MEASUREMENTS OF LIQUID HEAT CAPACITIES USING THE DU PONT MODULAR THERMAL ANALYSIS SYSTEM

By

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CHAPTER I

INTRODUCTION

The du Pont Modular Thermal Analysis System was used to measure calorimetrically heat capacities of organic liquids. The system has two types of differential scanning calorimetric cells. The cell that was designed to extend measurements to elevated pressure was used. In the measurement of liquid heat capacity, a reference pan was placed on a designated reference platform and a sample pan on a sample platform in the silver heating block of the calorimetric cell. The heat capacity of the test specimen was determined by comparing the thermal lag between sample and reference systems under "blank" condition, in which the sample pan was empty, and "sample" condition, in which liquid sample was encapsulated inside the sample pan. The du Pont Modular Thermal Analysis System enabled a continuous measurement of heat capacity over the desired temperature range. It required the use of only a small quantity of liquid sample. Since the heating rate and the sensitivity of measurement were automatically fixed by selecting the appropriate switches and buttons on the equipment, the accuracy of the result should depend on the accuracy of weighing samples and accuracy of measuring displacement representing the thermal lag between the "blank" and "sample" conditions on chart paper. The du Pont Modular Thermal Analysis System was tested under different experimental conditions, using air and nitrogen atmospheres in the calorimetric cell. Heat capacities of liquids with low vapor pressure and high vapor pressure were measured. For each compound, the temperature range selected was from the melting point to the boiling point of the particular compound. The results of measurements were used to evaluate the consistency and reproducibility of the du Pont Modular Thermal Analysis System.

The study of two recently proposed correlations for predicting saturated liquid heat capacities and a literature survey on experimentally determined liquid heat capacities are also included in this paper. Three new methods proposed by Tyagi (3) and the reversing of a correlation for thermal conductivity proposed by Narasimhan et al. (1) were tested with selected hydrocarbons. Mistakes found in the original Tyagi paper were corrected and the correct equations were used. Calculated results were compared to literature values so conclusion could be made if the proposed correlations were suitable for predicting heat capacities. These studies are presented in Appendix B and Appendix C.

A literature survey on experimentally determined liquid heat capacities is presented in Appendix D. In this survey, no evaluation of data was made, but every compound encountered in each article studied was listed and classified. Experimental conditions, the amount of data presented, the method of presentation and the source of data are tabulated along with each compound. The resulting table serves as a quick review of the experimental liquid heat capacity data in the articles studied.

CHAPTER II

DESCRIPTION OF EQUIPMENT (4)

The du Pont Modular Thermal Analysis System used for the measurement of liquid heat capacities consisted of a 990 thermal analyzer (serial number 4-001554), a pressure differential scanning cell or simply pressure DSC cell (serial number 00289) and a cell base module II (serial number 00436). A diagram of the system is shown in Figure 1.

The 990 thermal analyzer, as shown in Figure 2, was the basic console of the System. The analyzer had two complete and independent function units, a temperature programmer-controller and a two pen option X-Y-Y' recorder. Temperature of the sample under analysis was controlled by the programmer-controller and variances in the sample properties, energy absorption or release were read on the vertical Y or Y' axis as a function of sample temperature on the horizontal X-axis of the recorder.

The cell base module II, shown in Figure 3, was used to support the pressure DSC cell and was operated by the 990 thermal analyzer through an interconnecting cable. The cell base module II housed the electronic reference junction, compensation circuits for the sample and control thermocouples used, and the differential temprature amplifier. With the CELL switch at the appropriate position, the cell base automatically selected the proper reference junction circuit, the proper linearization circuit for heating rate and adjusted the gain of the

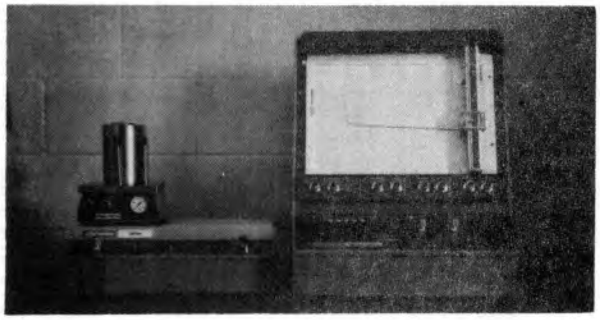

Figure 1. The du Pont Modular Thermal Analysis System

Figure 2. The 990 Thermal Analyser

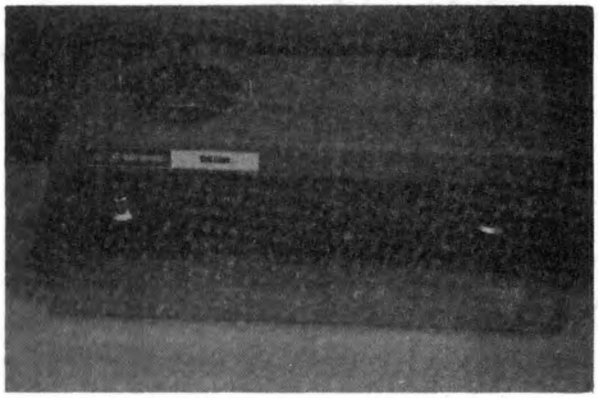

Figure 3. The Cell Base Module II

differential temperature amplifier in order to have the Y-axis and Y'-axis on the thermal analyzer read directly in the units of measurement. The cell base module II featured electronic linearization of the calibration coefficient. While this coefficient was nominally 1.0, the value should be determined for the particular differential scanning calorimetric cell. The calibration coefficient varied with the gas atmosphere and pressure used in the cell, therefore a new value had to be determined when experimental conditions were changed.

The du Pont pressure DSC cell, shown in Figure 4, was a plug-in module for the 990 thermal analyzer. The cell was designed to extend calorimetric measurements to elevated pressure as high as 1000 psig and to reduced pressure as low as approximately 10 microns. The cell temperature was controlled by using a sliver heating block, a resistant wound heater and a closely-couple Platinel II control thermocouples. The block temperature was monitored by the control thermocouple. The appropriate amount of power was supplied to the heater as determined by the difference signal between the control thermocouple and the output of the 990 programmer. A constantan disc was used as the primary means of heat transfer to the sample and reference platforms inside the block. Temperatures at the raised sample and reference platforms were monitored by chromel-constantan thermocouples formed by the junction of the constantan disc with a chromel wire centered on each platform. The difference signal between these two thermocouple junctions, Δq, was fed to the amplifier in the cell base module II and then monitored on the Y-axis and Y'-axis of the 990 X-Y-Y' recorder. The sample platform also had an alumel lead wire forming a chromel-alumel thermocouple junction. The output from this thermocouple was monitored on the temperature axis,

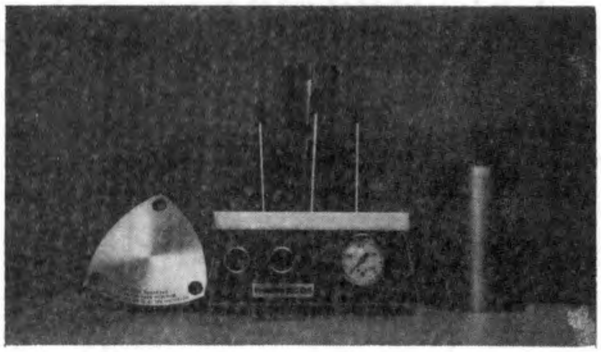

Figure 4. The Differential Scanning Calorimetric Pressure Cell

or X-axis of the 990 X-Y-Y' recorder after suitable cold junction compensation. The sample temperature was measured with this chromel-alumel thermocouple.

The du Pont sample encapsulating press (serial number 01159), shown in Figure 5, was a press with interchangable dies used for crimping the non-hermetic aluminum pans and for sealing hermetic containers. The press consisted of a base platform and a column, an adjustable lower die holder, a locking thumb nut for locking the lower die in position, and a movable upper die connected to a lever arm. The upper die was lowered by pulling the cam-mounted lever forward. Since the cam was mounted eccentrically, maximum pressure was exerted on the sample pan. The lower die was screw-mounted and could be adjusted in the vertical direction and then locked in place with the thumb nut positioned on the column.

There were two types of pans used, the regular non-hermetic aluminum pans and the hermetic pans as shown in Figure 6. The regular non-hermetic aluminum pans provided better thermal contact between the sample and the pan but were only used for non-volatile materials because the crimping was insufficient and poor in preventing vaporization of volatile compounds. The non-hermetic pans were used in the measurement of the calibration coefficient of the calorimetric cell. Three kinds of hermetic pans were used, the uncoated aluminum hermetic pans, the coated aluminum hermetic pans and the gold hermetic pans. For the measurement of heat capacities of liquid compounds, the hermetic pans were used because they were designed for the studies on volatile substances.

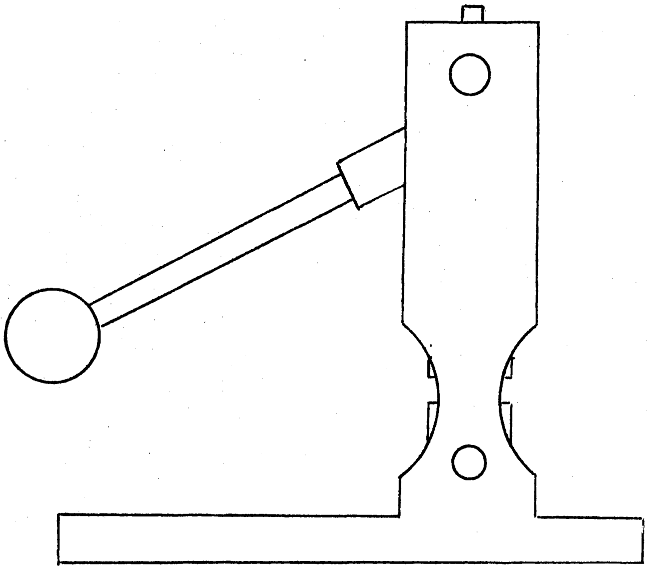

Figure 5. The Encapsulating Press

a. Non-Hermetic Pan

b. Hermetic Pan

Figure 6. Pans Used in the Measurements

CHAPTER III

EXPERIMENTAL PROCEDURE

The calibration coefficient was determined before measurements of heat capacities of liquid samples were made. The same experimental conditions were kept in both cases. The heating rate was kept constant at an appropriate rate in all measurements. The sensitivity range was fixed between blank run and sample run. To provide improved thermal contact with the differential thermocouple, Dow Corning #340 silicone heat sink compound was spread lightly on the sample and reference platforms, and aluminum discs of 1/4 inch diameter were affixed to the platforms to support the pans.

Measurement of the Calibration Coefficient

A weighed, empty, crimped non-hermetic aluminum pan and cover was placed on the reference platform and a similar pan and cover which were not crimped but whose weight was within 1% of the weight of the reference pan was placed on the sample platform. The silver lid of the pressure DSC cell block and the cover assembly were replaced. The starting temperature dial and the limit temperature dial were set so the temperature range of interest was covered. When the starting temperature was above ambient, the system was allowed to come to equilibrium at that temperature by depressing the Isothermal button on the 990 thermal analyzer. When the starting temperature was below ambient, the system was cooled to some temperature well below that temperature by using liquid nitrogen in the quench cooling can, and the temperature of the system was allowed to increase to the starting temperature. In either case, the Heat button on the 990 thermal analyzer was depressed when the starting temperature was reached. The system was heated at the selected rate until the limit temperature was reached when the system was allowed to cool to room temperature. A blank run was made. The same procedure was repeated in the sample run but with a weighed sapphire disc inside the crimped sample pan. A cathetometer was used to place the sample pan at the original position on the platform.

Measurements of the Heat Capacities of Liquids

The blank run was made as described in the calibration except that hermetic pans and lids were used on both reference and sample platforms. In the sample run, about one drop of liquid sample, equivalent to a weight less than 10 milligrams, was placed at the bottom of the hermetic pan using a syringe and the pan was sealed. The procedure of heating was repeated. The sample was weighed before and after the measurement. If loss of liquid sample occurred, the run was discarded and a new measurement on a new sample was made.

Under Different Experimental Conditions

For measurements at high pressure, the pressure cover assembly was put on and secured tightly by the knurled bolts. The pressure DSC cell was then pressurized through the IN valve. With starting temperature above ambient, the Isothermal button was depressed after the cell was pressurized. With starting temperature below ambient, the cell was cooled before being pressurized.

When a nitrogen atmosphere was wanted, the pressure cover assembly was put on and secured tightly by the knurled bolts. The cell was evacuated through the COOL control valve and nitrogen gas was introduced through the IN valve. This procedure was repeated several times to expel all the air. The nitrogen gas was then bled to atmospheric pressure. For starting temperature above ambient, the Isothermal button was depressed after the nitrogen gas was introduced. For starting temperature below ambient, the cell had to be cooled first.

Method of Calculation

The calibration coefficient was calculated by:

$$E = \frac{C_p \times H_r \times M}{60 \times \Delta q \times \Delta Y} \qquad (3\text{-}1)$$

where

C_p = heat capacity of the sapphire at the particular temperature, mcal/mg °C

E = calibration coefficient at the particular temperature

H_r = heating rate, °C/min.

M = mass of the sapphire disc, mg.

Δq = Y-axis sensitivity range, (mcal/sec)/in.

ΔY = difference in Y-axis deflection between sample and blank curves at temperature of interest, inch

To calculate the heat capacity of a liquid sample, equation (3-1) was arranged to

$$C_p = \frac{60 \times \Delta q \times \Delta Y}{H_r \times M} \tag{3-2}$$

where

C_p = heat capacity of the liquid sample, cal/gm °C

M = mass of the liquid sample

Since the coefficient E was determined at the temperature of interest, liquid heat capacity at the same temperature could be computed from equation (3-2).

Chemicals Used in the Evaluation

The organic compounds whose heat capacities were determined are listed in Table I. The results of the measurements were used to evaluate the du Pont Modular Thermal Analysis System.

TABLE I

LIST OF CHEMICALS USED IN THE MEASUREMENTS

n-Pentane	99 mole percent minimum pure grade by Phillips Petroleum Company.
n-Octane	99 mole percent minimum pure grade by Phillips Petroleum Company.
n-Nonane	99 mole percent minimum pure grade by Phillips Petroleum Company.
n-Decane	99.55 mole percent research grade by Phillips Petroleum Company.
Benzene	99 mole percent minimum pure grade by Phillips Petroleum Company.
Toluene	Certified A.C.S. by Fisher Scientific Company
Silicone oil	SF 1154 methyl phenyl silicone fluid by General Electric Silicone Products Department.

CHAPTER IV

EXPERIMENTAL RESULTS

The values of the calibration coefficient, using non-hermetic reference and sample pans and under the same experimental conditions, almost varied from measurement to measurement. Different gas atmosphere used in the pressure DSC cell did not give consistent values. The calibration coefficients measured under nitrogen atmosphere and under air atmosphere are shown in Figure 7 and Figure 8. In making each of the runs shown in the figures, new pans were used. Since the values measured were scattered, the effect of using different reference and sample pans was studied. Several sets of reference and sample pans were chosen. For each set of pans, one blank run was made but several repeated measurements were made in the sample run. Results showed that although data obtained from a particular set of reference and sample pans were reproducible, different sets of pans gave different calibration coefficients. The measured values are tabulated in Table II.

Another method was attempted to determine the calibration coefficient. The sapphire was crimped inside a sample pan and this pan was used in all measurements. In making blank runs, a pan having the same weight as the sample pan was used. Results of measurements are shown in Table III. The calibration coefficients were again found to be inconsistent.

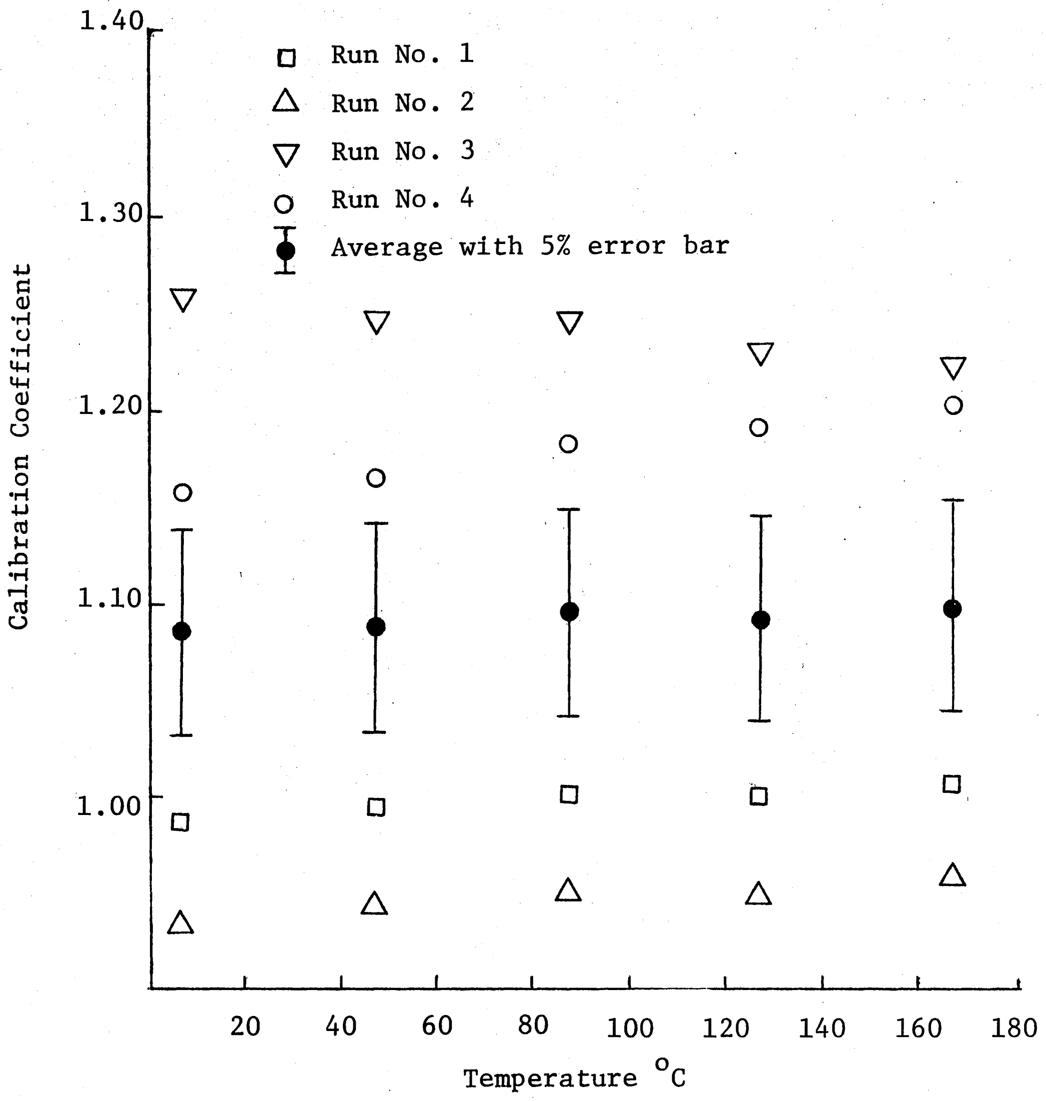

Figure 7. Calibration Measurement Using Non-Hermetic Aluminum Reference and Sample Pans Under Nitrogen Atmosphere

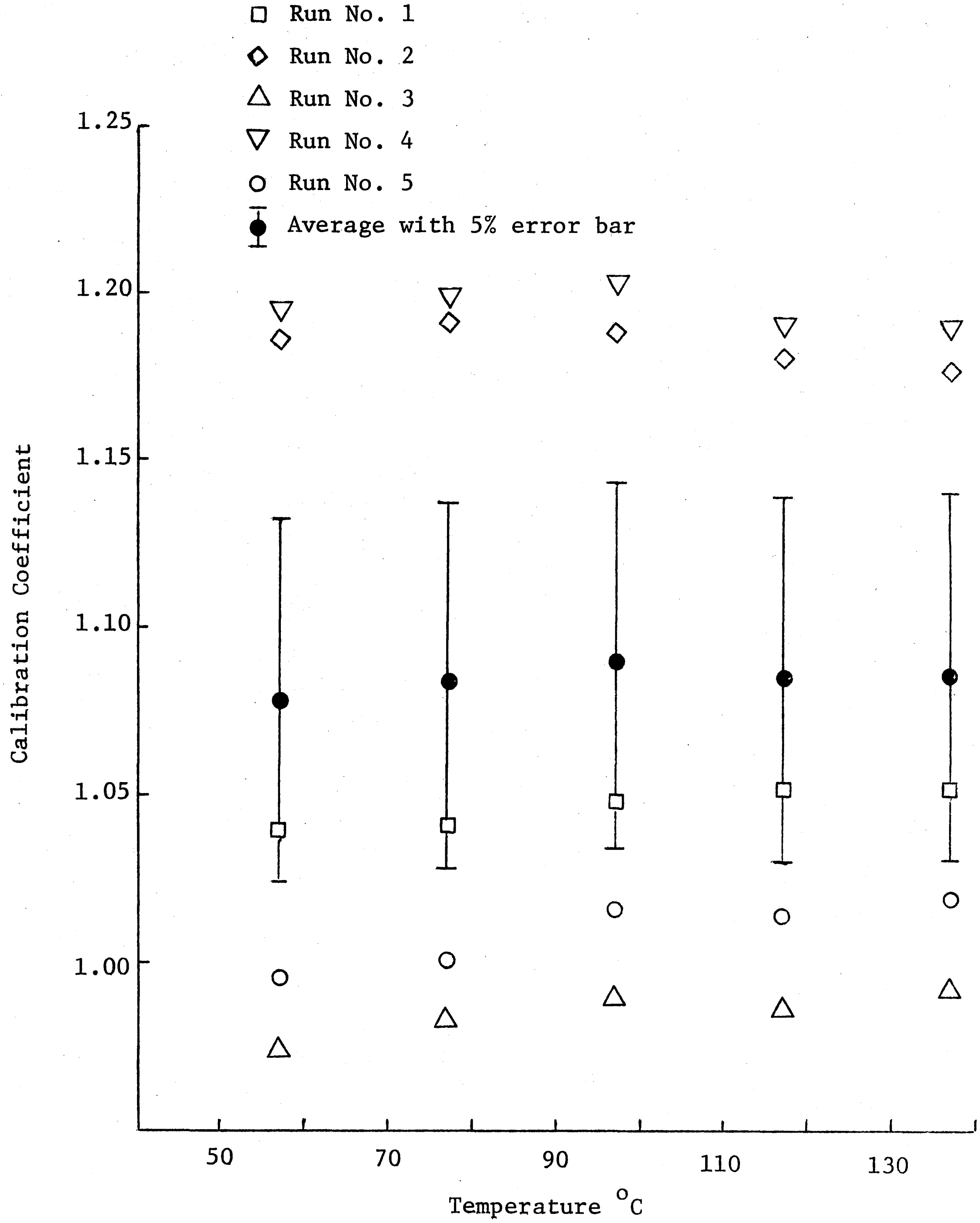

Figure 8. Calibration Measurement Using Non-Hermetic Aluminum Reference and Sample Pans Under Air Atmosphere

TABLE II

COMPARISON OF CALIBRATION COEFFICIENT OBTAINED FROM USING DIFFERENT SETS OF REFERENCE AND SAMPLE PANS

Temperature °C	E_1	E_2	E_3
57	1.101	1.0755	0.9955
77	1.101	1.0823	1.0032
97	1.107	1.0799	1.0182
107	1.109	1.0816	1.0162
117	1.103	1.0761	1.0152
137	1.104	1.0800	1.0181

TABLE III

COMPARISON OF CALIBRATION COEFFICIENT OBTAINED FROM USING THE SAME SAMPLE PAN CONTAINING THE SAPPHIRE IN DIFFERENT MEASUREMENTS

Temperature °C	E_1	E_2
137	1.0562	1.1149
167	1.0662	1.1163
197	1.0557	1.1046
227	1.0596	1.1134
257	1.0582	1.1119

Since consistent values of the calibration coefficient could not be obtained using non-hermetic reference and sample pans, a slight change was made in the procedure. In the determination of the coefficient, the sample pan that contained the sapphire was still a non-hermetic pan, but the reference pan was a sealed hermetic pan. A new sample pan was used in making each run but the same sealed hermetic reference pan was used in all measurements, also in the measurements of liquid heat capacities. Results are shown in Figure 9. The change of reference pan was found to make little improvement in the scattered values of the calibration coefficient. In the calculation of heat capacities of the liquid compounds, the calibration coefficient at a particular temperature was read from a curve drawn through the data points obtained.

The measurements of the heat capacities of the organic liquids chosen were made in a nitrogen atmosphere so that the effect of moisture in the air could be eliminated. For almost all of the liquid compounds measured, consecutive measurements made on different samples of the same compound produced considerably different heat capacity values. For each organic liquid compound, two samples were made and measured. The results are shown in Figures 10, 11, 12, 13, 14 and 15 for n-pentane, n-octane, n-nonane, n-decane, benzene and toluene. Literature values with ten percent error bar are also shown in the figures for comparison (2). The measured heat capacities showed that the results were not consistent.

Since the data obtained were scattered, the reproducibility and consistency of the equipment were tested by making repeated runs on the same sample of a liquid compound. For comparison, a volatile liquid of toluene and a non-volatile liquid of silicone oil were used. Air atmosphere was used in the pressure DSC cell so that the possibility of

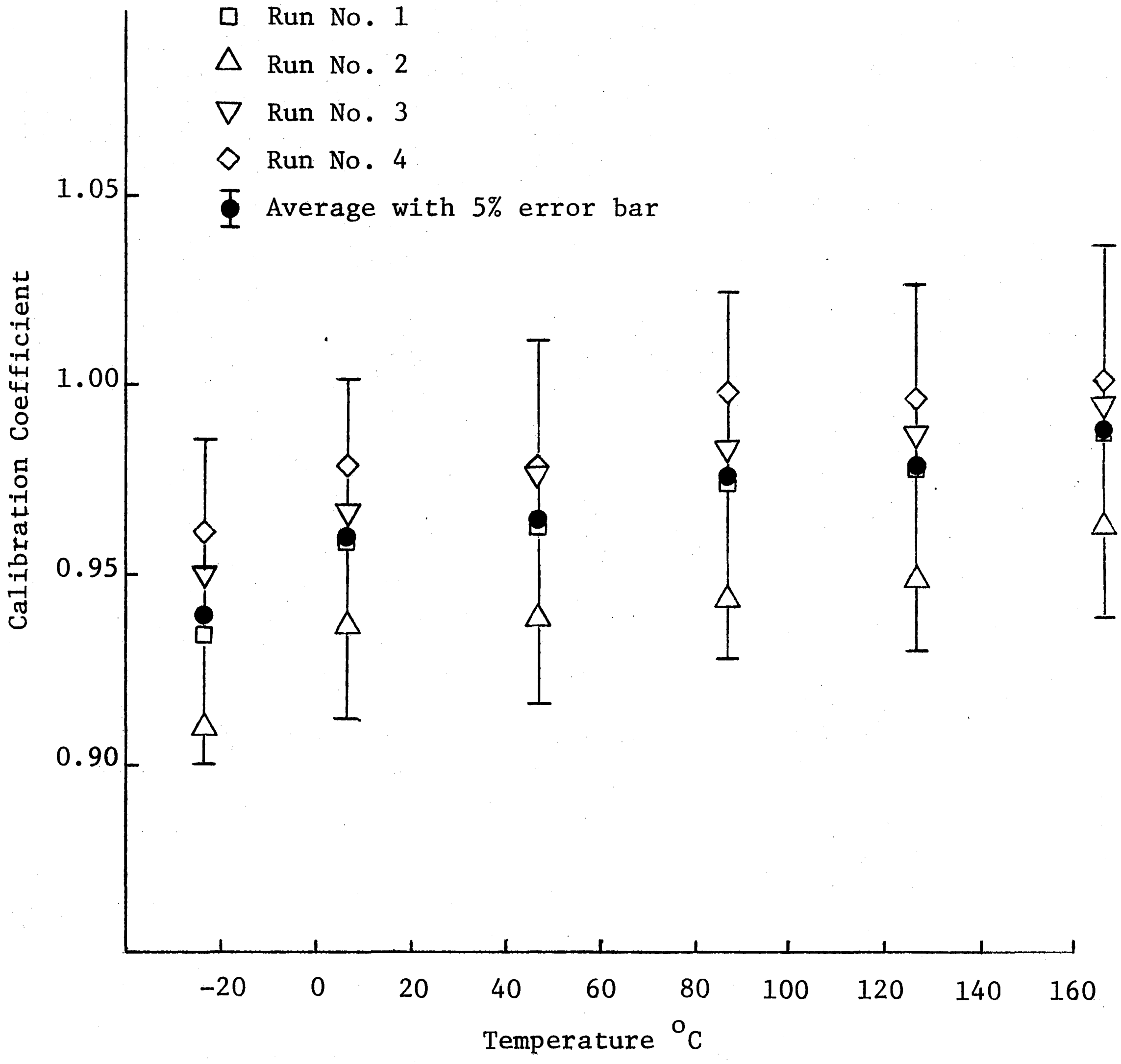

Figure 9. Calibration Measurement Using Sealed Gold Hermetic Pan Under Nitrogen Atmosphere

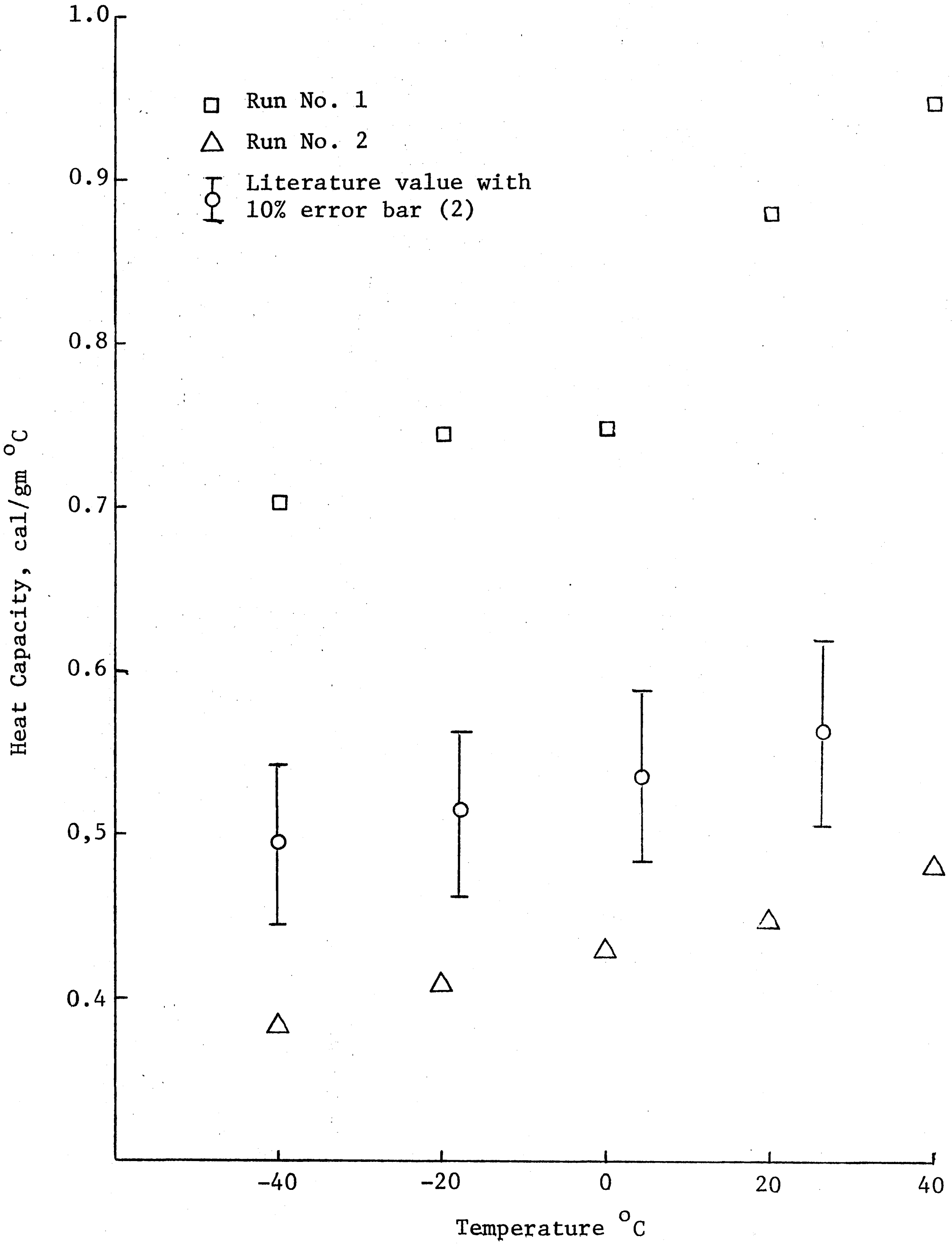

Figure 10. Measured Heat Capacity of n-Pentane

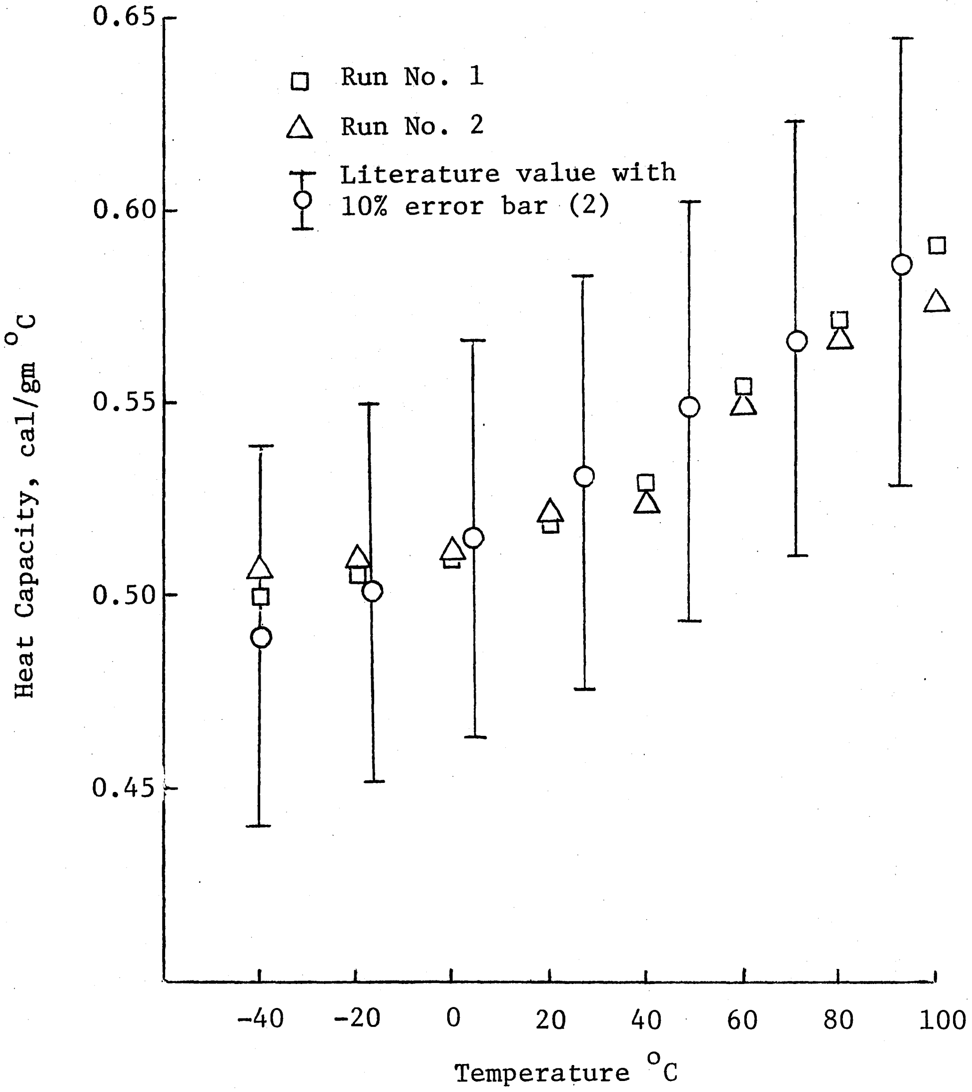

Figure 11. Measured Heat Capacity of n-Octane

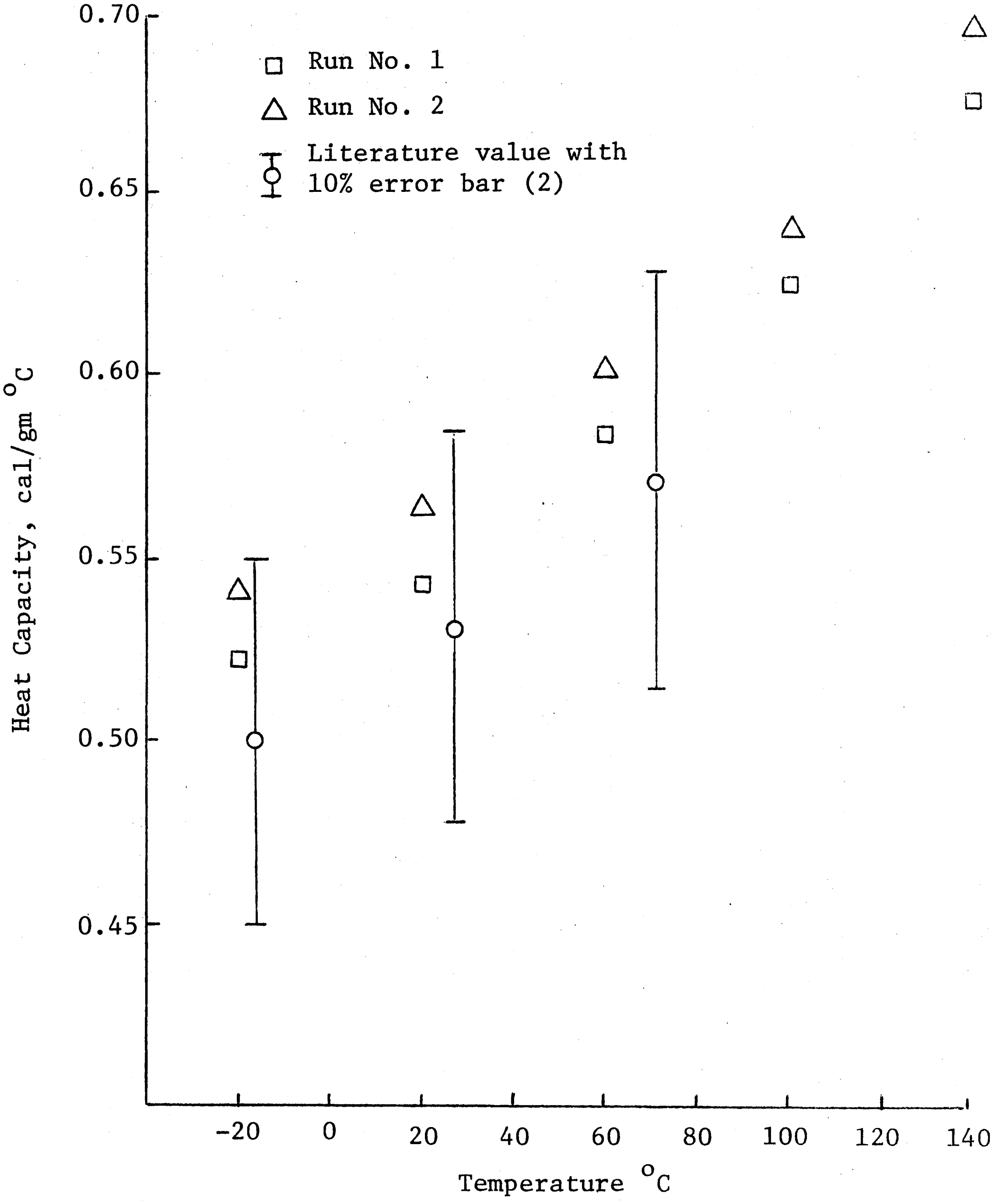

Figure 12. Measured Heat Capacity of n-Nonane

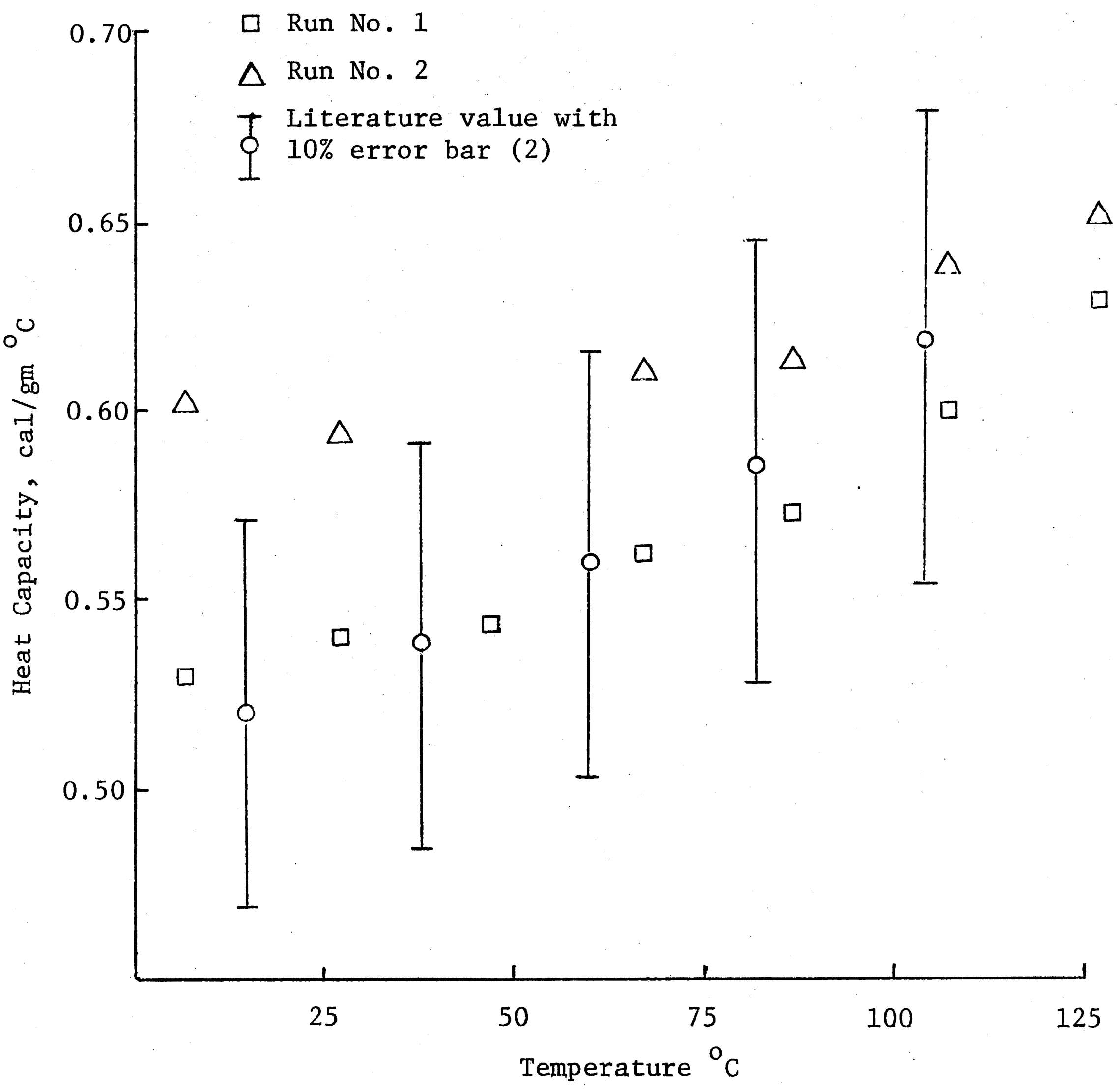

Figure 13. Measured Heat Capacity of n-Decane

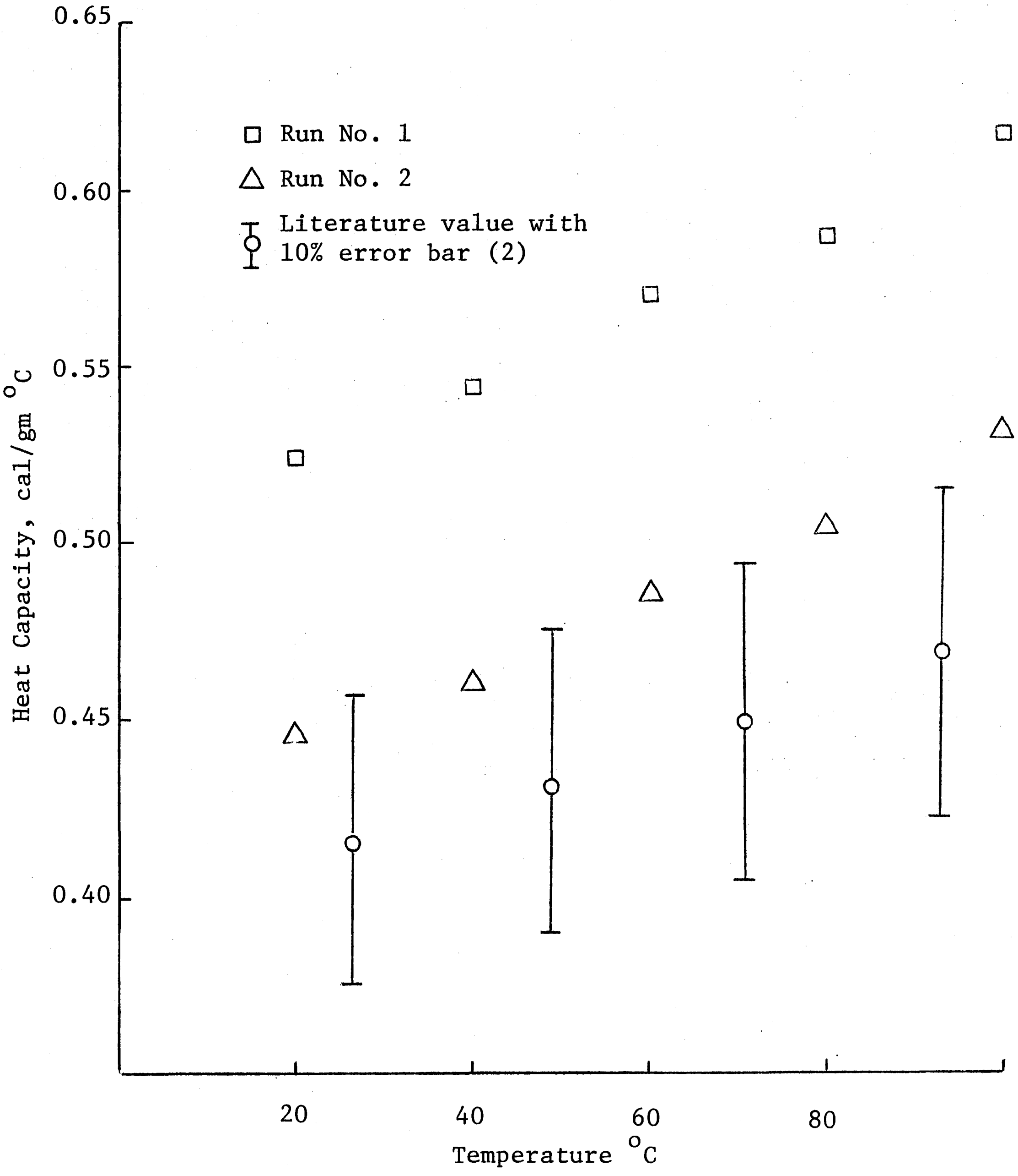

Figure 14. Measured Heat Capacity of Benzene

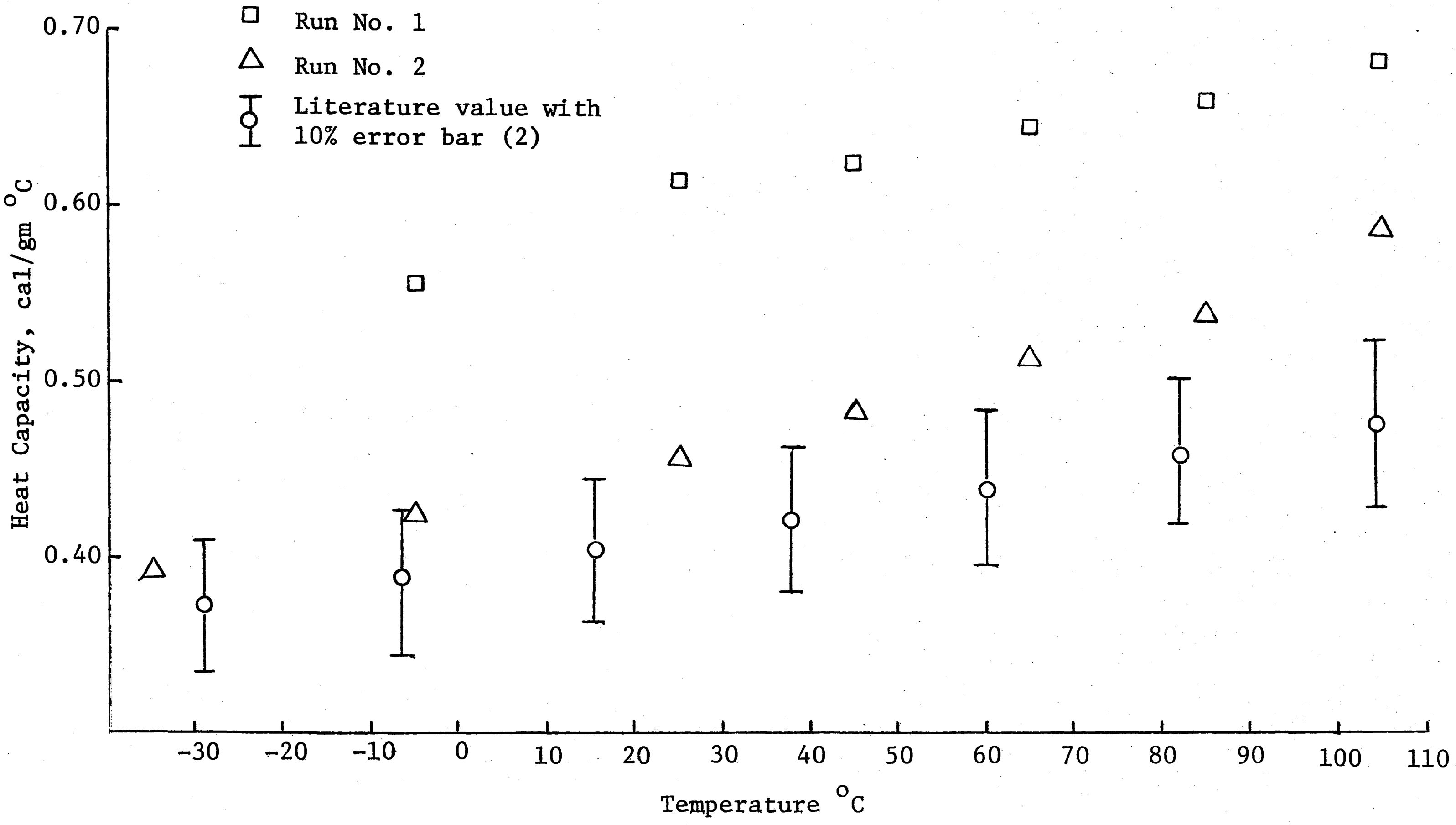

Figure 15. Measured Heat Capacity of Toluene

jarring the pans when nitrogen gas was introduced and when the pressure cover assembly was put on could be avoided. A calibration run was made using non-hermetic aluminum pans. In both measurements of the calibration coefficient and heat capacities, the sample pans were chosen such that the weights were within one percent of the weight of the reference pans.

Five measurements were repeated on a sample of toluene. At the end of each measurement, the sample was weighed to check for loss of sample and then was returned to the sample platform. A cathetometer was used so that the sample pan could be placed at the original position. The results obtained from five repeated measurements are shown in Figure 16. No loss of sample occurred during the measurements, but heat capacity values for the same compound deviated more than 5% of the average value.

Two samples of silicone oil were prepared. For one of the samples, the procedure was the same as the procedure used in the toluene measurement. Results of five repeated measurements are shown in Figure 17. In order to reduce further the possibility of disturbance of the pans, the second sample of silicone oil was not touched when repeated runs were made. The sample pan was weighed only before the start of the measurement and after the completion of five repeated measurements. The results are shown in Figure 18. No loss of sample was found in the samples, but the heat capacity values varied within 5% of the average value in either case. Comparing the average heat capacity values

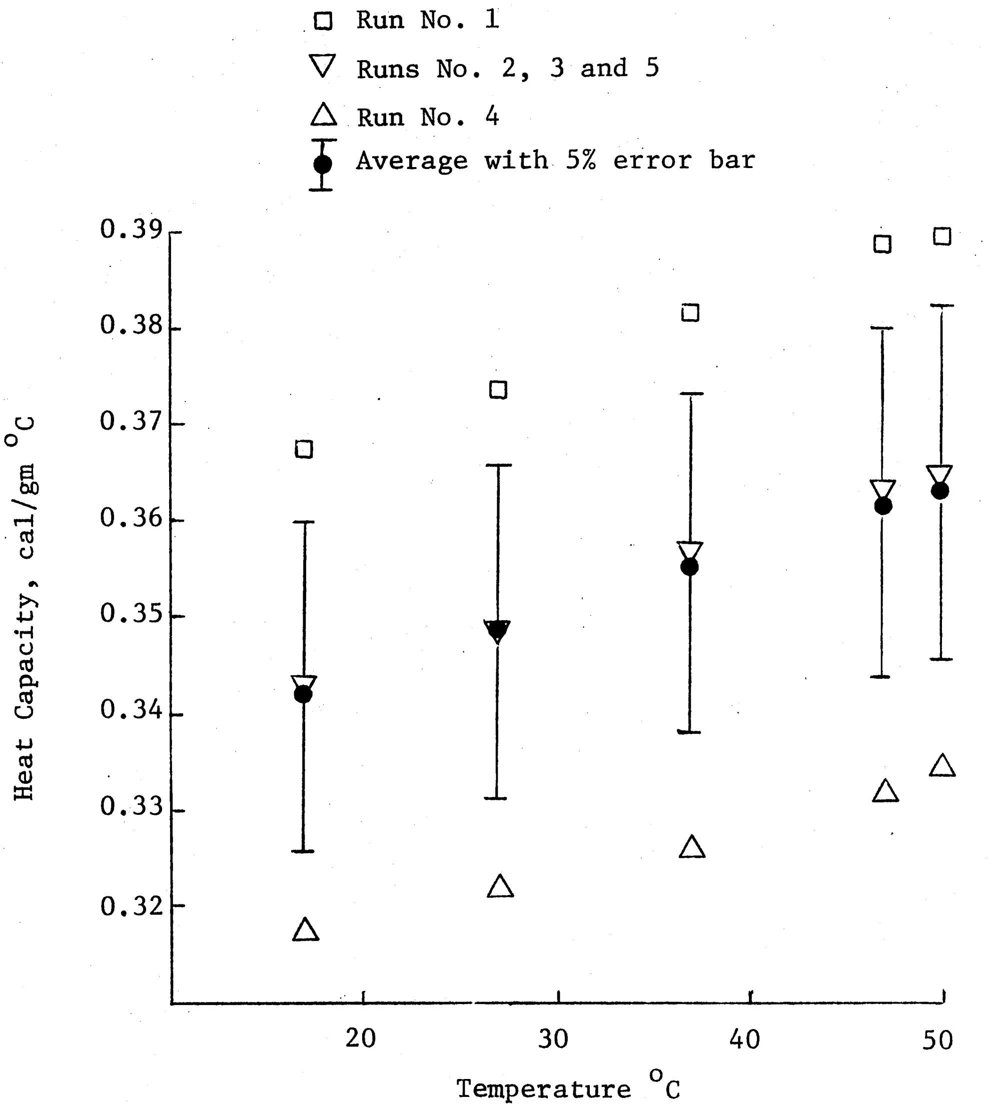

Figure 16. Five Repeated Runs on a Sample of Toluene with Weighing Between Runs

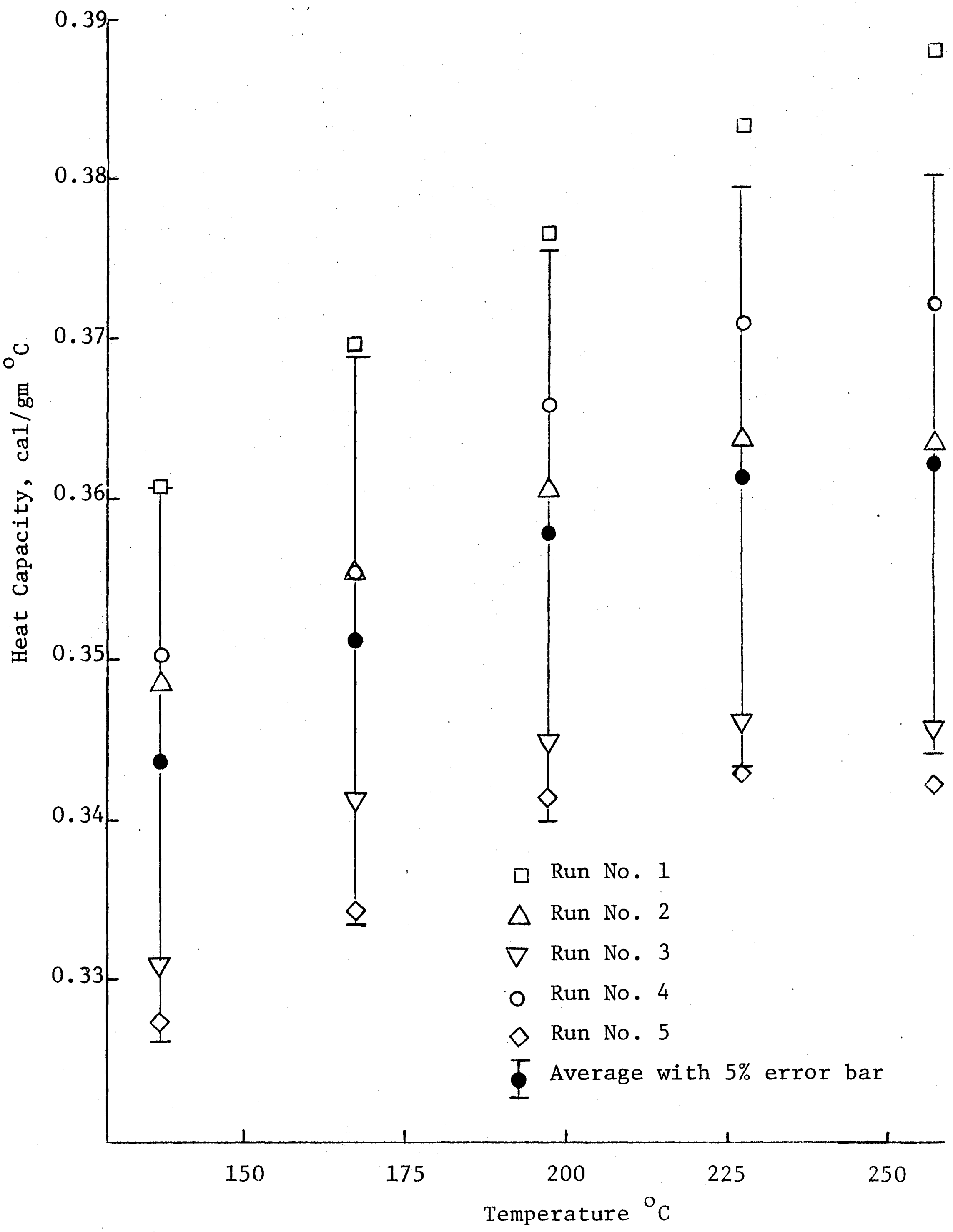

Figure 17. Five Repeated Runs on a Sample of Silicone Oil with Weighing Between Runs

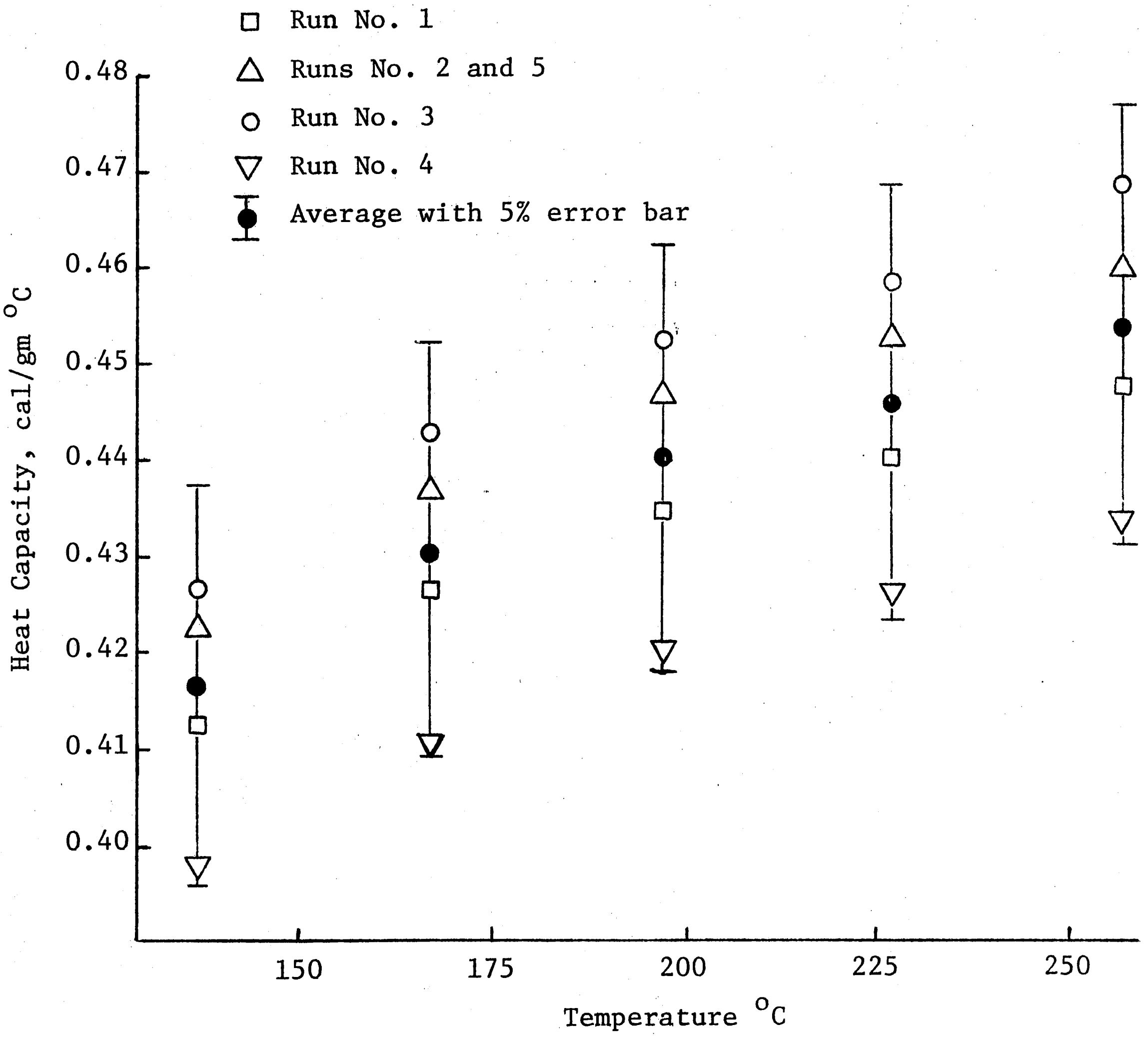

Figure 18. Five Repeated Runs on a Sample of Silicone Oil Without Weighing Between Runs

of the two samples of silicone oil, two distinct and different values were observed.

Though the results of repeated blank runs were found to reproduce exactly, the results of the repeated sample runs show that for either volatile or non-volatile liquids, the reproducibility of results were poor and consistent heat capacity values not obtained.

Measurement of heat capacity at high pressure was attempted but no sample was measured after a hermetic reference pan was found collapsed under a high pressure of 1000 psig.

CHAPTER V

CONCLUSIONS

Results of measurements using the du Pont Modular Thermal Analysis System showed that consistent values could not be obtained. This was true for both volatile and non-volatile compounds. Consecutive measurements usually produced two different values. For solid compound like sapphire, results were reproducible using the same sample, but values obtained from using different samples were different. The heat capacity data of the organic liquids measured were inconsistent, seldom reproducible and disagreed with literature values. The same unsatisfactory results remained even in the absence of disturbance and in the absence of the possibility of vaporization of liquid sample as in the measurement of the non-volatile silicone oil. Based on the above facts, the du Pont Modular Thermal Analysis System with the differential scanning calorimetric pressure cell was not able to measure heat capacities of liquids satisfactorily.

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APPENDIX A

SAMPLE CALCULATIONS

Calculation of the Calibration Coefficient E

Instrument Parameters:

1. Cell Base Module II

   CELL -- BSC

   MODE -- DSC CALIBRATED

2. 990 Thermal Analyzer

   Y' range, Δq -- 0.5 (mcal/sec)/in.

   Heating rate -- 10 °C/min.

   Atmosphere -- Air at atmosphere pressure

   Temperature -- Starting +2 °C, Limit +65 °C.

Mass of sapphire disc = 52.85 mg.

Displacement ΔY at 50 °C = 3.183 in.

C_p, heat capacity of sapphire at 50 °C = 0.19707 mcal/mg °C

$$E = \frac{C_p \times H_r \times M}{60 \times \Delta q \times \Delta Y}$$

$$= \frac{0.19707 \times 10 \times 52.85}{60 \times 0.5 \times 3.183}$$

$$= 1.0907$$

Calculation of the Heat Capacity of Toluene

Instrument Parameters:

1. Cell Base Module II

   CELL -- DSC

   MODE -- DSC CALIBRATED

2. 990 Thermal Analyzer

   Y' range, Δq -- 0.1 (mcal/sec)/in.

   Heating rate -- 10 ^{o}C.min.

   Atmosphere -- Air at atmosphere pressure

   Temperature -- Starting +2 ^{o}C, Limit +65 ^{o}C.

Mass of sample pan = 58.61 mg.

Mass of sample pan + toluene = 61.91 mg.

Mass of toluene, M = 3.30 mg.

Calibration coefficient E at 50 ^{o}C = 1.0907

Displacement ΔY of toluene at 50 ^{o}C = 1.783 in.

$$C_p = \frac{E \times 60 \times \Delta q \times \Delta Y}{H_r \times M}$$

$$= \frac{1.0907 \times 60 \times 0.1 \times 1.783}{10 \times 3.30} \qquad \text{mcal/mg } ^{o}\text{C}$$

$$= 0.3536 \text{ cal/gm } ^{o}\text{C}$$

APPENDIX B

EVALUATION OF THREE NEW METHODS FOR THE ESTIMATION OF SATURATED LIQUID HEAT CAPACITIES

There are many correlations for estimating liquid heat capacities. Three new methods have been suggested by K. P. Tyagi (13). In the proposed methods, the equation derived by Reid and Sobel (7) was modified and the enthalpy correlations by Lee and Edmister (4) and Stevens and Thodos (11) were used in the modification. The new methods have the advantage that graphical computation may be avoided and they present a simple straight forward calculation. The only quantities required are the critical constants and the density of the particular compounds of interest. Tyagi (13) tested the new methods with 31 organic liquids and the percentage deviation was calculated to be less than 2%. Investigation showed the equations of method 1 and method 2 in the paper were incorrectly derived. The three methods were studied with the derivation of the corrected formulae included in the corresponding methods. The methods were tested for some common organic liquids to check if the same accuracy could be obtained. The incorrect equations presented in the paper had also been used and the results were compared to results obtained using the correct formulae.

The heat capacity at constant pressure is a temperature derivative of enthalpy and is a point function. From a simple thermodynamic cycle, Reid and Sobel (7) obtained the following expression

$$\frac{d}{dT} H_{sl} = C_p^o - \frac{d\lambda}{dT} - \frac{d}{dT} (H^o - H_{sv}) \tag{B-1}$$

There are three terms of liquid phase heat capacities that are generally used. C_{PL} represents the change in enthalpy with temperature at constant pressure; C_{sL} is the change in enthalpy of the saturated liquid with temperature and the $(dQ/dT)_{sL}$ represents the heat that is necessary to effect a temperature change if the liquid is held in a saturated state. Except near the critical point, all three forms are in close agreement. The third term $(dQ/dT)_{sL}$ is the one usually measured in the laboratory. The relation among the three terms is given by (7)

$$\begin{aligned} \frac{d}{dT} H_{sL} &= C_{sL} = C_{pL} + [V_{sL} - T (\frac{\partial V}{\partial T})_p] (\frac{dP}{dT})_{sL} \\ &= (\frac{dQ}{dT})_{sL} + V_{sL} (\frac{dP}{dT})_{sL} \end{aligned} \tag{B-2}$$

From equations (B-1) and (B-2)

$$\begin{aligned} (\frac{dQ}{dT})_{sL} &= C'_{sL} = C_p^o - \frac{d\lambda}{dT} - \frac{1}{T_c} [\frac{\partial}{\partial T_r} (H^o - H_{sv})]_{P_r} \\ &- \frac{1}{T_c} [\frac{\partial}{\partial P_r} (H^o - H_{sv})]_{T_r} - V_{sL} (\frac{dP}{dT})_{sL} \end{aligned} \tag{B-3}$$

In evaluating the terms on the right hand side of equation (B-3), Lydersen, Greenkorn and Hougen's (5) tabulated values of enthalpy deviation, the Klein (3) correlation for enthalpy of vaporization, Watson's (14) temperature function, Clapeyron equation for vapor pressure, the equation of state, PV = ZRT, and the saturated liquid density were used by Reid and Sobel (7) to obtain

$$C'_{sL} = C_p^o + \phi_o \left[\frac{\phi_1}{\phi_o} - \phi_2 + \phi_4 \left(\frac{P_{vpr}}{\Delta Z_v}\right) \left(\phi_3 + \frac{RZ_c}{\rho_{sLr}} \right)\right] \qquad \text{(B-4)}$$

where

$$\phi_o = \ln P_{vr} \left(1 - \frac{P_{br}}{T_{br}^3}\right)^{1/2}$$

$$\phi_1 = -\left[\frac{\partial}{T_c \, \partial T_r} (H^o - H_{sv})\right]_{P_r}$$

$$\phi_2 = \frac{(0.38)\ (1.04)\ R\ T_{br}\ (1 - T_r)^{-0.62}}{(1 - T_{br})^{1.38}}$$

$$\phi_3 = \left[\frac{\partial}{T_c \, \partial P_r} (H^o - H_{sv})\right]_{T_r}$$

$$\phi_4 = \frac{(1.04)\ T_{br}\ (1 - T_r)^{0.38}}{(1 - T_{br})^{1.38}\ T_r^2}$$

Equation (B-1) can also be reduced to

$$C_{sL} = C_p^o - \frac{d}{dT} (H^o - H_{sv} + \lambda)$$

$$= C_p^o - \frac{d}{dT} (H^o - H_{sl})$$

or

$$C_{sL} = C_p^o + \frac{d}{dT} (H_{sl} - H^o) \qquad \text{(B-5)}$$

Equation (B-4) and B-5) were the basic equations that were used by Tyagi (13) in the estimation of the saturated liquid heat capacities. In all the methods, the ideal heat capacity C_p^o was calculated by Rihani and Daraiswamy's (10) group contribution method. The equation used was

$$C_p^o = a + bT + cT^2 + dT^3 \qquad \text{(B-6)}$$

All the critical constants were found in Reid and Sherwood (8).

Method 1

Equation (B-5) was the starting equation. Lee and Edmister's (4) enthalpy expression was used to evaluate the term $\frac{d}{dT}(H_{sl} - H^o)$. The enthalpy expression

$$\frac{H_{sl} - H^o}{RT_c} = A_2 - A_3T_r - 2A_4T_r^3 - 6A_5T_r^7 + (A_6 - A_7T_r - 2A_8T_r^3)\,P_r - 3A_9T_r^4P_r^2 + \omega(A_{10}T_r^2 + A_{11} + A_{12}P_r - 3A_{13}T_r^4P_r^2) \qquad \text{(B-7)}$$

was differentiated with respect to temperature

$$\frac{d}{dT}(H_{sl} - H^o) = RT_c \frac{d}{dT}\{A_2 - A_3\frac{T}{T_c} - 2A_4\left(\frac{T}{T_c}\right)^3 - 6A_5\left(\frac{T}{T_c}\right)^7 + [A_6 - A_7\left(\frac{T}{T_c}\right) - 2A_8\left(\frac{T}{T_c}\right)^3]P_r - 3A_9\left(\frac{T}{T_c}\right)^4 P_r^2 + \omega\,[A_{10}\left(\frac{T}{T_c}\right)^2 + A_{11} + A_{12}P_r - 3A_{13}\left(\frac{T}{T_c}\right)^4 P_r^2]\}$$

$$= R \{-A_3 - 6A_4 (\frac{T}{T_c})^2 - 42A_5 (\frac{T}{T_c})^6$$

$$+ [-A_7 - 6A_8 (\frac{T}{T_c})^2]P_r - 12A_9 (\frac{T}{T_c})^3 P_r^2$$

$$+ \omega [2A_{10} (\frac{T}{T_c}) - 12A_{13} (\frac{T}{T_c})^3 P_r^2]\}$$

or

$$\frac{d}{dT} (H_{sl} - H^o) = R [-A_3 - 6A_4 T_r^2 - 42A_5 T_r^6 + (-A_7 - 6A_8 T_r^2) P_r - 12A_9 T_r^3 P_r^2 + \omega (2A_{10} T_r - 12A_{13} T_r^3 P_r^2)] \quad \text{(B-8)}$$

The acentric factor ω was determined using Edmister's (1) method

$$\omega = \frac{3}{7} (\frac{\log P_c}{\frac{T_c}{T_B} - 1}) - 1 \quad \text{(B-9)}$$

By substituting equation (B-8) into equation (B-5), the estimated heat capacity was calculated by

$$C_{sL} = C_p^o + R [-A_3 - 6A_4 T_r^2 - 42A_5 T_r^6 + (-A_7 - 6A_8 T_r^2) P_r - 12A_9 T_r^3 P_r^2 + \omega (2A_{10} T_r - 12A_{13} T_r^3 P_r^2)] \quad \text{(B-10a)}$$

The incorrect formula given in the paper is

$$C_{sL} = C_p^o + R \{-A_3 - 6A_4 T_r^2 - 42A_5 T_r^6 + [-A_7 - 6A_8 T_r^2 - 12A_9 T_r^3 P_r^2 + \omega (2A_{10} T_r - 12A_{13} T_r^3 P_r^2)] P_r\} \tag{B-10b}$$

The results obtained using both equations (B-10a) and (B-10b) are compared in Table IV.

Method 2

Another expression for $(H_{sl} - H^o)$ was derived by Stevens and Thodos (11).

$$\frac{H^o - H_{sl}}{T_c} = 10 (\alpha - \beta T_r)^{\frac{1}{\gamma}} \tag{B-11}$$

where

$$\alpha = -317.49 + 2559.5Z_c - 5012.5Z_c^2$$

$$\beta = -335.52 + 2686.5Z_c - 5237.5Z_c^2$$

$$\gamma = 25Z_c - 2.25$$

Differentiating equation (B-11) with respect to temperature

$$\frac{d}{dT} (H^o - H_{sl}) = T_c . 10 . \frac{d}{dT} (\alpha - \beta \frac{T}{T_c})^{\frac{1}{\gamma}}$$

$$= T_c . 10 . \frac{d}{dT} (\alpha T_c - \beta T)^{\frac{1}{\gamma}} . \frac{1}{T_c^{\frac{1}{\gamma}}}$$

TABLE IV

COMPARISON BETWEEN HEAT CAPACITIES CALCULATED BY EQUATION (B-10a) AND (B-10b) VALUES IN cal/gm °C

Compound	Temp. °F	Literature Value	Using Eq (B-10a)	% Error[a]	Using Eq (B-10b)	% Error[a]
n-Butane[c]	80	0.5820	0.6055	4.04	0.5214	-10.41
	120	0.6190	0.6378	3.03	0.5474	-11.56
	160	0.6650	0.6803	2.30	0.5837	-12.22
n-Heptane[c]	80	0.5373	0.5579	3.83	0.4933	- 8.19
	120	0.5576	0.5802	4.05	0.5108	- 8.39
	160	0.5799	0.6029	3.96	0.5287	- 8.83
	200	0.6040	0.6266	3.73	0.5476	- 9.34
	240	0.6300	0.6519	3.47	0.5682	- 9.82
	280	0.6578	0.6797	3.33	0.5912	-10.13
n-Octane[c]	80	0.5308	0.5493	3.48	0.4879	- 8.08
	120	0.5481	0.5720	4.35	0.5060	- 7.68
	160	0.5668	0.5946	4.90	0.5241	- 7.54
	200	0.5867	0.6175	5.25	0.5424	- 7.54
Cyclohexane[b]	68	0.4325	0.4594	6.23	0.4130	- 4.51
	104	0.4530	0.4812	6.22	0.4315	- 4.74
	140	0.4765	0.5029	5.55	0.4501	- 5.53
	176	0.5010	0.5251	4.82	0.4691	- 6.36
	212	0.5280	0.5482	3.82	0.4890	- 7.38
Acetone[c]	80	0.5288	0.5514	4.28	0.4428	-16.26
	100	0.5357	0.5590	4.34	0.4463	-16.69
	120	0.5421	0.5669	4.58	0.4502	-16.95
Chloroform[c]	80	0.2280	0.2282	0.10	0.1913	-16.09
	120	0.2324	0.2301	-0.98	0.1905	-18.05
	160	0.2380	0.2327	-2.21	0.1903	-20.03

TABLE IV (Continued)

Compound	Temp. °F	Literature Value	Using Eq (B-10a)	% Error[a]	Using Eq (B-10b)	% Error[a]
Carbon Tetrachloride[c]	80	0.2043	0.1953	- 4.39	0.1718	-15.89
	120	0.2068	0.1970	- 4.75	0.1717	-16.96
	160	0.2140	0.1989	- 7.05	0.1719	-19.66
Methanol[b,d]	68	0.6010	0.9715	61.64	0.6286	4.59
	104	0.6170	0.9884	60.20	0.6221	0.83
	140	0.6270	1.0087	60.87	0.6189	- 1.29
	176	0.7700	1.0337	34.25	0.6206	-19.41
	212	0.8380	1.0654	27.14	0.6289	-24.96
	248	0.9075	1.1060	21.87	0.6460	-28.81
Ethanol[c]	80	0.5850	0.8412	43.79	0.5636	- 3.66
	120	0.6353	0.8647	36.10	0.5665	-10.83
	160	0.6955	0.8911	28.13	0.5724	-17.70
	200	0.7666	0.9222	20.30	0.5829	-23.97
	240	0.8491	0.9597	13.03	0.5998	-29.36
Benzene[c]	80	0.4160	0.4048	- 2.69	0.3533	-15.08
	120	0.4323	0.4216	- 2.47	0.3663	-15.27
	160	0.4498	0.4386	- 2.48	0.3795	-15.64
	200	0.4690	0.4564	- 2.69	0.3934	-16.12
	240	0.4890	0.4756	- 2.74	0.4088	-16.40
Toluene[c]	80	0.4114	0.4142	0.68	0.3625	-11.90
	120	0.4291	0.4323	0.76	0.3768	-12.19
	160	0.4472	0.4503	0.69	0.3909	-12.59
	200	0.4665	0.4683	0.60	0.4051	-12.98
	240	0.4834	0.4869	0.73	0.4199	-13.15

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[a] % error = (calculated - literature)/literature x 100.

[b] literature value from Gallant (2).

[c] literature value from Touloukian (12).

[d] literature value from Pachaiyappan (6).

TABLE V

COMPARISON BETWEEN HEAT CAPACITIES CALCULATED BY EQUATION (B-13a) AND (B-13b) VALUES IN cal/gm °C

Compound	Temp. °F	Literature Value	Using Eq (B-13a)	% Error[a]	Using Eq (B-13b)	% Error[a]
Methanol[b,d]	68	0.6010	0.5199	-13.50	0.5586	- 7.05
	104	0.6170	0.5345	-13.57	0.5694	- 7.71
	140	0.6270	0.5493	-12.39	0.5801	- 7.48
	176	0.7700	0.5643	-26.71	0.5907	-23.29
	212	0.8380	0.5796	-30.83	0.6011	-28.27
	248	0.9075	0.5952	-34.41	0.6114	-32.63
Chloroform[c]	80	0.2280	0.1563	-31.45	0.1357	-40.48
	120	0.2324	0.1626	-30.06	0.1400	-39.76
	160	0.2380	0.1689	-29.02	0.1442	-39.41
	200	0.2440	0.1755	-28.07	0.1481	-39.30

---

[a] % error = (calculated - literature)/literature x 100.
[b] literature value from Gallant (2).
[c] literature value from Touloukian (12).
[d] literature value from Pachaiyappan (6).

$$= \frac{10}{T_c^{\frac{1}{\gamma}-1}} \frac{d}{dT} (\alpha\ T_c - \beta\ T)^{\frac{1}{\gamma}}$$

$$= \frac{-10\beta}{\gamma} \left(\frac{\alpha\ T_c - \beta\ T}{T_c} \right)^{\frac{1}{\gamma}-1}$$

or

$$\frac{d}{dT} (H_{sl} - H^o) = \frac{10\beta}{\gamma} (\alpha - \beta\ T_r)^{\frac{1}{\gamma}-1} \qquad \text{(B-12)}$$

Substituting equation (B-12) to equation (B-5), the heat capacity was calculated by

$$C_{sL} = C_p^o + \frac{10\beta}{\gamma} (\alpha - \beta\ T_r)^{\frac{1}{\gamma}-1} \qquad \text{(B-13a)}$$

But the equation presented in the paper is

$$C_{sL} = C_p^o + \frac{10\beta}{\gamma} (\gamma - \beta)^{\frac{1}{\gamma}-1} \qquad \text{(B-13b)}$$

For most of the compounds, the term $(\gamma - \beta)$ is negative and γ is greater than 1. Mathematically a negative number raised to some non-integer number is impossible and no values could be calculated using equation (B-13b) for many compounds. Table V compares the results using equation (B-13a) and equation (B-13b) for compounds having a positive $(\gamma - \beta)$ term.

Method 3

In this method, equation (B-4) was the basic equation used to calculate the saturated liquid heat capacities. Graphical computation which was used originally was avoided by the present method. Steven and Thodos' (11) expression for enthalpy departure of saturated vapor from ideal gas state was used to evaluate the functions ϕ_1 and ϕ_3. The expression given by Steven and Thodos (11) is

$$\frac{H^o - H_{sv}}{T_c} = (mT_r + k)^{\frac{1}{p}} \qquad \text{(B-14)}$$

where

$m = -7.424 + 45.65Z_c - 48.75Z_c^2$

$k = 7.401 -39.65Z_c + 43.75Z_c^2$

$p = 2.5Z_c - 0.525$

By differentiating equation (B-14), the functions ϕ_1 and ϕ_3 were evaluated as shown in the following

$$\phi_1 = - [\frac{\partial}{T_c \partial T_r} (H^o - H_{sv})]_{P_r} = \frac{-m}{p} (mT_r + k)^{\frac{1}{p} -1} \qquad \text{(B-15)}$$

$$\phi_3 = [\frac{\partial}{T_c \partial P_r} (H^o - H_{sv})]_{T_r} = 0.0 \qquad \text{(B-16)}$$

The other terms in equation (B-4) were found as follows. The difference between the compressibility factor was determined from (13)

$$\Delta Z_v = (1 - \frac{1}{P_c T_{br}^3})^{\frac{1}{2}} \qquad \text{(B-17)}$$

Yamada and Gunn's (15) method was used to determine molar volume V

$$V = V_{scr} Z_c^{(1-T_r)^{\frac{2}{7}}} \qquad \text{(B-18)}$$

The scaling volume V_{scr} was determined at reduced temperatures in the region of maximum accuracy for liquid density measurement

$$V_{scr} = V' \exp\left[-(1-T_r)^{\frac{2}{7}} \ln Z_c\right] \tag{B-19}$$

In the calculation, the average V_{scr} was used. The reduced liquid density was calculated by

$$\rho_{sLr} = \frac{V_c}{V} \tag{B-20}$$

In estimating the reduced vapor pressure, Riedel-Plank-Miller (9) correlation was used

$$\log P_{vpr} = \frac{-G}{T_r}\left[1 - T_r^2 + g\,(1 - T_r)^3\right] \tag{B-21}$$

where

$$G = 0.2471 + 0.4525\,h \qquad 10 < P_{vp} < 1500 \text{ mmHg}$$

$$= 0.2271 + 0.4525\,h \qquad P_{vp} > 1500 \text{ mmHg}$$

$$h = T_{br}\left[\frac{\log P_c}{(1-T_{br})}\right]$$

$$g = \frac{\left[\frac{h}{G} - (1 + T_{br})\right]}{(1 - T_{br})^2}$$

Thus all terms in equation (B-4) were evaluated and the heat capacities were calculated by

$$C'_{sL} = C_p^o + \phi_o\left[\frac{\phi_1}{\phi_o} - \phi_2 + \phi_4\left(\frac{P_{vpr}}{\Delta Z_v}\right)\left(\frac{RZ_c}{\rho_{sLr}}\right)\right] \tag{B-22}$$

The incorrect equations given in the paper, when used to predict heat capacities of some compounds, were not able to produce the accuracy claimed by Tyagi (13). The incorrect formula in method 1 predicted smaller heat capacities and produced larger deviation in most of the cases when compared to the correct equation. The original equation in method 2, though gave similar results for a few compounds as the correct equation, could not be computed for most of the compounds because the expression involves a negative number raised to some power of non-integer number.

Summarized in Table VI is the comparison of the three methods using the correct equations for the prediction of heat capacities. The results are also compared to experimental results. For the compounds selected, method 1 and method 3 gave best result with aromatic compounds. For paraffin hydrocarbons, all three methods predicted heat capacity values that were within 5% of the experimental values in a wide range of temperature. However, for alcohols, except at high temperatures, more than 40% deviation was obtained. Generally, smaller deviation were found at higher temperatures for the three methods. Comparing the three methods, heat capacities predicted by method 2 were always lower than the experimental values and this method produced the largest deviation among the three; the claimed accuracy using this method could not be verified by testing with the selected compounds. Method 1 and method 3 gave more satisfactory results and values obtained by the two methods were similar, but method 1 was much simpler to use.

In conclusion, the three methods enable a simple and straight forward calculation for the prediction of heat capacities. For the

TABLE VI

COMPARISON BETWEEN LITERATURE AND CALCULATED HEAT CAPACITIES, VALUES IN cal/gm °C

Compound	Temp. °F	Literature Value	Method 1	% Error[a]	Method 2	% Error[a]	Method 3	% Error[a]
n-Butane[c]	80	0.5820	0.6055	4.04	0.5595	- 3.87	0.6818	6.21
	120	0.6190	0.6378	3.03	0.6054	- 2.19	0.6416	3.65
	160	0.6650	0.6803	2.30	0.6605	- 0.67	0.6648	- 0.02
n-Heptane	80	0.5373	0.5579	3.83	0.4849	- 9.76	0.5455	1.52
	120	0.5576	0.5802	4.05	0.5135	- 7.90	0.5735	2.85
	160	0.5799	0.6029	3.96	0.5425	- 6.44	0.6004	3.54
	200	0.6040	0.6266	3.73	0.5722	- 5.27	0.6261	3.66
	240	0.6300	0.6519	3.47	0.6029	- 4.30	0.6503	3.23
	280	0.6578	0.6797	3.33	0.6355	- 3.39	0.6733	2.36
n-Octane[c]	80	0.5308	0.5493	3.48	0.4748	-10.56	0.5327	0.35
	120	0.5481	0.5420	4.35	0.5021	- 8.39	0.5604	2.25
	160	0.5668	0.5946	4.90	0.5295	- 6.58	0.5874	3.64
	200	0.5867	0.6175	5.25	0.5570	- 5.06	0.6134	4.56

TABLE VI (Continued)

Compound	Temp. °F	Literature Value	Method 1	% Error[a]	Method 2	% Error[a]	Method 3	% Error[a]
Cyclohexane[b]	68	0.4325	0.4594	6.23	0.3883	-10.21	0.4470	3.34
	104	0.4530	0.4812	6.22	0.4183	- 7.77	0.4759	5.07
	140	0.4765	0.5029	5.55	0.4483	- 5.92	0.5039	5.74
	176	0.5010	0.5251	4.82	0.4786	- 4.47	0.5306	5.90
	212	0.5280	0.5482	3.82	0.5094	- 3.51	0.5559	5.28
Methanol[b,d]	68	0.6010	0.9715	61.64	0.5199	-13.50	0.8713	44.98
	104	0.6170	0.9884	60.20	0.5345	-13.37	0.8955	45.13
	140	0.6270	1.0087	60.87	0.5493	-12.39	0.9161	46.11
	176	0.7700	1.0337	34.25	0.5643	-26.71	0.9306	20.86
	212	0.8380	1.0654	27.14	0.5796	-30.83	0.9356	11.65
	248	0.9075	1.1060	21.87	0.5952	-34.41	0.9263	2.07
Ethanol[c]	80	0.5850	0.8412	43.79	0.5704	- 2.49	0.7717	31.91
	120	0.6353	0.8647	36.10	0.5986	- 5.78	0.8025	26.31
	160	0.6955	0.8911	28.13	0.6289	- 9.57	0.8326	19.71
	200	0.7666	0.9222	20.30	0.6624	-13.60	0.8616	12.39
	240	0.8491	0.9597	13.03	0.7003	-17.53	0.8896	4.77

TABLE VI (Continued)

Compound	Temp. °F	Literature Value	Method 1	% Error[a]	Method 2	% Error[a]	Method 3	% Error[a]
Chloroform[c]	80	0.2280	0.2282	0.10	0.1563	-31.45	0.2216	- 2.79
	120	0.2324	0.2301	- 0.98	0.1626	-30.06	0.2281	- 1.84
	160	0.2380	0.2327	- 2.21	0.1689	-29.02	0.2339	- 1.74
	200	0.2440	0.2366	- 3.05	0.1755	-28.07	0.2388	- 2.13
Carbon Tetrachloride[c]	80	0.2043	0.1953	- 4.39	0.1597	-21.81	0.1901	- 6.95
	120	0.2068	0.1970	- 4.75	0.1665	-19.47	0.1960	- 5.21
	160	0.2140	0.1989	- 7.05	0.1736	-18.88	0.2014	- 5.91
Acetone[c]	80	0.5288	0.5514	4.28	0.4515	-14.62	0.5372	1.59
	100	0.5357	0.5590	4.34	0.4646	-13.27	0.5493	2.54
	120	0.5421	0.5669	4.58	0.4780	-11.82	0.5610	3.48
Benzene[c]	80	0.4160	0.4048	- 2.69	0.3258	-21.68	0.3910	- 6.01
	120	0.4323	0.4216	- 2.47	0.3521	-18.55	0.4161	- 3.75
	160	0.4498	0.4386	- 2.48	0.3786	-15.82	0.4398	- 2.22
	200	0.4690	0.4564	- 2.69	0.4056	-13.52	0.4620	- 1.50
	240	0.4890	0.4756	- 2.74	0.4334	-11.36	0.4823	- 1.36

TABLE VI (Continued)

Compound	Temp. °F	Literature Value	Method 1	% Error[a]	Method 2	% Error[a]	Method 3	% Error[a]
Toluene[c]	80	0.4114	0.4142	0.68	0.3336	-18.91	0.3944	- 4.13
	120	0.4291	0.4323	0.76	0.3586	-16.42	0.4195	- 2.25
	160	0.4472	0.4503	0.69	0.3836	-14.22	0.4435	- 0.82
	200	0.4655	0.4683	0.60	0.4086	-12.22	0.4665	0.21
	240	0.4834	0.4869	0.73	0.4340	-10.22	0.4882	0.99
	230	0.5000	0.5066	1.31	0.4600	- 8.01	0.5085	1.70

[a] % error = (Calculated - literature)/literature x 100.
[b] literature value from Gallant (2).
[c] literature value from Touloukian (12).
[d] literature value from Pachaiyappan (6).

compounds selected, prediction for alcohols was not satisfactory. Method 1 and method 3 were found to be superior than method 2 and these two methods are preferred to be used for more accurate results. The incorrect equations given in the original paper either predicted heat capacities which were not within the claimed accuracy or could not be computed mathematically, and therefore the original equations should not be used.

NOMENCLATURE

A_1 = 6.32873

A_2 = -8.45167

A_3 = -6.90287

A_4 = 1.87895

A_5 = -0.33448

A_6 = -0.018706

A_7 = -0.286517

A_8 = 0.18940

A_9 = -0.002584

A_{10} = 8.7015

A_{11} = -11.201

A_{12} = -0.05044

A_{13} = 0.002255

a,b,c,d = Constants used in equation (B-6)

C_p^o = Ideal heat capacity, cal/gm-mole ^oC

C_{pL} = Heat capacity at constant pressure, cal/gm ^oC

C_{sL} = Saturated liquid heat capacity, cal/gm ^oC

C'_{sL} = $(dQ/dT)_{sL}$ term, cal/gm ^oC

G,g = Parameters used in equation (B-21)

H = Enthalpy, cal/gm-mole

H^o = Enthalpy at ideal state, cal/gm-mole

H_{sl} = Saturated liquid enthalpy, cal/gm-mole

H_{sv} = Saturated vapor enthalpy, cal/gm-mole

k, m, p = Parameters used in equation (B-14)

P = Pressure, atm.

P_c = Critical pressure, atm.

P_r = Reduced pressure

P_{vp} = Vapor pressure, atm.

P_{vpr} = Reduced vapor pressure

Q = Heat, cal.

R = Gas constant

T = Temperature, ^{o}K

T_B = Boiling temperature, ^{o}K

T_{br} = Reduced boiling temperature

T_c = Critical temperature, ^{o}K

T_r = Reduced temperature

V = Molar volume, cc/gm-mole

V_{sL} = Saturated liquid volume, cc/gm-mole

V_c = Critical volume, cc/gm-mole

V_{scr} = Scaling volume, cc/gm-mole

Z_c = Critical compressibility

ΔZ_v = Difference between saturated vapor and liquid compressibility

α, β, γ = Parameters used in equation (B-11)

λ = Enthalpy of vaporization, cal/gm-mole

ρ_{sLr} = Reduced saturated liquid density

ω = Acentric factor

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APPENDIX C

CALCULATING HEAT CAPACITY FROM THERMAL CONDUCTIVITY

A new general correlation for predicting thermal conductivity was proposed by Narasimhan et al. (3). In the temperature range from 32 °F to 106 °F, the accuracy was claimed to be within ±8% of the experimental values for a wide range of organic liquids. Since a heat capacity term was included in the correlation, an attempt was made to reverse the original equation and use it for prediction of heat capacities.

The thermal conductivity correlation was derived by combining and comparing with some previous correlations. Sakiadis and Coates (5) formulated

$$k = C_p \rho U_s L \tag{C-1}$$

and Jacobson (2) obtained

$$U_s L \rho^{\frac{1}{2}} = \text{constant} \tag{C-2}$$

Substituting equation (3-2) into equation (C-1),

$$k \alpha C_p \rho^{\frac{1}{2}} \tag{C-3}$$

But Weber (7) proposed the following expression earlier,

$$k \alpha C_p \rho^{\frac{4}{3}} \tag{C-4}$$

Comparing the two equations, Narasimhan et al. (3) obtained the generalization

$$k = a\ C_p\ \rho^b \tag{C-5}$$

Equation (C-5) was reversed and the heat capacity was expressed as a function of thermal conductivity k and density ρ

$$C_p = \frac{k}{a\ \rho^b} \tag{C-6}$$

With the available experimental data at 293 $^{\circ}$K (4), given in Table VII, the constants a and b were determined by plotting the equation

$$\log\ \left(\frac{C_p}{k} \right)_{293} = \log \frac{1}{a} - b\ \log \rho_{293} \tag{C-7}$$

The result is shown in Figure 19 for 47 compounds. The resulting equation became, at 293 $^{\circ}$K

$$C_{p_{293}} = \frac{1}{0.000877} \left(\frac{k}{\rho^{0.83}} \right)_{293} \tag{C-8}$$

Narasimhan et al. (3) incorporated a temperature factor to predict thermal conductivity values at other temperatures. The equation given was

$$k_T = 0.000877\ (C_p\ \rho^{0.83})_{293}\ \left(\frac{293}{T} \right)^{0.38} \tag{C-9}$$

Similarly, for predicting heat capacity values at other temperature,

$$C_{p_T} = \frac{1}{0.000877} \left(\frac{k}{\rho^{0.83}} \right)_{293} \left(\frac{T}{293} \right)^n \tag{C-10}$$

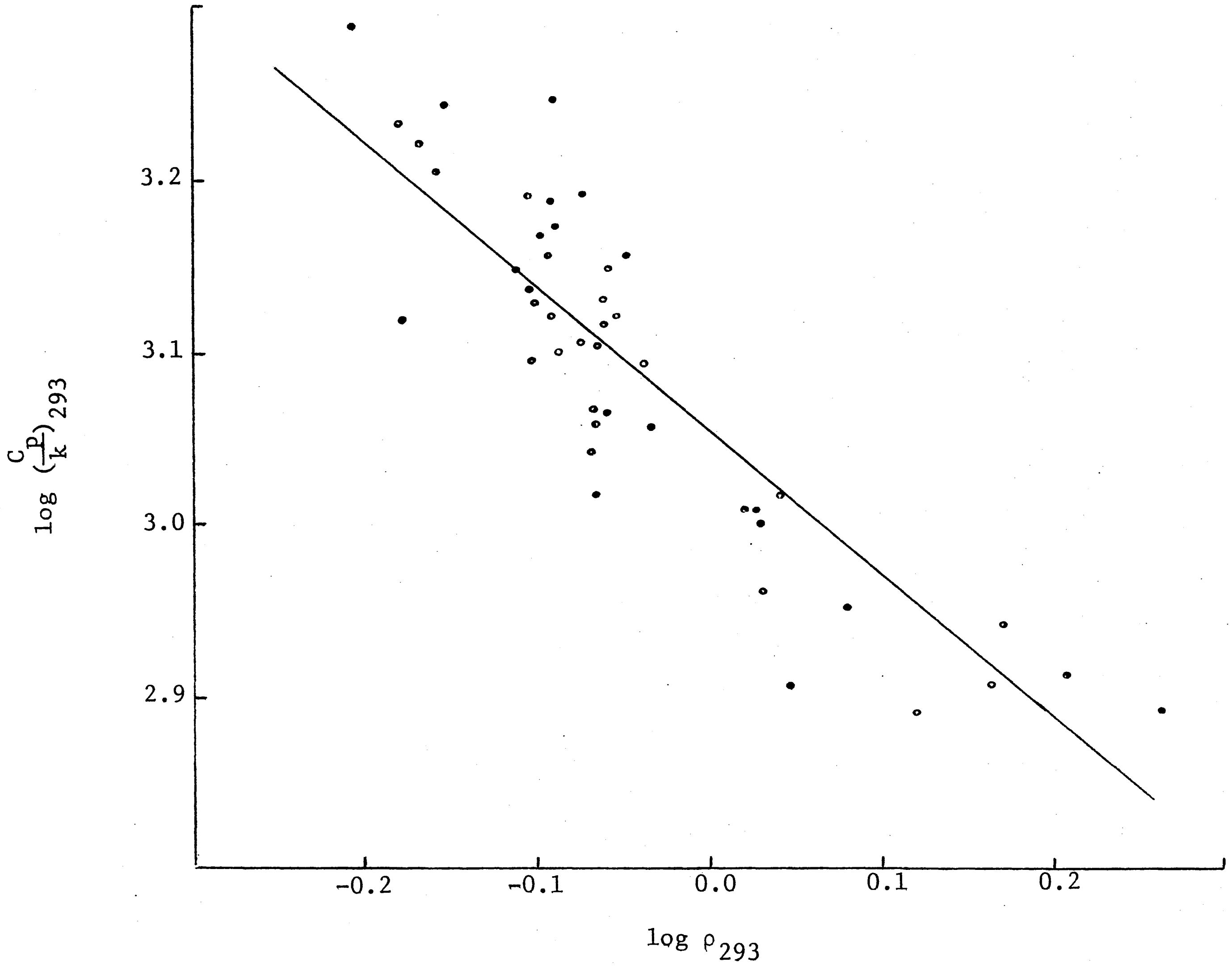

Figure 19. Determination of the constants a and b

TABLE VII

EXPERIMENTAL VALUES OF HEAT CAPACITY, THERMAL CONDUCTIVITY AND DENSITY AT 293 °K.

Compounds	C_p cal/gm °C	k cal/sec cm °C	ρ gm/cc
Carbon Tetrachloride	0.201	0.000247	1.621
Chloroform	0.234	0.000246	1.483
Methylene Chloride	0.287	0.000368	1.326
Nitromethane	0.412	0.000510	1.131
Acetic Acid	0.488	0.000411	1.069
n-Pentane	0.558	0.000286	0.626
Acetone	0.528	0.000386	0.791
Methanol	0.601	0.000483	0.792
Trichloro Ethylene	0.223	0.000278	1.466
Ethanol	0.569	0.000421	0.789
Methyl Acetate	0.468	0.000410	0.993
n-Propanol	0.563	0.000395	0.804
Propionic Acid	0.473	0.000390	1.049
Acetic Anhydride	0.480	0.000528	1.082
Methyl Ethyl Ketone	0.549	0.000374	0.805
Methyl Propionate	0.459	0.000371	0.915
Ethyl Propionate	0.457	0.000351	0.896
n-Propyl Propionate	0.459	0.000348	0.886
Bromo Benzene	0.231	0.000266	1.494
Nitrobenzene	0.339	0.000380	1.203
Chlorobenzene	0.318	0.000308	1.106
Ethyl Benzene	0.402	0.000316	0.867
Benzene	0.406	0.000351	0.879
Aniline	0.496	0.000412	1.022
Cyclohexane	0.417	0.000297	0.778
Cyclohexene	0.429	0.000325	0.811
n-Butyl Acetate	0.459	0.000327	0.882
Ethyl n-Butyrate	0.457	0.000341	0.874
n-Hexane	0.534	0.000313	0.659

TABLE VII (Continued)

Compounds	C_p cal/gm ^oC	k cal/sec cm ^oC	ρ gm/cc
n-Heptane	0.526	0.000317	0.684
n-Heptanol	0.505	0.000384	0.659
Toluene	0.364	0.000317	0.867
p-Chloro Toluene	0.315	0.000320	1.070
Methyl Aniline	0.512	0.000442	0.860
n-Octane	0.517	0.000326	0.720
n-Octanol	0.499	0.000396	0.825
o-Xylene	0.419	0.000321	0.880
m-Xylene	0.387	0.000376	0.864
p-Xylene	0.406	0.000370	0.861
Mesitylene	0.412	0.000325	0.860
Ether	0.538	0.000307	0.708
Iodobenzene	0.186	0.000244	1.831
Allyl Alcohol	0.665	0.000429	0.855
i-Propyl Alcohol	0.602	0.000389	0.785
n-Butyl Alcohol	0.563	0.000367	0.810
i-Butyl Alcohol	0.603	0.000343	0.809
i-Amyl Alcohol	0.535	0.000364	0.814

Experimental values for a number of compounds were used to obtain an average of the exponential n's. Equation (C-10) was written in another form

$$\log C_{p_T} = \log \left[\frac{1}{0.000877} \left(\frac{k}{\rho^{0.83}}\right)_{293}\right] + n \log \left(\frac{T}{293}\right) \qquad \text{(C-11)}$$

The terms $\log (C_{p_T})$ and $\log (\frac{T}{293})$ are plotted in Figure 20. The n value for each compound was measured by the slope of the line, and the result is shown in Table VIII. The average value was calculated to be 0.38 for the compounds considered. The final equation is

$$C_{p_T} = \frac{1}{0.000877} \left(\frac{k}{\rho^{0.83}}\right)_{293} \left(\frac{T}{293}\right)^{0.38} \qquad \text{(C-12)}$$

Equation (C-12) was used to predict the heat capacities for some hydrocarbon compounds, including those used to obtain the average exponential n. The results are shown in Table IX. For the compounds selected, the heat capacities predicted by the equation were generally lower than the experimental values. In many cases the percent error increased as temperature increased. Deviation of more than ten percent were calculated for most of the compounds.

The large deviation of the predicted values was mainly caused by error introduced when the constants a and b were determined in equation (C-7). As shown in Figure 19, the ratios of heat capacity to thermal conductivity of the 47 compounds are scattered and the curve drawn through them cannot truly represent the line of average values for all compounds. Ratios that are below the curve have their actual values increased and ratios that are above the curve have their actual

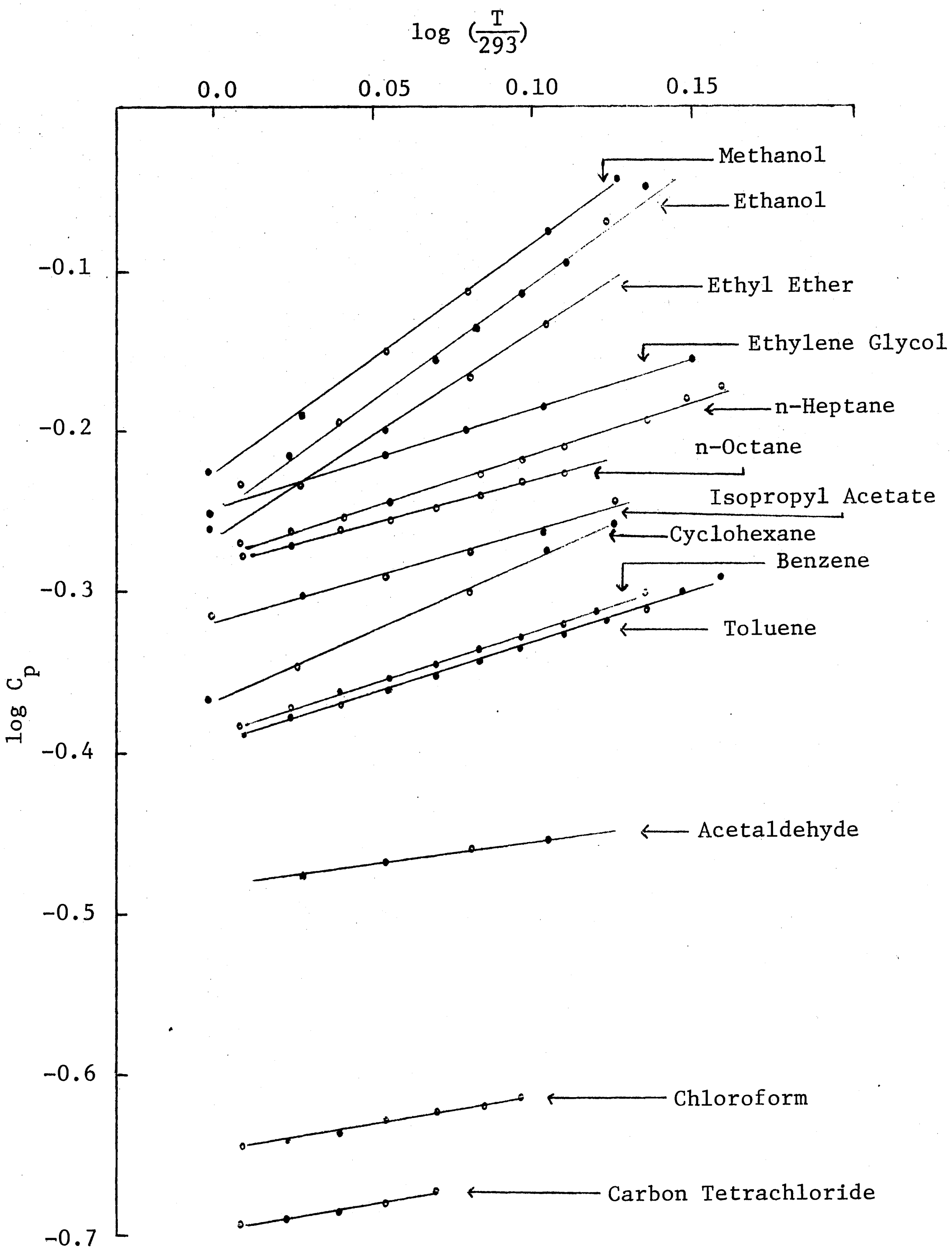

Figure 20. Determination of the Exponential n

TABLE VIII

EXPONENTIAL n OF THE SELECTED COMPOUNDS

Compounds	n
Carbon Tetrachloride	0.1853
Chloroform	0.1853
Acetaldehyde	0.1548
Toluene	0.3340
Benzene	0.3249
Cyclohexane	0.4642
Isopropyl Acetate	0.2962
n-Octane	0.2773
n-Heptane	0.3249
Ethylene Glycol	0.3249
Ethyl Ether	0.6371
Ethanol	0.7107
Methanol	0.7265

TABLE IX

COMPARISON BETWEEN CALCULATED AND LITERATURE HEAT CAPACITIES, VALUES IN cal/gm °C

Compound	Temperature °F	Literature Value	Calculated Value	% Error[a]
n-Heptane[c]	80	0.5373	0.4656	-13.34
	120	0.5576	0.4784	-14.20
	160	0.5799	0.4907	-15.38
	200	0.6040	0.5025	-16.80
	240	0.6300	0.5139	-18.43
	280	0.6578	0.5249	-20.21
n-Octane[c]	80	0.5308	0.4830	- 9.00
	120	0.5481	0.4963	- 9.44
	160	0.5668	0.5091	-10.18
	200	0.5867	0.5213	-11.15
	240	0.6077	0.5331	-12.28
Cyclohexane[b]	68	0.4325	0.4621	6.85
	104	0.4530	0.4739	4.60
	140	0.4765	0.4851	1.81
	176	0.5010	0.4960	- 0.99
	212	0.5280	0.5065	- 4.07
	248	0.5540	0.5167	- 6.74
Benzene[c]	80	0.4160	0.4529	8.86
	120	0.4323	0.4653	7.64
	160	0.4498	0.4773	6.11
	200	0.4690	0.4888	4.21
	240	0.4890	0.4998	2.21
Toluene[c]	80	0.4112	0.4262	3.60
	120	0.4291	0.4379	2.06
	160	0.4472	0.4492	0.44

TABLE IX (Continued)

Compound	Temperature °F	Literature Value	Calculated Value	% Error[a]
Toluene[c] (Con't.)	200	0.4655	0.4600	- 1.19
	240	0.4834	0.4704	- 2.70
	280	0.5000	0.4804	- 3.92
Ethanol[c]	80	0.5850	0.5820	- 0.50
	120	0.6353	0.5981	- 5.86
	160	0.6955	0.6134	-11.80
	200	0.7666	0.6282	-18.06
	240	0.8491	0.6424	-24.35
Methanol[b]	68	0.5950	0.7016	17.91
	104	0.6425	0.7194	11.97
	140	0.7040	0.7365	4.62
	176	0.7700	0.7530	- 2.20
	212	0.8380	0.7690	- 8.24
	248	0.9075	0.7844	-13.57
Butanol[b]	68	0.5300	0.5119	- 3.41
	104	0.5670	0.5249	- 7.42
	140	0.6100	0.5375	-11.89
	176	0.6630	0.5495	-17.12
	212	0.7220	0.5611	-22.28
	248	0.7850	0.5724	-27.08
Chloroform[c]	80	0.2280	0.2358	3.43
	120	0.2324	0.2423	4.27
	160	0.2380	0.2485	4.43
	200	0.2440	0.2545	4.31
Carbon Tetrachloride[c]	80	0.2043	0.1963	- 3.94
	120	0.2068	0.2017	- 2.49
	160	0.2140	0.2068	- 3.36

TABLE IX (Continued)

Compound	Temperature °F	Literature Value	Calculated Value	% Error[a]
Acetaldehyde[b]	68	0.3280	0.5833	77.83
	104	0.3350	0.5981	78.54
	140	0.3400	0.6123	80.09
	176	0.3480	0.6261	79.90
	212	0.3550	0.6393	80.09
	248	0.3600	0.6521	81.15
Isopropyl[a] Acetate	68	0.4850	0.4244	-12.50
	104	0.4980	0.4351	-12.62
	140	0.5110	0.4455	-12.82
	176	0.5280	0.4555	-13.73
	212	0.5460	0.4651	-14.81
	248	0.5700	0.4745	-16.76
Ethyl Ether[b]	104	0.5850	0.4657	-20.39
	140	0.6300	0.4768	-24.32
	176	0.6800	0.4875	-28.31
	212	0.7370	0.4978	-32.46
	248	0.8000	0.5078	-36.53
	284	0.8750	0.5174	-40.86
Ethylene[b] Glycol	68	0.5600	0.7131	27.34
	104	0.5830	0.7312	25.42
	140	0.6050	0.7486	23.74
	176	0.6270	0.7654	22.08
	212	0.6500	0.7816	20.25
	248	0.6730	0.7973	18.47

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[a] % error = (calculated - literature)/literature x 100.

[b] data source from Gallant (1).

[c] data source from Touloukian (6).

values decreased. Consequently the changed ratios determined an incorrect constant a which when used in equation (C-12) predicted incorrect heat capacities. The effect becomes more noticeable for compounds having their ratios of heat capacity to thermal conductivity at considerable distance from the curve. The second error source came from the determination of the exponential term in equation (C-11). As shown in Table VIII, the values of n are different for many compounds. Therefore the heat capacities were predicted lower for some compounds and higher for the other using the average n.

Since average deviation for many compounds is not within an acceptable level, the reverse of the thermal conductivity correlation was found not to be satisfactory. The equation, in the form of equation (C-12), predicted inaccurate results and is not suitable for the prediction of heat capacities.

NOMENCLATURE

a = Constant

b = Constant

C_p = Heat capacity, cal/gm °C

k = Thermal conductivity, cal/sec cm °C

L = Intermolecular free length, A°

n = Exponential in equation (C-10)

T = Temperature, °K

U_s = Sonic velocity, cm/sec

ρ = Density, gm/cc

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APPENDIX D

LITERATURE SURVEY ON EXPERIMENTAL LIQUID HEAT CAPACITIES

The heat capacities of both organic and inorganic compounds can be found in many sources such as handbooks and technical journals. Usually the available data which could be experimentally determined or calculated from correlations are presented in tabular and/or graphical form. The purpose of this literature survey was to locate sources that contained the above information and to tabulate all compounds, whose liquid heat capacities had been determined experimentally, in the articles that would be checked.

The organic compounds that were of primary interest were the paraffins, alcohols and aromatic hydrocarbons and their derivatives. Sources that contained these compounds were located in "Thermophysical Properties Research Literature Retrieval Guide" (47). All articles which had been checked dated from the 1920's to the 1960's and only those articles that had experimental heat capacity values were listed. For each article, all compounds encountered were tabulated. Information about the data include the number of data points cited, the method of presentation, the temperature and pressure ranges and the reported experimental accuracy. The compounds had also been classified in the table. In preparing the reference, unless not available, the English versions of foreign articles were given. The results of the survey are shown in Table X.

In all the articles checked, the temperature range was given and generally the reported accuracy was also included. The pressure range was seldom stated. Heat capacities at elevated pressure had been determined only for a limited number of compounds. No evaluation of any data was made and Table X merely shows what compound is included in a particular source and the experimental conditions.

By tabulating all information about a source, the usefulness of that source can be found almost immediately. Table X serves this purpose for locating sources that contain experimental liquid heat capacity data.

TABLE X

A LIST OF COMPOUNDS WITH EXPERIMENTAL HEAT CAPACITIES CITED DURING THE SURVEY

Compound	Data Points	Temperature Range	Pressure Range	Reported Accuracy	Data Source
Elements					
Helium	25	1.79 to 5.04 °K	Saturation		20
Hydrogen	8	13.95 to 20.0 °K	Saturation		20
Nitrogen	7	65.02 to 77.71 °K	Saturation		20
Oxygen	24	-357.2 to -297.1 °F			20
Paraffins					
Methane	1	-276 °F			42
Ethane	2	-150 to 60 °F			42
Propane	2	60 to 125 °F			42
	15	90 to 230 °K			20
	12	-17.82 to 18.44 °C			11
n-Butane	10	-16.2 to 16.78 °C			11
	14	140 to 270 °K			3
	2	12 to 60 °F			42
	14	140 to 270 °K			20

TABLE X (Continued)

Compound	Data Points	Temperature Range	Pressure Range	Reported Accuracy	Data Source
2-Methyl Propane	11	-12.53 to 17.5 °C			11
	2	8.3 to 60 °F			42
n-Pentane	15	150 to 290 °K			27
n-Hexane	1				39
	1	20 °C			33
	24	180.42 to 300.98 °K		.1 to .2%	12
	15	180 to 320 °K		.75 to 1.25%	46
2-Methyl Pentane	29	103.56 to 303.27 °K		.1 to .2%	12
	20	130 to 320 °K		.75 to 1.25%	46
3-Methyl Pentane	36	50.89 to 302.14 °K		.1 to .2%	12
	24	90 to 320 °K		.75 to 1.25%	46
2,2-Dimethyl Butane	17	177.25 to 296.1 °K		.1 to .2%	12
	15	180 to 320 °K		.75 to 1.25%	46
2,3-Dimethyl Butane	38	149.37 to 306.46 °K		.1 to .2%	12
	18	150 to 320 °K		.75 to 1.25%	46
n-Heptane	11	20 to 70 °C			23
	1	20 °C			33
2-Methyl Hexane	19	160.41 to 301.17 °K		.1 to .2%	17
3-Ethyl Pentane	46	145.19 to 298.79 °K		.1 to .2 %	17

TABLE X (Continued)

Compound	Data Points	Temperature Range	Pressure Range	Reported Accuracy	Data Source
2,2-Dimethyl Pentane	20	154.68 to 298.36 °K		.1 to .2%	17
2,4-Dimethyl Pentane	40	160.81 to 307.09 °K		.1 to .2%	17
2,2,3-Trimethyl Butane	10	253.03 to 313.26 °K		.1 to .2%	17
n-Octane	1	20 °C			33
	18	222.61 to 297.58 °K		.1 to .2%	14
2,2,4-Trimethyl Pentane	1				39
	6	100 to 500 °F			6
n-Nonane	7	100 to 600 °F			6
	22	225.03 to 313.88 °K		.1 to .2%	14
2,2,5-Trimethyl Hexane	6	100 to 500 °F			6
n-Decane	17	247.02 to 318.62 °K		.1 to .2%	14
	13	80 to 200 °F		1%	36
n-Undecane	12	251.74 to 298.92 °K		.1 to .2%	14
n-Dodecane	11	266.69 to 317.41 °K		.1 to .2%	14
n-Tridecane	8	271.66 to 306.38 °K		.1 to .2%	14
n-Tetradecane	7	282.71 to 302.77 °K		.1 to .2%	14

TABLE X (Continued)

Compound	Data Points	Temperature Range	Pressure Range	Reported Accuracy	Data Source
n-Pentadecane	7	285.51 to 312.78 °K		.1 to .2%	14
n-Hexadecane	Graphical	-90 to 50 °F			37
	12	100 to 800 °F			6
	9	295.41 to 320.28 °K		.1 to .2%	14
2,2,4,4,6,8,8-Heptamethyl Nonane	8	100 to 700 °F			6
Miscellaneous Hydrocarbons					
Diphenyl Methane	2	310.7 to 322.6 °K		.9 to 1.33%	41
1,1-Diphenyl Ethane	9	100 to 900 °F			6
	4	259.8 to 298.5 °K		1.4 to 1.5%	41
1,1-Dicyclohexyl Ethane	12	100 to 800 °F			6
1,1-bis(4-Methylcyclohexyl) Ethane	11	100 to 900 °F			6
Spiro(5,5)undecane	11	100 to 800 °F			6
Isopropylibicyclohexyl	12	100 to 800 °F			6

TABLE X (Continued)

Compound	Data Points	Temperature Range	Pressure Range	Reported Accuracy	Data Source
Monocyclic Hydrocarbons					
Cyclohexane	8	6.84 to 28.14 °C			5
	6	100 to 500 °F			6
	11	20 to 70 °C			23
	3	280 to 295 °K		.5%	4
	7	282.27 to 301.3 °K		.1%	34
	4	24.85 to 54.57 °C	1 atm	.5%	18
	11	10 to 60 °C		.2 to .3%	29
	3	20 to 40 °C		.4%	49
Methyl Cyclohexane	32	-98.4 to 35 °C		.2%	19
Diethyl Cyclohexane	9	100 to 600 °F			6
Cyclododecane	10	200 to 800 °F			6
Olefins					
Propylene	2	-57.6 to 60 °F			42
1-Butene	2	5.8 to 60 °F			42
	5	246 to 298.5 °K		2. to 3.%	41
2-Methyl-1-Butene	2	-4 to 60 °F			42

TABLE X (Continued)

Compound	Data Points	Temperature Range	Pressure Range	Reported Accuracy	Data Source
Cis-2-Butene	13	80 to 200 °F		1.5%	36
	2	0 to 60 °F			42
Trans-2-Butene	2	-2.8 to 60 °F			42
1,1-Diphenyl Ethylene	2	286 to 298.5 °K		2. to 3.%	41
1,3-Butadiene	2	20 to 60 °F			42
Alkynes					
Phenyl Acetylene	6	231.7 to 298.5 °K			41
Diphenyl Acetylene	8	231.7 to 322.6 °K			41
Aromatics					
Benzene	9	0 to 140 °C			52
	13	15.21 to 73.73 °C		1.%	45
	10	5.53 to 76.84 °C			5
	7	100 to 500 °F			6
	5	10 to 30 °C		1.%	32
	3	Ambient			26

TABLE X (Continued)

Compound	Data Points	Temperature Range	Pressure Range	Reported Accuracy	Data Source
Benzene (Con't.)	1	20 °C			35
	3	8.18 to 45.61 °C			53
	2				39
	1	18 °C		1.7%	1
	1	20 °C			33
	5	280 to 320 °K		.75 to 1.25%	46
	1	287.87 °K			25
	1	5.4 °C			2
Toluene	9	0 to 140 °C			52
	Graphical	25 to 70 °F			37
	14	50.6 to 241.3 °C	3 to 19 atm	5.%	28
	7	18.38 to 244.79 °K		.5%	44
	1	20 °C			35
	3	5.31 to 47.22 °C			53
	1	20 °C			33
	11	183.83 to 284.44 °K			22
	9	184.4 to 298.5 °K		.9 to 1.3%	41
	24	160.09 to 371.02 °K		.1%	38
	34	-92.3 to 31.3 °C		.2%	19
	8	26.7 to 71.1 °C	1 atm		40
Ethyl Benzene	9	184.4 to 298.5 °K		1.4 to 1.5%	41
Isopropyl Benzene	13	80 to 200 °F		1.%	36
n-Butyl Benzene	9	100 to 700 °F			6

TABLE X (Continued)

Compound	Data Points	Temperature Range	Pressure Range	Reported Accuracy	Data Source
1,2,3,5-Tetramethyl Benzene	8	100 to 700 °F			6
o-Dihydroxybenzene	1	104.3 °C			2
m-Dihydroxybenzene	1	109.7 °C			2
p-Dihydorxybenzene	1	172.3 °C			2
o-Dinitrobenzene	1	116.93 °C			2
m-Dinitrobenzene	1	90.08 °C			2
p-Dinitrobenzene	1	173.5 °C			2
Hydrindan	10	100 to 700 °F			6
Naphthalenes					
Naphthalene	1	79.98 °C			2
α-Methyl Naphthalene	11	100 to 900 °F			6
Tetrahydronaphthalene	11	100 to 800 °F			6
Cis-Decahydronaphthalene	10	100 to 700 °F			6

TABLE X (Continued)

Compound	Data Points	Temperature Range	Pressure Range	Reported Accuracy	Data Source
Trans-Decahydronaphthalene	10	100 to 700 °F			6
β-Ethyldecahydronaphthalene	11	100 to 800 °F			6
Dimethyldecahydronaphthalene	11	100 to 800 °F			6
Halo Substituted Hydrocarbons					
Chloroform	11	10.81 to 55.87 °C		1.%	45
	1	27 to 118 °C			15
	1	20 °C			35
	1	20 °C			33
Carbon Tetrachloride	7	22.76 to 65.60 °C		1.%	45
	1	20 °C			35
	25	5.19 to 45.79 °C			53
	1				39
	Graphical	30 to 70 °C		1.%	16
	1	20 °C			33
	7	260 to 320 °K		.75 to 1.25%	46
	1	288.31 °K			25

TABLE X (Continued)

Compound	Data Points	Temperature Range	Pressure Range	Reported Accuracy	Data Source
1,2-Dibromoethane	3	20 to 40 °C		.4%	49
1,2-Dichloroethane	14	11 to 74.88 °C		1.%	45
	3	20 to 40 °C		.4%	49
Tetrachloroethane	1				39
Ethylene Bromide	1	20 °C			33
1,1,3-tetrachloropropane	11	239.56 to 288.5 °K			24
1,1,1-Trifluoro-3-Chloropropane	33	184.36 to 299 °K			24
Diphenylchloromethane	2	298.5 to 310.7 °K			41
Fluorobenzene	9	240 to 320 °K		.75 to 1.25%	46
Chlorobenzene	10	230 to 320 °K		.75 to 1.25%	46
	1	20 °C			35
Bromobenzene	8	250 to 320 °K		.75 to 1.25%	46
Iodobenzene	8	250 to 320 °K		.75 to 1.25%	46
Benzyl Chloride	5	246 to 298.5 °K			41

TABLE X (Continued)

Compound	Data Points	Temperature Range	Pressure Range	Reported Accuracy	Data Source
Alcohols					
Methanol	1	20 °C			50
Ethanol	1	20 °C			50
	2	0 to 80 °C			7
	9	15 to 55 °C		.1%	32
	11	20 to 70 °C			23
	Graphical	0 to 70 °C		1.%	16
	1	20 °C			33
	19	160 to 250 °K			30
	20	163.51 to 294.31 °K		.5%	21
	41	-107.8 to 31.1 °C		.2%	19
	7	27.65 to 70.2 °C	1 atm		40
	Graphical	0 to 700 °C		.3%	8
Propanol	10	293 to 398 °K			13
	26	5.19 to 45.79 °C			53
	48	153.9 to 361.5 °K		.1 to .15%	10
2-Methyl-1-Propanol	1	20 °C			50
	8	27.2 to 75.6 °C	1 atm		40
	66	101.0 to 355.0 °K		.1 to .15%	10
1-Butanol	Graphical	0 to 70 °C		1.%	16
	1				39
	25	188 to 322 °K			9
	40	184 to 340 °F	3.89 to 73.62 psia		43

TABLE X (Continued)

Compound	Data Points	Temperature Range	Pressure Range	Reported Accuracy	Data Source
3-Methyl-1-Butanol	18	4.37 to 46.33 °C			53
1-Pentanol	54	200.1 to 389.2 °K		.1 to .15%	10
4-Methyl-1-Pentanol	2	0 to 100 °C			7
	1	20 °C			33
1-Hexanol	7	229.64 to 290.01 °K		1.%	21
1-Heptanol	Graphical	40 to 70 °C		1.%	16
	7	240 to 300 °K		1.%	31
1-Octanol	Graphical	80 to 240 °K			44
4-Octanol	Graphical	80 to 160 °K			44
1-Decanol	Graphical	35 to 70 °C		1.%	16
Cyclopentanol	5	260 to 300 °K		1.%	31
Benzyl Alcohol	4	259.8 to 298.5 °K			41
Furfuryl Alcohol	5	260 to 300 °K		1.%	31
α-Naphthol	1	95.0 °C			2
β-Naphthol	1	120.6 °C			2

TABLE X (Continued)

Compound	Data Points	Temperature Range	Pressure Range	Reported Accuracy	Data Source
Dialcohols (Diols)					
Ethylene Glycol	1	20 °C			50
	1	20 °C			53
Triols					
Glycerol	1	20 °C			50
	2	26.5 to 68.0 °C			7
Aldehydes					
n-Butyraldehyde	13	180 to 300 °K		1.%	31
n-Heptaldehyde	8	230 to 300 °K		1.%	31
Ketones					
Acetone	1	20 °C			33
	10	14.7 to 50.58 °C		1.%	45
	1	26 to 110 °C			15
	1				39
	1	18°C		3.1%	1

TABLE X (Continued)

Compound	Data Points	Temperature Range	Pressure Range	Reported Accuracy	Data Source
Methyl Ethyl Ketone	13	180 to 300 °K		1.%	31
	1	297.01 °K			25
Quinone	1	112.9 °C			2
Ethers					
Ether	1	20 °C			33
Ethyl Ether	1	25 to 111 °C			15
Anisol	1	297.21 °K			25
Tetrahydropyran	4	24.47 to 54.32 °C	1 atm	.5%	18
Dioxan	1				39
Esters					
Ethyl Formate	1	294.72 °K			25
Methyl Acetate	1	20 °C			33
Ethyl Acetate	1	20 °C			33
	1				39

TABLE X (Continued)

Compound	Data Points	Temperature Range	Pressure Range	Reported Accuracy	Data Source
Benzyl Acetate	1	292.71 °K			25
Ethyl Propionate	1	20 °C			33
Ethyl Butyrate	1	20 °C			33
	1	297.28 °K			25
Ethyl Carbonate	1	294.70 °K			25
Ethyl Benzoate	1	292.75 °K			25
Ethyl Malonate	1	294.64 °K			25
Ethyl Succinate	1	292.62 °K			25
Ethyl Acetyl Acetate	1	297.59 °K			25
Methyl Salicylate	1	295.20 °K			25
<u>Acids</u>					
Acetic Acid	1				39
Benzoic Acid	1	121.8 °C			2
o-Toluic Acid	1	103.7 °C			2

TABLE X (Continued)

Compound	Data Points	Temperature Range	Pressure Range	Reported Accuracy	Data Source
m-Toluic Acid	1	103.7 °C			2
p-Toluic Acid	1	179.6 °C			2
o-Chlorobenzoic Acid	1	140.2 °C			2
m-Chlorobenzoic Acid	1	154.25 °C			2
p-Chlorobenzoic Acid	1	239.7 °C			2
o-Aminobenzoic Acid	1	145.0 °C			2
m-Aminobenzoic Acid	1	180.0 °C			2
p-Aminobenzoic Acid	1	188.5 °C			2
o-Nitrobenzoic Acid	1	145.8 °C			2
m-Nitrobenzoic Acid	1	141.1 °C			2
p-Nitrobenzoic Acid	1	239.2 °C			2
<u>Miscellaneous Compounds</u>					
Water	1 Graphical	20 °C 32 to 70 °F			50 37

TABLE X (Continued)

Compound	Data Points	Temperature Range	Pressure Range	Reported Accuracy	Data Source
Water	7	0 to 110 °C			7
(Con't.)	1	18 °C		3.1%	1
	22	273.15 to 473.15 °K	1 to 48.4 atm		20
Perchloryl Fluoride	31	226.09 to 360.18 °K			20
Chlorine Trifluoride	12	196.84 to 278.25 °K			20
Perhydrofluorine	12	100 to 800 °F			6
9-(2'-Ethylhexyl)perhydrofluorine	13	100 to 900 °F			6
Pinane	20	100 to 700 °F			6
Limonene	1	293.40 °K			25
Sabinene	1	297.04 °K			25
Linalool	1	293.15 °K			25
Pulegone	1	293.38 °K			25
Hydroxy-Acetanilide	1	91.3 °C			2
Carbon Disulphide	1	20 °C			33
	1	20 °C			35

TABLE X (Continued)

Compound	Data Points	Temperature Range	Pressure Range	Reported Accuracy	Data Source
Nitrogen Compounds					
Ammonia	10	-26.3 to 17.22 °C			11
	4	200 to 230 °K			20
Hydrazine	9	274.69 to 340 °K			20
Dimethyl Hydrazine	18	388.7 to 536.6 °K			20
Piperidine	4	24.44 to 54.16 °C	1 atm	.5%	18
o-Nitroaniline	1	69.3 °K			2
m-Nitroaniline	1	111.8 °K			2
p-Nitroaniline	1	147.5 °K			2
Deuterated Compounds					
Deuterium Oxide	12	293 to 398 °K			13
Deutero Ethanol	9	15 to 55 °C		.1%	32
	19	160 to 250 °K			30
Deutero Cyclohexane	11	10 to 60 °C		.2 to .3%	29

TABLE X (Continued)

Compound	Data Points	Temperature Range	Pressure Range	Reported Accuracy	Data Source
Deutero Benzene	5	10 to 30 °C		.1%	32
	9	283.5 to 322.6 °K		2.%	54
Refrigerants					
Freon-11	9	100 to 600 °K			20
Freon-12	9	100 to 600 °K			20
Freon-13	9	100 to 600 °K			20
Freon-14	9	100 to 600 °K			20
Paraffin Hydrocarbon Mixture					
n-Heptane and Carbon Tetrachloride	3	25 °C			48
n-Heptane and Ethanol	44	20 to 70 °C			23
n-Heptane and Benzene	3	25 °C			48

TABLE X (Continued)

Compound	Data Points	Temperature Range	Pressure Range	Reported Accuracy	Data Source
<u>Halo Substituted Paraffin Hydrocarbon Mixtures</u>					
Chloroform and Acetone	43	14.56 to 50.58 °C		1.%	45
	15	20 to 40 °C			51
Chloroform and Carbon Tetrachloride	20	20 to 50 °C			51
Carbon Tetrachloride and Benzene	41	20.16 to 71.85 °C		1.%	45
	25	20 to 60 °C			51
	8	25 °C			48
Carbon Tetrachloride and Ethanol	Graphical	35 to 65 °C		1.%	16
Carbon Tetrachloride and 1-Propanol	3	5.66 to 46.45 °C			53
Carbon Tetrachloride and 2-Propanol	3	5.06 to 46.92 °C			53
Carbon Tetrachloride and 1-Butanol	Graphical	35 to 65 °C		1.%	16
Carbon Tetrachloride and 1-Heptanol	Graphical	35 to 65 °C		1.%	16

TABLE X (Continued)

Compound	Data Points	Temperature Range	Pressure Range	Reported Accuracy	Data Source
Carbon Tetrachloride and 1-Decanol	Graphical	35 to 65 °C		1.%	16
Carbon Tetrachloride and Silicone Tetrachloride	11	25 °C			48
Ethylene Chloride and Benzene	35	16.19 to 75.70 °C		1.%	45
<u>Monocyclic Saturated Hydrocarbon Mixtures</u>					
Cyclohexane and Ethanol	44	20 to 70 °C			23
Cyclohexane and Benzene	171	-25 to 32.9 °C			5
Cyclohexane and Tetrahydropyran	8	24.49 to 54.32 °C	1 atm	.5%	18
Methyl Cyclohexane and Ethanol	103	-67.6 to 34.7 °C		.2%	19

TABLE X (Continued)

Compound	Data Points	Temperature Range	Pressure Range	Reported Accuracy	Data Source
<u>Aromatic Hydrocarbon Mixtures</u>					
Benzene and Ethylene Chloride	35	16.19 to 75.70 °C		1.%	45
Benzene and Carbon Tetrachloride	41	20.16 to 71.85 °C		1.%	45
	25	20 to 60 °C			51
	8	25 °C			48
Benzene and n-Heptane	3	25 °C			48
Benzene and Cyclohexane	171	-25 to 32.9 °C			5
Benzene and Toluene	35	20 to 60 °C			51
Benzene and 1-Propanol	3	5.23 to 45.68 °C			53
Benzene and Methyl Ethyl Ketone	3	5.19 to 45.65 °C			53
Chlorobenzene and Bromobenzene	20	20 to 80 °C			51
Toluene and Ethanol	218	-93.7 to 36.4 °C		.2%	19
Toluene and 1-Propanol	3	5.24 to 45.21 °C			53

TABLE X (Continued)

Compound	Data Points	Temperature Range	Pressure Range	Reported Accuracy	Data Source
Toluene and 2-Propanol	Graphical	25 to 80 °C	1 atm		40
Toluene and 2-Methyl-1-Propanol	3	5.42 to 44.55 °C			53
Toluene and 3-Methyl-1-Butanol	4	5.05 to 46.57 °C			53
<u>Alcohol Mixtures</u>					
Ethanol and Water	Graphical	25 to 75 °C	1 atm		40
Ethanol and n-Heptane	44	20 to 70 °C			23
Ethanol and Cyclohexane	44	20 to 70 °C			23
Ethanol and Toluene	218	-93.7 to 36.4 °C		.2%	19
<u>Ketone Mixtures</u>					
Acetone and Carbon Tetrachloride	27	11.54 to 44.18 °C		1.%	45

TABLE X (Continued

Compound	Data Points	Temperature Range	Pressure Range	Reported Accuracy	Data Source
Acetone and Chloroform	43 15	14.56 to 50.58 °C 20 to 40 °C		1.%	45 51
Methyl Ethyl Ketone and Benzene	3	5.19 to 45.65 °C			53
<u>Miscellaneous Mixtures</u>					
Piperidine and Tetrahydroxypyran	12	24.4 to 54.43 °C	1 atm	.5%	18

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