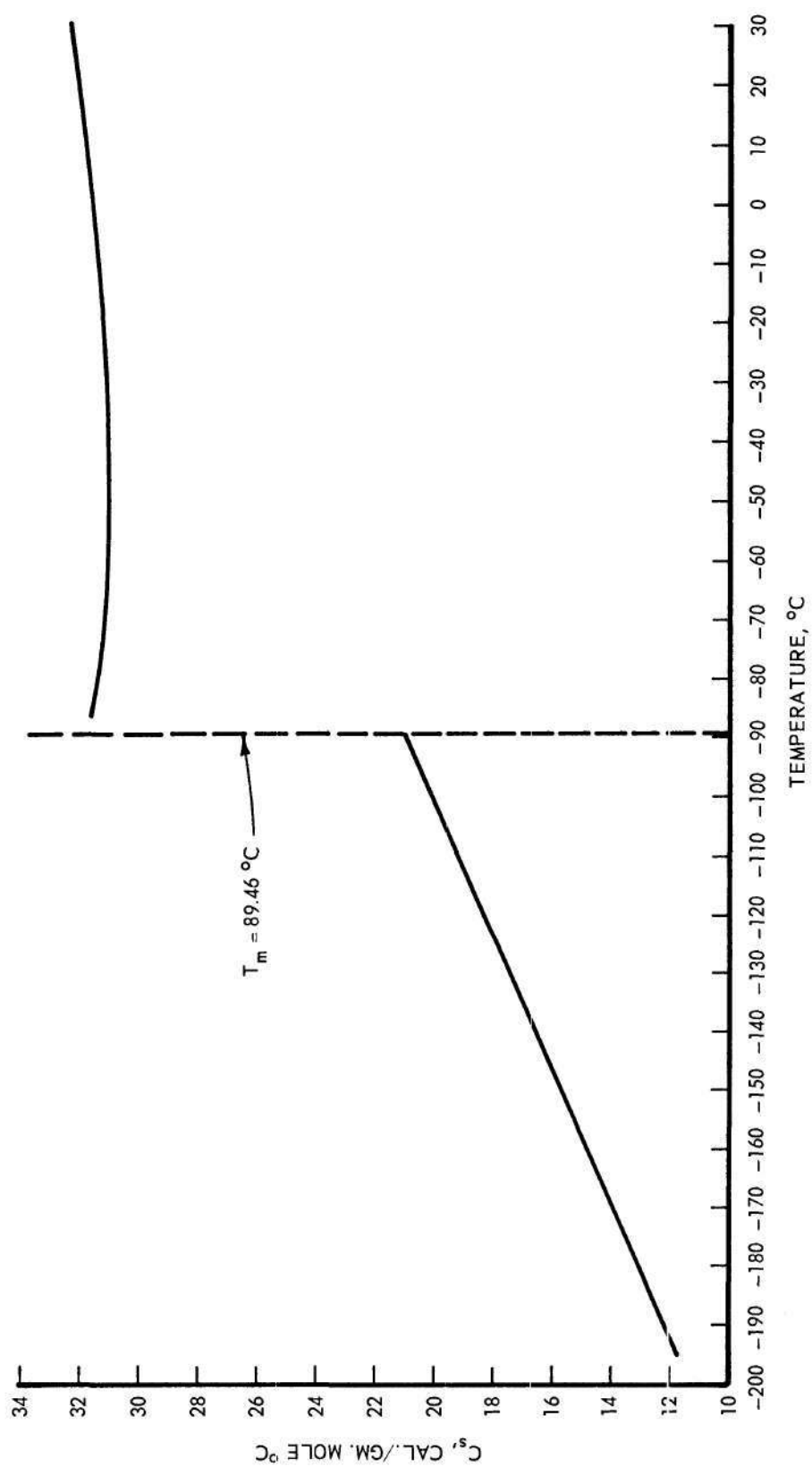


Figure 2. Smoothed Values of Heat Capacity of Nitroethane.

Table 2. Equilibrium Temperature - Fraction Melted*

Equilibrium Temperature (°C)	Fraction Melted
Series A	
-90.492	0.024
-89.555	0.219
-89.494	0.527
-89.479	0.843
-89.470	0.961
Melting point = -89.474° C.	
Heat of fusion = 2360 cal./gm. mole	
Purity = 99.92 mole percent	
Series B	
-90.384	0.027
-89.508	0.328
-89.471	0.634
-89.462	0.841
-89.454	0.976
Melting point - -89.457° C	
Heat of fusion = 2351 cal./gm. mole	
Purity = 99.91 mole percent	
Average melting point = -89.46 ± 0.02° C.	
Average heat of fusion = 2355 ± 4 cal./gm. mole	
Average purity = 99.92 mole percent	

* Appendix C, Table 5: Run 1700

traverses is 9 cal./gm. mole, so that the reproducibility of the heat of fusion is 0.4 percent. The calorimetric purity of the sample is 99.9⁺ mole percent, which may be compared with the gas chromatographic value of 99.2⁺ mole percent (see remarks on p. 9 and p. 30). Beard¹ (Appendix E) measured the heat capacity of nitroethane at 25, 35, 45, and 50° C. His value at 25° C. was 0.441 cal./gm. °C. The corresponding value as calculated from Equation 2 is 0.427 cal./gm. °C. No heat of fusion measurements have been made previously.

The values of the heat capacity from Table 1 have been plotted in Figure 2. It is interesting to note that the heat capacity passes through a minimum near -45° C. It was suspected that this may be due, at least in part, to the contribution of internal rotation to the heat capacity. Assuming different barrier heights of 0 to 3000 cal./gm. mole for the C-C bond, an analysis similar to that in Hcugen and Watson⁸ was done. The barrier for the C-N bond was assumed to be the same as that in nitromethane²² (6.0 cal./gm. mole) and neglected. The results could not account for the observed behavior of the heat capacity. However, the calculations were only a rough approximation. If values for the actual barrier heights for the C-C and C-N bonds in nitroethane were available, a more conclusive examination could be made.

APPENDICES

APPENDIX A

NUMERICAL CONSTANTS AND CONVERSION FACTORS

Temperature Scale

All the temperature measurements were made with a platinum resistance thermometer which had been calibrated by the National Bureau of Standards on the International Temperature Scale. All the temperature measurements are reported in degrees centigrade. Where the Kelvin scale is used, the conversion relation used is

$$T^{\circ}\text{K.} = 273.15 + t^{\circ}\text{C.}$$

Molecular Weight

The molecular weight of nitroethane was based on the atomic weights published in 1956,²⁶ which gave the following atomic weights:

oxygen 16

hydrogen 1.008

nitrogen 14.008

carbon 12.011.

The molecular weight, calculated from the above atomic weights, of nitroethane is 75.070.

Energy Conversion

All the electrical measurements were in absolute units, which gave the calculated energy in absolute joules. The absolute joules

were converted into defined calories (the units used in this work) by the following relation:

$$1 \text{ defined calorie} = 4.1840 \text{ absolute joules} .$$

APPENDIX B

CALCULATION OF HEAT CAPACITY, HEAT OF FUSION, AND PURITY

Calculation of the Heat Capacity

The heat capacity that is measured in this experiment consists of two parts: the heat capacity of the calorimeter can and that of the sample. The heat capacity of the calorimeter can has been determined by Hwa⁹ and is represented by Equation 4.

$$C_p(\text{can}) = 16.150851 + 1.4611653 \times 10^{-2} t - 9.826999 \times 10^{-6} t^2 + 1.1551778 \times 10^{-7} t^3 - 1.963681 \times 10^{-9} t^4 \quad (4)$$

$$t = ^\circ\text{C}.$$

Equation 4 was used to calculate the heat capacity of the calorimeter can. The difference between the measured heat capacity and that of the can is the heat capacity of the sample. The mean temperature of an interval is taken as the temperature at which the heat capacity has been evaluated.

The data obtained during a measurement were the initial resistance of the thermometer (same as the final resistance of the preceding measurement), the potential across the calorimeter heater (measured across the volt box), P, the potential across the one-ohm standard resistor, Q, the elapsed time of the heating interval, S, and the final resistance of the thermometer.

The main assumption in this experiment is that all the energy

supplied goes into the can and the sample. Actually, this is not quite true because heat losses do occur by conduction through the electrical leads, by conduction of the residual gas in the vacuum jacket, and by radiation. The conduction loss is nearly eliminated by keeping the ring, R, around which the leads are wound, at the same temperature as the can. At the vacuum of better than 1×10^{-5} torr the gaseous conduction and loss is also negligible. At the lower temperatures the radiation loss, which is proportional to the fourth power of the absolute temperature, is unnoticeable. At the higher temperatures, or when there is a large difference between the temperature of the bath and that of the can, the radiation effect shows up as a drift in the temperature of the can at the rate of a few ten-thousandths of a degree per minute. This drift was practically eliminated by Hwa⁹ by means of an automatic device for maintaining the bath temperature close to the temperature of the can. A way of correcting for this drift would be to compute a drift rate that was the average of the drift rate of a measurement and that of the preceding measurement. When multiplied by the heating interval, this average drift would give a reasonable correction for the drift. But such corrections amount to less than 0.001° C., and are tedious to make. So, as a demonstration, this was taken into account only in Run 1500 (Appendix C: Table 5).

Theoretically, the energy input to the calorimeter should be integrated over the heating interval. However, by means of a ballast circuit having the same resistance as the calorimeter heater circuit, and which drew current all the time that the latter was not in use, the input current was stabilized. Over a heating interval the potential

across the heater would drop by about 2 to 3 parts in 10,000. The average potential was taken to calculate the energy input.

The Callendar-van Dusen Equation for the thermometer has been approximated⁹ with a fourth degree polynomial with resistance as the independent variable. This polynomial was used to calculate a first approximation of the temperature from the resistance of the thermometer. The Callendar-van Dusen Equation is convergent for the method of successive iteration for the solution of the zeros of functions. So, the first approximation of the temperature was substituted into the Callendar-van Dusen Equation and the temperature iterated until the absolute difference between two successive values was less than 0.0001°C .

The maximum effect of partial vaporization of the sample on the heat capacity occurred in heating the sample from 25°C to 30°C . Since the heat of vaporization⁷ at 25°C of nitroethane is $9940\text{ cal./gm. mole}$, for a gas volume of 10 ml. , this effect was computed to be $0.007\text{ cal./}^{\circ}\text{C}$. This effect rapidly decreases with decreasing temperature, so no such corrections were made.

The calorimeter can is sealed at room temperature and atmospheric pressure. The gas space above the sample is about 10 ml. and filled with nitrogen. At room temperature this nitrogen has a heat capacity of about $0.003\text{ cal./}^{\circ}\text{C}$. Again, this is a diminishing effect with decreasing temperature and has been neglected. The effect of pressure on the heat capacity is usually negligibly small.

Over the temperature range of this work only very slight variations in the pressure would be expected within the calorimeter

can. Therefore, the effect of pressure on the heat capacity was not considered.

The variation in the amount of solder used each time the can is sealed is such that its effect on the heat capacity of the can is negligible.

A sample calculation of the heat capacity will now be presented. The following is a set of data for a typical measurement (Appendix C, Table 5: Run 1800):

Initial resistance readings from the Mueller bridge,

$$N = 26.17235 \text{ ohms}$$

$$R = 26.150667 \text{ ohms}$$

Potential across volt box, of heater, $P = 0.0573439$ volts

Potential across one ohm standard resistor, $Q = 0.0774643$ volts

Heating interval, $S = 1730.32$ seconds

Final resistance readings from the Mueller bridge,

$$N = 26.6249 \text{ ohms}$$

$$R = 26.6018 \text{ ohms}$$

The resistance of the thermometer is taken to be $(N + R)/2$. Therefore,

Initial resistance of the thermometer = 26.16151 ohms

Initial temperature = $6.5105^{\circ} \text{ C.}$

Final resistance of the thermometer = 26.61335 ohms

Final temperature = $10.9708^{\circ} \text{ C.}$

Temperature increment, Δt = $4.4603^{\circ} \text{ C.}$

Mean temperature = $8.7407^{\circ} \text{ C.}$

The volt box, which was connected in parallel across the heater, reduced the potential across the heater by a factor of 200. Therefore, the actual potential across the heater is 200P. The total current in the circuit is $Q/1.00044$, where 1.00044 is the resistance of the standard resistor. The current through the heater is $(Q/1.00044 - 200P/60000)$, where 60000 is the resistance of the volt box. Let H be the energy input to the calorimeter during the heating interval.

$$H = (Q/1.00044 - 200P/60000) \cdot 200P \cdot S / 4.1840 \text{ calories}$$

For the data above, $H = 366.344$ calories. The overall heat capacity is $H/\Delta t$, equal to $82.1344 \text{ cal./}^\circ\text{C}$. The heat capacity of the calorimeter can be calculated from Equation 4 is $16.2778 \text{ cal./}^\circ\text{C}$. The number of moles of nitroethane is 2.07815.

$$\begin{aligned} C_s(\text{nitroethane}) &= (82.1344 - 16.2778)/2.07815 \\ &= 31.690 \text{ cal./gm. mole } ^\circ\text{C}. \end{aligned}$$

In summary, the results of this measurement are:

<u>Initial temperature</u> <u>°C</u>	<u>Mean temperature</u> <u>°C</u>	<u>Heat capacity</u> <u>cal./gm. mole °C.</u>
6.511	8.741	31.690

The above procedure has been programmed for the Burroughs B-220 computer by Hwa,⁹ and the calculations were made with that program.

Consideration of the data in the overlap region (Appendix C, Table 5: Run 1500 and Run 1800) and the data in Appendix D leads to the conclusion that the experimental heat capacity values are reproducible to within $0.03 \text{ cal./gm. mole } ^\circ\text{C}$.

Calculation of Heat of Fusion and Purity

For an almost pure component, its fusion process can be analyzed by assuming that the liquid phase is an ideal solution, the solid phase is pure, and that the solid and liquid phases are in equilibrium. Such an analysis has been done by Rossini¹⁸ and the result is Equation 5.

$$T = T_1^* - \left(\frac{N_2^s}{A}\right) \cdot \left(\frac{1}{r}\right) \quad (5)$$

where T = equilibrium temperature,

T_1^* = melting point of the absolutely pure major component,

N_2^s = mole fraction of impurities,

$A = \Delta H_{m1}/R(T_1^*)^2$, ΔH_{m1} being the heat of fusion of the major component,

r = fraction melted.

Where Equation 5 is applicable, a plot of T against $1/r$ would be a straight line. Corresponding to $1/r$ equal to zero would be the temperature T_1^* , the melting point of the absolutely pure sample. Corresponding to $1/r$ equal to one is the temperature T_m , the melting point of the actual sample. The slope of the straight line is N_2^s/A , from which the mole fraction of the impurities, N_2^s , is readily calculated.

Tables 3 and 4 summarize the heat of fusion calculations.

T_{start} (the same as T_{end} of the preceding interval) is the starting temperature of a heating interval in a traverse of the melting region. Δt is the temperature increment. Q , the total energy input is exactly equal to $C_s(\Delta T)$. On the low side of the melting point (assuming that this known roughly) Q consists of two parts, the energy that went into

Table 3. Evaluation of the Heat of Fusion and Purity. Series A*

Interval	T _{start}	T _{end}	Δt	C _s	Q	C _{sn}	Q _n	Q - Q _n	Fract.melt.	1/Fract.melt.
1	-105.776	-101.467	4.309	19.963	86.021	19.834	85.465	0.556	2.356x10 ⁻⁴	4.244x10 ³
2	-101.467	-97.278	4.189	20.697	86.700	20.195	84.597	2.103	1.127x10 ⁻³	8.873x10 ²
3	-97.278	-93.583	3.695	22.380	82.694	20.510	75.784	6.910	4.055x10 ⁻³	2.466x10 ²
4	-93.583	-90.492	3.091	36.188	111.857	20.761	64.172	47.685	2.426x10 ⁻²	41.220
5	-90.492	-89.555	0.937	509.989	477.860	20.899	19.582	458.278	0.219	4.577
6	-89.555	-89.494	0.061	11940.194	728.352	20.932	1.277	727.075	0.527	1.899
7	-89.494	-89.479	0.015	49820.636	747.310	20.934	0.314	746.996	0.843	1.186
8	-89.479	-89.470	0.009	30824.612	277.422	20.935	0.188	277.234	0.961	1.041
9	-89.470	-85.993	3.477	58.390	203.022	31.697	110.210	92.812	1.000	1.000

Sum (Q - Q_n) = Heat of fusion: 2359.649 cal./gm. mole

$$T_m = -89.474^\circ \text{C.}$$

Purity = 99.92 mole percent

* Appendix C: Table 5, Run 1700

Table 4. Evaluation of the Heat of Fusion and Purity. Series B*

Interval	T _{start}	T _{end}	ΔT	C _s	Q	C _{sn}	Q _n	Q - Q _n	Fract.melt. l	Fract.melt. l/Fract.melt.
1	-105.431	-101.124	4.307	19.988	86.088	19.864	85.554	0.534	2.272x10 ⁻⁴	4.401x10 ³
2	-101.124	-96.968	4.156	20.782	86.370	20.221	84.038	2.332	1.219x10 ⁻³	8.203x10 ²
3	-96.968	-93.263	3.711	22.631	83.984	20.534	76.202	7.782	4.530x10 ⁻³	2.208x10 ²
4	-93.263	-90.384	2.879	38.997	112.272	20.776	59.814	52.458	2.685x10 ⁻²	37.244
5	-90.384	-89.508	0.876	828.007	725.334	20.904	18.312	707.022	0.328	3.053
6	-89.508	-89.471	0.037	19482.125	720.839	20.934	0.775	720.064	0.634	1.577
7	-89.471	-89.462	0.009	53994.163	485.947	20.936	0.188	485.759	0.841	1.189
8	-89.462	-89.454	0.008	39765.154	318.121	20.936	0.167	317.954	0.976	1.025
9	-89.454	-86.117	3.337	48.659	162.375	31.699	105.780	56.595	1.000	1.000

Sum (Q - Q_n) = Heat of fusion: 2350.500 cal./gm. mole

T_m = -89.457° C.

Purity = 99.91 mole percent

* Appendix C: Table 5, Run 1700

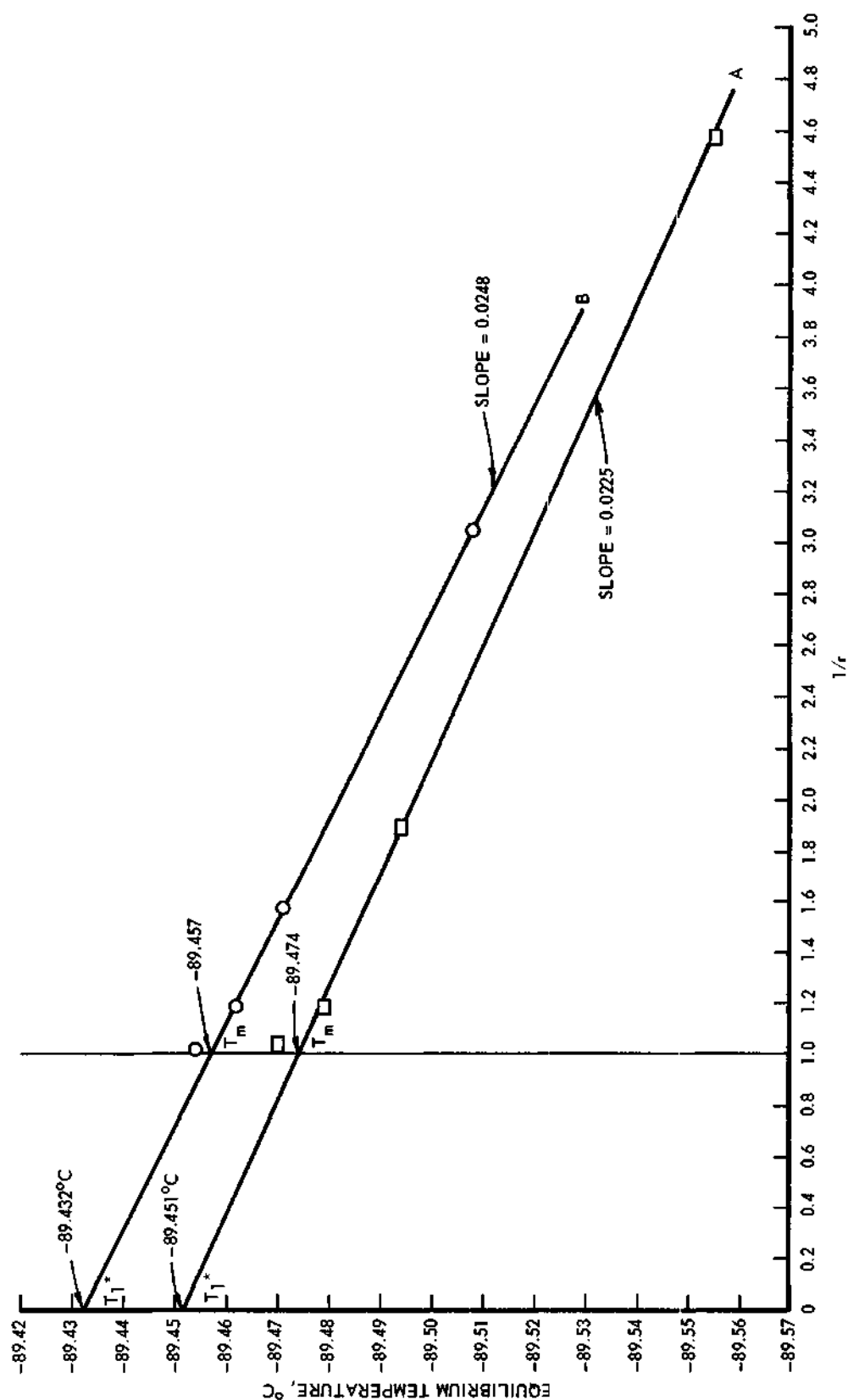


Figure 3. Equilibrium Temperature versus $1/\text{Fraction Melted}$.

melting the solid and, the energy, Q_n , that raised the temperature of the solid to the equilibrium temperature. The latter is given by $C_{sn}(\Delta T)$, where C_{sn} is the heat capacity of the solid if there were no premelting. C_{sn} for the solid was calculated from Equation 1. $(Q - Q_n)$ is then attributable to the heat of fusion. On the high side of the melting point the same argument is applied to the liquid, and C_{sn} for the liquid was calculated from Equation 2. The heat of fusion is the sum of the individual $(Q - Q_n)$ terms, and the fraction melted, r , is given by dividing the accumulative sum of $(Q - Q_n)$ by the heat of fusion.

Figure 3 is a plot of T_{end} versus $1/r$, showing the appropriate quantities. When the melting point is not known precisely, the above procedure is a trial and error process that is carried on until the value of the heat of fusion is such that Figure 3 yields a melting point that is the same as assumed in obtaining the heat of fusion. In Series A the difference between the assumed and calculated melting points is 0.004°C . In Series B, the difference is 0.003°C . The calculation of the purity of the sample is straightforward.

For Series A:

$$T_1^* = -89.451^\circ \text{C. or } 183.699^\circ \text{K.}$$

$$\begin{aligned} A &= \Delta H_{m1}/R(T_1^*)^2 = 2359.649/(1.987) \cdot (183.699)^2 \\ &= 0.03519 \end{aligned}$$

$$\begin{aligned} N_2^s/A &= \text{slope of the straight line, from Figure 3} \\ &= 0.0225 \end{aligned}$$

$$N_2^s = (0.0225) \cdot (0.03519) = 0.0008$$

Therefore, the calorimetric purity of the sample is 99.92 mole percent nitroethane, which may be compared with gas chromatographic value of

99.2 mole percent. As had been mentioned before (p.9) the chromatograph used for analysis was not calibrated for quantitative analysis. This probably is the main reason for the difference in the calorimetric and chromatographic values for the purity of the sample. To a smaller extent, the effects of the assumptions inherent in the two analytic methods would contribute to the difference.

APPENDIX C

HEAT CAPACITY DATA AND LEAST SQUARES FIT

Table 5. Experimental Heat Capacity Data
(Sample Weight: 156.007 gm.)

Initial Temperature °C	Mean Temperature °C	Heat Capacity, C_s^* cal./gm. mole °C
<u>Run 1500</u>		
0.037	1.557	31.513
3.078	4.806	31.561
6.534	8.144	31.658
9.754	11.296	31.713
12.838	14.414	31.781
15.989	17.542	31.877
19.095	20.728	31.942
22.362	23.998	32.048
25.634	27.111	32.155
<u>Run 1600</u>		
-195.642	-193.622	11.782
-191.602	-190.137	12.145
-188.672	-187.303	12.398
-185.935	-184.530	12.658
-183.125	-181.930	12.915
-180.734	-179.369	13.153
-178.003	-176.794	13.389
-175.585	-174.136	13.642
-172.686	-171.229	13.902
-169.776	-168.224	14.172
-166.782	-165.440	14.433
-164.098	-162.511	14.724
-160.925	-159.170	15.001
-157.416	-156.036	15.275
-154.655	-153.159	15.498

* C_s : Heat capacity of the saturated solid, or liquid.

(continued)

Table 5. Experimental Heat Capacity Data
(Sample Weight: 156.007 gm.)
(continued)

Initial Temperature °C	Mean Temperature °C	Heat Capacity, C _s cal./gm. mole °C
<u>Run 1600 (continued)</u>		
-154.402	-152.763	15.555
-151.123	-149.326	15.847
-147.529	-145.666	16.140
-143.802	-141.936	16.422
-140.147	-138.361	16.756
-136.576	-134.850	17.070
-133.125	-131.548	17.345
-129.972	-128.302	17.637
-126.633	-125.000	17.935
-123.368	-121.725	18.240
-120.083	-118.446	18.550
-116.810	-115.259	18.783
-113.762	-112.228	19.027
-110.693	-109.191	19.333
-107.688	-106.022	19.652
-104.356	-102.728	20.838
-101.101*	-99.454	19.809
-97.808*	-96.265	21.635
-94.721*	-93.492	24.519
-92.262*	-91.369	40.060
-90.475*	-90.207	132.343
-89.938*	-89.861	376.082
-89.784*	-89.730	740.734
-89.675*	-89.615	1691.186
-89.554*	-89.533	5513.230
-89.512*	-89.501	20389.581
-89.490	-89.188	2042.212
<u>Run 1700 - Melting Region Traverses - Series A</u>		
-109.662	-107.719	19.467
-105.776	-103.622	19.963
-101.467	-99.372	20.697
-97.278	-95.430	22.380
-93.583	-92.037	36.188

* Exploratory traverse of the melting region.

(continued)

Table 5. Experimental Heat Capacity Data
(Sample Weight: 156.007 gm.)
(continued)

Initial Temperature °C	Mean Temperature °C	Heat Capacity, C_p cal./gm. mole °C
<u>Run 1700 - Melting Region Traverses - Series A (continued)</u>		
-90.492	-90.024	509.989
-89.555	-89.525	11940.194
-89.494	-89.487	49820.636
-89.479	-89.475	30824.612
-89.470	-87.731	58.390
-85.993	-84.340	31.582
-82.687	-81.102	31.509
<u>Series B</u>		
-105.431	-103.277	19.988
-101.124	-99.046	20.782
-96.968	-95.117	22.631
-93.263	-91.824	38.997
-90.384	-89.946	828.007
-89.508	-89.489	19482.125
-89.471	-89.466	53994.163
-89.462	-89.458	39765.154
-89.454	-87.786	48.659
-86.117	-84.533	31.537
-82.948	-81.321	31.474
-79.694	-77.862	31.379
-76.031	-73.656	31.264
-71.280	-68.890	31.195
<u>Run 1800</u>		
-76.183	-74.417	31.248
-72.651	-70.907	31.203
-69.163	-67.361	31.156
-65.558	-63.714	31.096
-61.871	-59.898	31.073
-57.924	-55.937	31.036
-53.950	-51.929	31.026
-49.908	-47.885	31.011
-45.863	-43.748	31.002

(continued)

Table 5. Experimental Heat Capacity Data
 (Sample Weight: 156.007 gm.)
 (continued)

Initial Temperature °C	Mean Temperature °C	Heat Capacity, C_p cal./gm. mole °C
Run 1800 (continued)		
-41.634	-39.342	31.032
-37.049	-34.811	31.035
-32.574	-30.197	31.090
-40.137	-37.571	31.048
-35.005	-32.395	31.064
-29.784	-26.864	31.111
-23.943	-21.433	31.175
-18.924	-16.350	31.224
-13.777	-11.286	31.307
-8.796	-6.168	31.384
-3.539	-0.988	31.493
1.564	4.037	31.580
6.511	8.741*	31.690

* Data used in sample calculation.

Table 6. Polynomial Fit for the Solid Range

Temperature °C	Heat Capacity, cal./gm. mole °C		Calc. - Observ.
	Observed	Calculated*	
-193.622	11.782	11.794	0.012
-190.137	12.145	12.125	-0.020
-187.303	12.398	12.396	-0.002
-184.530	12.658	12.662	0.004
-181.930	12.915	12.910	-0.005
-179.369	13.153	13.154	0.001
-176.794	13.389	13.397	0.008
-174.136	13.642	13.645	0.003
-171.229	13.902	13.914	0.012
-168.224	14.172	14.187	0.015
-165.440	14.433	14.438	0.005
-162.511	14.724	14.697	-0.027
-159.170	15.001	14.990	-0.011
-156.036	15.275	15.261	-0.014
-153.159	15.498	15.508	0.010
-152.763	15.555	15.542	-0.013
-149.326	15.847	15.835	-0.012
-145.666	16.140	16.145	0.005
-141.936	16.422	16.462	0.040
-138.361	16.756	16.766	0.010
-134.850	17.070	17.067	-0.003
-131.548	17.345	17.352	0.007
-128.302	17.637	17.635	-0.002
-125.000	17.935	17.926	-0.009
-121.725	18.240	18.217	-0.023
-118.446	18.550	18.511	-0.039
-115.259	18.783	18.797	0.014
-112.228	19.027	19.070	0.043
-109.191	19.333	19.343	0.010
-106.022	19.652	19.624	-0.028
-107.719	19.466	19.474	0.008

$$\begin{aligned}
 * \text{Heat Capacity} = & -28.2972 - 0.19882149 \times 10^{-1} t - 0.29578408 \times 10^{-1} t^2 \\
 & - 0.20672040 \times 10^{-3} t^3 - 0.70838749 \times 10^{-6} t^4 \\
 & - 0.95205115 \times 10^{-9} t^5
 \end{aligned}$$

t = °C

Table 7. Polynomial Fit for the Liquid Range

Temperature °C	Heat Capacity, cal./gm. mole °C		Calc. - Observ.
	Observed	Calculated*	
-84.340	31.582	31.570	-0.012
-81.102	31.509	31.463	-0.046
-84.533	31.537	31.577	0.040
-81.321	31.474	31.470	-0.004
-77.862	31.379	31.370	-0.009
-73.656	31.264	31.269	0.005
-68.890	31.195	31.177	-0.018
-74.417	31.248	31.286	0.038
-70.907	31.203	31.213	0.010
-67.361	31.156	31.153	-0.003
-63.714	31.096	31.103	0.007
-59.898	31.073	31.064	-0.009
-55.937	31.036	31.035	-0.001
-51.929	31.026	31.018	-0.008
-47.885	31.011	31.011	0.000
-43.748	31.002	31.014	0.012
-39.342	31.032	31.028	-0.004
-34.811	31.035	31.052	0.017
-30.197	31.090	31.085	-0.005
-37.571	31.048	31.036	-0.012
-32.395	31.064	31.068	0.004
-26.864	31.111	31.114	0.003
-21.433	31.175	31.171	-0.004
-16.350	31.224	31.233	0.009
-11.286	31.307	31.304	-0.003
-6.168	31.384	31.383	-0.001
-0.988	31.493	31.473	-0.020
4.037	31.580	31.568	-0.012
8.741	31.690	31.666	-0.024
1.557	31.513	31.520	0.007
4.806	31.561	31.584	0.023
8.144	31.658	31.653	-0.005
11.296	31.713	31.723	0.010

(continued)

Table 7. Polynomial Fit for the Liquid Range
(concluded)

Temperature °C	Heat Capacity, cal./gm. mole °C		Calc. - Observ.
	Observed	Calculated*	
14.414	31.781	31.796	0.015
17.542	31.877	31.874	-0.003
20.728	31.942	31.958	0.016
23.998	32.048	32.049	0.001
27.111	32.155	32.142	-0.013

$$\begin{aligned}
 \text{* Heat Capacity} = & 31.490681 + 0.18468551 \times 10^{-1} t + 0.17348328 \times 10^{-3} t^2 \\
 & + 0.73103250 \times 10^{-6} t^3 + 0.16627775 \times 10^{-7} t^4
 \end{aligned}$$

t = °C.

APPENDIX D

VERIFICATION OF THE CONDITION OF THE CALORIMETER

When Hwa⁹ completed his measurements with the calorimeter, the last sample was left in the calorimeter. That sample contained an ethanol-methylcyclohexane mixture consisting of 53.24 mole percent ethanol, and weighed 118.58 gm. As a check on the operation of the calorimeter at the outset of the present work, the heat capacity of this sample was redetermined at three points and compared with the values that had been obtained by Hwa. Tables 8 and 9 present the results that have been obtained in this work and Hwa's values respectively. The same data are plotted in Figure 4. It can be seen that the data agree to within 0.03 cal./gm. mole °C. The elapsed time between the two sets of measurements was sixteen months.

Table 8. Heat Capacity of Ethanol-Methylcyclohexane
(This work: Run 1400)

Initial Temperature °C.	Mean Temperature °C.	Heat Capacity, C cal./gm. mole °C. ^s
17.005	18.960	36.241
20.915	22.844	36.813
24.773	26.676	37.391

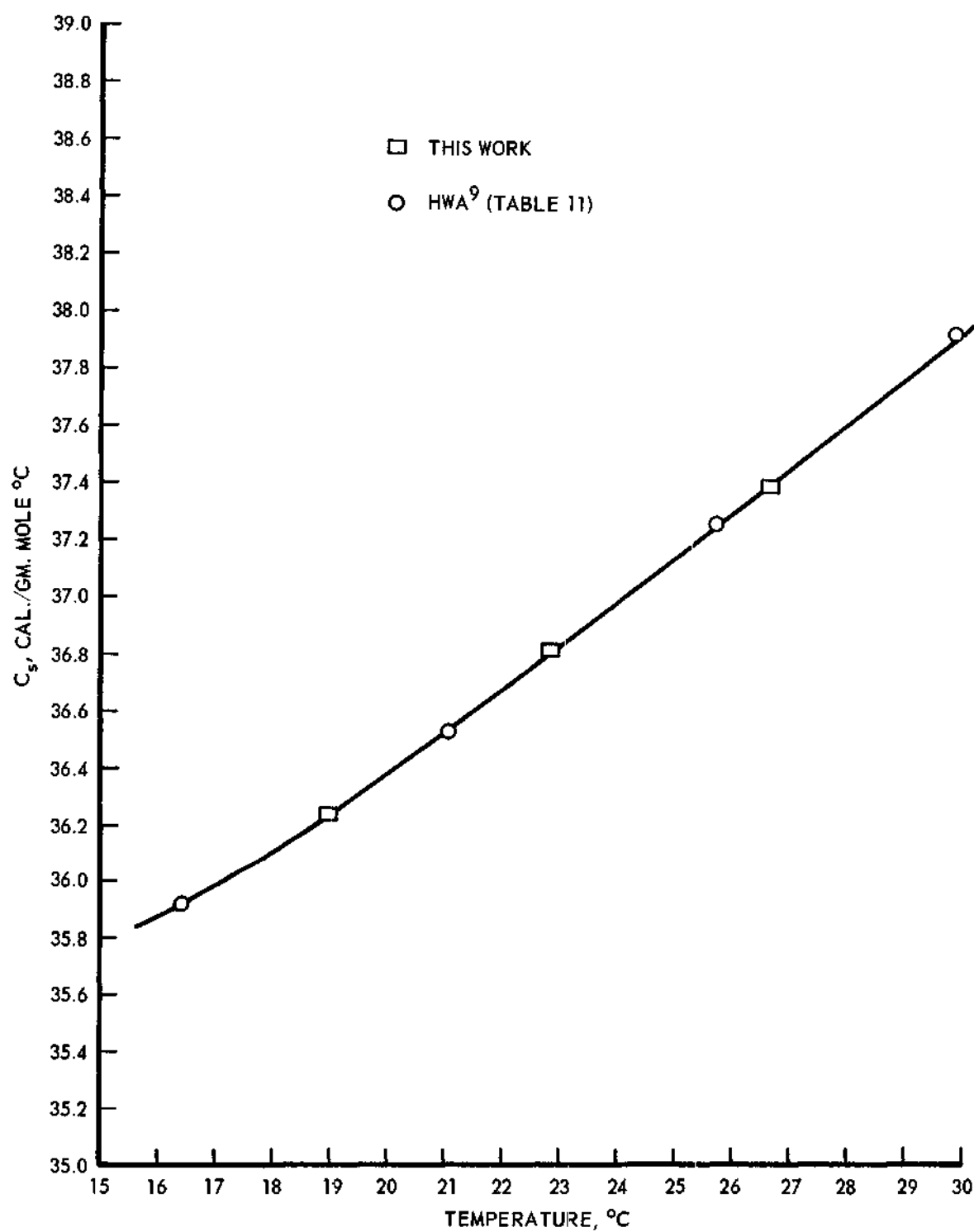


Figure 4. Heat Capacity of Ethanol-Methylcyclohexane.

Table 9. Heat Capacity of Ethanol-Methylcyclohexane
(Data of Hwa:⁹ Table 11)

Initial Temperature °C.	Mean Temperature °C.	Heat Capacity, C cal./gm. mole °C. ^s
14.061	16.412	35.920
18.763	21.059	36.533
23.354	25.726	37.254
28.099	29.915	37.909

APPENDIX E

LIQUID HEAT CAPACITY DATA OF BEARD

Beard¹ measured the heat capacity of liquid nitroethane and 1-nitropropane over a narrow range of temperatures. Table 10 presents his results for nitroethane.

Table 10. Heat Capacity of Nitroethane
(Data of Beard¹)

Temperature °C	Heat Capacity cal./gm. °C.
25*	0.441 ± 1%
35	0.437 ± 1%
45	0.437 ± 1%
50	0.438 ± 1%

* At 25° C. the value of the heat capacity as calculated from Equation 2 is 0.427 cal./gm. °C.

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* Abbreviations follow the form used by Chemical Abstracts 55, (1961).

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