67-14,247

KEMME, Herbert Rudolph Conrad, 1941-
RELATIONSHIPS BETWEEN SOME PROPERTIES OF PURE HOMOLOGOUS ORGANIC LIQUIDS.

Newark College of Engineering, D. Eng. Sc., 1967
Engineering, chemical

University Microfilms, Inc., Ann Arbor, Michigan

RELATIONSHIPS BETWEEN SOME PROPERTIES OF PURE HOMOLOGOUS ORGANIC LIQUIDS

BY

HERBERT R. KEMME

A DISSERTATION

PRESENTED IN PARTIAL FULFILLMENT OF

THE REQUIREMENTS FOR THE DEGREE

OF

DOCTOR OF SCIENCE IN CHEMICAL ENGINEERING

AT

NEWARK COLLEGE OF ENGINEERING

Newark, New Jersey
1967

ABSTRACT

The vapor pressures of eleven primary straight chain alkyl chlorides and eleven primary straight chain alcohols between C_3 and C_{16} were determined within a range of 5 to 760 mm Hg. These data were obtained by determining the boiling points of the pure materials at various pressures by using differential thermal analysis. The boiling points were determined with a precision of $\pm$.1 degree Centigrade at a 95 per cent C.I. The Antoine equation was used to analytically describe the data. The constants for this equation were determined by a multiple linear regression technique for each individual compound. The heats of vaporization were generated for each compound from the experimental vapor pressure data by the Haggenmacher and Fishtine method.

A correlation was developed, based on a hole model for a liquid, which relates vapor pressures between 5 and 760 mm Hg with corresponding liquid densities and the number of carbon atoms in a molecular chain for an homologous series. The correlation constants were determined from a multiple linear regression analysis by the use of available literature density data. Any missing density

data were then predicted from the knowledge of experimental vapor pressure data. The maximum error in correlating the available density data was 2.7 per cent.

A relationship was also developed which relates vapor pressures between 5 and 760 mm Hg, internal heats of vaporization and the number of carbon atoms in a molecular chain for an homologous series. The maximum error in correlating the internal heat of vaporization data was 8.2 per cent. This relationship was also used to determine energies of vaporization which can be ascribed to different functional groups independently of the remaining molecule.

Both of the above correlations were applied to the straight chain homologous series consisting of the n-alkanes, n-alkenes, n-alkyl chlorides, and the n-alkanols.

APPROVAL OF DISSERTATION

RELATIONSHIPS BETWEEN SOME PROPERTIES OF

PURE HOMOLOGOUS ORGANIC LIQUIDS

BY

HERBERT R. KEMME

FOR

DEPARTMENT OF CHEMICAL ENGINEERING

NEWARK COLLEGE OF ENGINEERING

BY

FACULTY COMMITTEE

APPROVED: _____ Chairman

_____

_____

_____

_____

NEWARK, NEW JERSEY

JUNE 1967

ACKNOWLEDGEMENTS

I want to express my heartfelt gratitude to Dr. Saul I. Kreps for his continued guidance and encouragement. I especially want to thank Dr. Kreps for his deep interest and concern during the course of this investigation. Without him this work would never have been completed.

A three year grant from the United States Government through the National Defense and Education Act and additional support from the Newark College of Engineering Research Foundation is also gratefully acknowledged.

I also want to thank my wife Doris for her understanding and patience as this work was in progress and for typing the manuscripts.

H.R.K.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

INTRODUCTION

In order to describe the state of pure liquids, certain physical and thermodynamic properties must be defined. Such properties as density, vapor pressure, temperature, viscosity, heat of vaporization and the critical properties are among the more common of these. Each of these properties is dependent upon the same molecular parameters. Very simply, these parameters concern themselves with the molecular structure, the molecular energy, and the inter- and intramolecular potentials. Realizing this dependency, one might hope to find relationships between some of the defined properties. This would be of great utility in predicting unmeasured properties from a knowledge of others. These expressions might also find applicability in computer work since they could be easily stored and recalled whenever liquid properties are desired. The result would be a great saving in computer storage space over that required to store the individual bits of data.

In reviewing the properties of a liquid, it can be seen that vapor pressure is one of the more variable properties. For example, while the density of a pure

organic liquid varies by about 25 per cent, the vapor pressure will vary over one hundred fold. Over this same range the absolute temperature and the heat of vaporization will vary by about 30 per cent and 50 per cent respectively. Thus it would be desirable to relate other properties to vapor pressure since reasonably accurate vapor pressure data could be used to predict these unknown properties with good precision and accuracy.

The purpose of this work is two-fold in nature, the first being to investigate some of the "inter-property" relationships. This objective, if it is not to be entirely trivial as merely an empirical correlation, should be based at least in part on an acceptable theory of liquid structure.

The second purpose is to improve and expand upon the existing vapor pressure data. This is here accomplished by a method known as differential thermal analysis. As this work was started, only imprecise vapor pressure data for toluene had been determined using this technique. Thus a good deal of development work was necessary so that vapor pressure data could be determined simply, rapidly, and accurately.

This study concentrates on the relationships which exist within several normal straight chain homologous

series. In this way the effect of structure can be more easily ascertained since such compounds present an orderly and consistent variation. The basic series considered is the normal alkanes. Subsequent to this series, consideration is given to the normal olefins, the normal alkyl chlorides, and the normal primary alcohols. The different functional end groups present a chance to study the effect of substituents characterized by varying amounts of polarity. This work is primarily concerned with the relationships between vapor pressure, temperature, liquid density, heat of vaporization and molecular structure.

LITERATURE SURVEY

Available Vapor Pressure Data

Vapor pressure-temperature data for four normal homologous series were obtained. These include the alkanes, the primary olefins, the primary alkyl chlorides and the primary alcohols containing straight chains of one to twenty carbon atoms. Winslow (71) has performed a survey of the available experimental data on many homologous series. His findings are among those reported below.

Alkanes and primary olefins. Winslow's search has shown that there has been a great deal of data collected for the alkanes and the primary olefins. The American Petroleum Institute (57) has compiled all of the worthwhile data and presented it analytically in terms of the Antoine equation between 10 and 1500 mm Hg. Great care was exercised by the API in analyzing the data so that accurate results would be obtained. It was felt that this information was of sufficient quality so that it could be applied with confidence in this work.

Primary alkyl chlorides. Li and Rossini (42) have surveyed the available data and have shown that only 170 pairs of vapor pressure-temperature points exist for this

series. One hundred twenty-four of these points consist of data for the first four members of the series. Within these data one finds much variation. For example, the boiling point of 1-butyl chloride at 760 mm Hg is reported by Dreisbach and Martin (14) as 78.44 degrees Centigrade while Lenth (40) measures 77.5 degrees Centigrade. This discrepancy is equivalent to a variation in vapor pressure of about 25 mm Hg at this pressure. On this basis it was decided to use the estimates of Li and Rossini (42) only when first-hand experimental data were lacking.

Normal primary alcohols. A fair amount of data exists for the first eight members of the series, expecially for the even numbered compounds. Above this point the data are very sparse and of unknown accuracy. The American Petroleum Institute (57) has published vapor pressure data on these alcohols, but no source is indicated. The boiling points at different pressures are given only to the closest degree above octanol. This might indicate that the data presented are only estimates based on the information available in the literature. Because of the uncertainty involved, the API data were used only when experimental data were not available.

In summary, it was found necessary to obtain vapor pressure data for the normal primary alkanols and alkyl

chloride homologous series by precise experimentation.

Vapor Pressure Equations

In order to apply the experimental vapor pressure data in an analytical fashion, it is advantageous to fit the results to an equation. It is desirable that such an equation be relatively easy to handle and yet describe the data as accurately as the experimental results warrant. Many vapor pressure equations have been proposed, some possessing a semitheoretical background, others purely empirical in nature. Many vapor pressure equations require the use of reduced parameters. These equations were not considered because many of the critical properties are not known, especially for the higher members of homologous series. Computational methods are available to estimate the critical properties, but even these are of doubtful accuracy (22).

Thompson (62) presents a review of the important equations which have been used. A set of vapor pressure equations was developed from the Clapeyron equation, each one based upon different simplifying assumptions. The Clapeyron equation may be written in the following form:

$$\frac{d(\ln P)}{d(1/T)} = -\left[\frac{1}{R}\right]\left[\frac{\Delta H_v}{\Delta Z}\right] \qquad (1)$$

where: $\Delta Z = Z_g - Z_l$

$Z_g = Pv'_g/RT$

$Z_l = Pv'_l/RT$

P = Vapor pressure

T = Absolute temperature

ΔH_v = Heat of vaporization

v'_g = Molecular volume of the gaseous phase

v'_l = Molecular volume of the liquid phase.

The simplest vapor pressure equation could be obtained by assuming v'_l negligible compared to v'_g, ΔH a constant, and that the ideal gas law is obeyed. The resulting equation would be

$$\ln P = A - \frac{B}{T} \qquad (2)$$

where A and B are constants.

This equation is known as a "1/T" form. Nernst (62) presented one of the first of the more important equations in this class. In order to integrate the Clapeyron equation he assumed ΔH and ΔZ to be functions of temperature and pressure respectively. The resulting equation is

$$\log_{10} P = \frac{\Delta H_o}{2.3RT} + \frac{\beta}{2} \log_{10} T - \frac{\epsilon T}{2.3R} + C \qquad (3)$$

where ΔH_o, β, ϵ, and C are empirical constants. This equation has been used widely because the addition of two extra terms to the 1/T form improves the precision to a great extent. One of the latest representative equations in this group is the equation presented by Frost and Kalkwarf (24). This equation makes use of van der Waals' equation in expressing the change in volume from the liquid to the gaseous state and assumes ΔH to be linear in temperature. The resulting equation might be shown in the following form:

$$\log_{10} P = A + \frac{B}{T} + C \log_{10} T + D \frac{P}{T^2} \qquad (4)$$

where A, B, C, and D are empirical constants. It can be readily seen that a disadvantage exists in solving for P since a recursive method must be used.

The empirical school suggested many equations, some of which describe vapor pressure data very accurately over extended ranges. They offer very little, if any, theoretical basis and in many cases are quite complex. Because they are so numerous and offer no insight into the problem of expressing vapor pressure data in an analytical fashion, they will not be discussed in this work.

In considering the entire mass of available equations,

it becomes apparent that the more complex equations describe the data with greater accuracy but the required constants are difficult and tedious to determine. An example is the complex water equation of Osborne and Meyers (49) shown as

$$\log P = A - \frac{B}{T} + \frac{Cx}{T}\left[10^{Dx^2} - 1\right] - E\left[10^{Fy^{5/4}}\right] \qquad (5)$$

where: A, B, C, D, E, K, and F are constants

$x = T^2 - K$

$y = 374.11 - t$

t = temperature, ^{o}C

T = absolute temperature, ^{o}K

After considering the range of available equations it was decided to use the Antoine equation expressed as

$$\log_{10} P = A - \frac{B}{C+t} \quad . \qquad (6)$$

This equation provides the desired degree of accuracy, offers a direct and simple solution for either T or P and is well known in vapor pressure studies. It is the equation of choice in the API tables of physical properties.

Density Correlations

There are a wide variety of density correlations which are functions of the critical constants of substances.

These relations are not mentioned here because critical parameters were not utilized or considered in this work.

Schroeder (52) and Le Bas (54) present additive methods of estimating densities of hydrocarbons at the normal boiling point. They are additive methods in the sense that each atom or functional group in a molecule is represented by a volume increment. The summation of these increments results in the molal volume. Only the molecular structure is considered in utilizing these methods. Egloff and Kuder (16) relate molal volumes at the normal boiling point as a function of the number of carbon atoms and three constants. This purely empirical equation was used by them to correlate the data for fourteen different series of aliphatic hydrocarbons.

Kurtz and Sankin (38), using similar structural considerations, empirically related the density of liquid hydrocarbons of a molecular weight greater than 170. By the use of graphically presented multiplication factors the structural values are corrected for pressure and temperature. Thus density can be estimated between -100 and 200 degrees Centigrade and 1 to 10,000 psia.

Several purely empirical relations are presented which relate the density of liquid hydrocarbons at a single temperature to the number of carbon atoms and some structural

factors. Francis (20) correlates the density of several homologous series at 20 degrees Centigrade with the number of carbon atoms and two constants, one of which is fairly universal, and the other depends on the structural configuration of the series. A similar relationship is presented by Calingaert et al (6) in which the density of the normal and branched chain alkanes are empirically correlated as a function of the number of carbon atoms and four constants. A related approach is taken by Greenshields and Rossini (27) and Li et al (43) to obtain densities at 25 degrees Centigrade. Calingaert and Hladky (7) graphically correlate the densities of the alkanes at 20 degrees Centigrade. They claim that the graph can be used to predict unknown densities.

A four constant equation was proposed by Francis (21) to correlate the densities of saturated liquid hydrocarbons up to temperatures approaching the critical. The constants have to be evaluated for each individual compound.

Miller (47) found that the density was a linear function of the internal heat of vaporization for non-polar simple hydrocarbon liquids.

Pratap and Narsimhan (53) derived a relationship based on Eyring's theory of the liquid state. The equation relates viscosity, heat of vaporization, density, velocity of sound

in the liquid and temperature in the range of 0 to 50 degrees Centigrade.

Meissner and Paddison (46) inter-relate density, normal boiling point, molar refraction based on the sodium D line, surface tension and vapor pressure. Their equation contains a constant which varies only with the class of compound.

Heat of Vaporization Correlations

Again it should be mentioned that correlations requiring critical parameters are not reviewed because they were not applied in this work.

The most common correlation is based upon the well known Clapeyron equation. Its major disadvantages are that it requires an accurate knowledge of the slope of the vapor pressure curve, and a knowledge of the difference in the saturated molal volumes of the liquid and vapor. The slope of the vapor pressure curve can be obtained by differentiating an analytical expression for vapor pressure in terms of temperature. Haggenmacher (29) suggested the use of the Antoine equation as the vapor pressure function. The volume difference can be expressed in terms of the ideal gas equation and a delta compressibility factor, ΔZ, which is equal to the difference between the compressibility factors for the liquid and vapor. Fishtine (18) relates this ΔZ to the

ratio $\frac{T}{T_b}$

where: T = temperature, ^oK

T_b = normal boiling point, ^oK.

Dreisbach (13), starting with Haggenmacher's equations for ΔZ in terms of critical parameters, shows ΔZ to be a function of temperature and molecular weight.

Othmer (50) and Gorden (26) both apply a reference substance equation for the correlation of latent heats. This method is based upon the assumption that the ratio of the latent heats of any one known substance to another is a constant. Thus the ratio of the differential form of the Clausius-Clapeyron equation for one substance to that of another substance can be integrated. The result is a linear equation of the form

$$\log P = \left[\frac{L_v}{L_{vR}}\right]_T \log P + k \qquad (7)$$

where: P = vapor pressure

L_v = latent heat of unknown substance

L_{vR} = latent heat of reference substance

k = constant.

By knowing the latent heat of the reference substance as a function of temperature and knowing two values of the vapor

pressure of the unknown substance, the latent heat may be determined.

Several methods have been proposed for the determination of the latent heat at the normal boiling point. Kistiakowsky (34) proposed a very simple relationship between the latent heat of vaporization and the normal boiling point for unassociated liquids. The equation requires only the knowledge of the boiling point itself. Chipman (9) proposed correction factors for the Kistiakowski equation to make it applicable to several series of polar liquids. Fishtine (18) improved upon Chipman's work by increasing the number of available Kistiakowsky factors for different classes of compounds. Chu et al (11) and Bowden and Jones (54) proposed equations based upon structure, including such terms as parachor, polarity number, and path length. These methods were reported to be good within 2 per cent for the paraffin hydrocarbons.

McCurdy and Laidler (45) correlate the heats of vaporization of several alcohols by assigning to various types of bonds different latent heat values. Thus by summing these values for any individual molecule the total latent heat value will be obtained. Errors of only a few tenths of a per cent are claimed for fourteen alcohols.

Some work has been done in deriving semi-empirical

equations based upon the free volume concept of Eyring, including his hole theory of liquids. Pratap and Narsimhan (53) show the latent heat to be a function of the velocity of sound in liquids, the viscosity of the liquid and the molal volume. The equation has only been applied between 0 and 50 degrees Centigrade. Marcus (44) relates the internal energy of vaporization with density, temperature and vapor pressure. The equation is difficult to use since the energy of vaporization must be obtained by iteration techniques. Errors of 20 to 30 per cent are not uncommon using this equation. Kurata and Isida (37) developed a model for the liquid structure of the normal paraffins based upon the hole theory of liquids. In their derivation it was assumed that the cell size was somewhat larger than a methane molecule and that a paraffin molecule occupied a multiple number of cells. Based upon this model, equation (8) was derived, relating internal heat of vaporization at constant pressure to the number of carbon atoms in a chain.

$$E_v = N^{2/3}(z\epsilon/2) \tag{8}$$

where: E_v = internal heat of vaporization

N = number of carbon atoms

z = number of nearest neighbor cells

ϵ = energy required for the separation of two cells

Nakanishi, Kurata and Tamura (48) improved upon this work by developing a relationship, equation (9), which relates the heat of vaporization with the number of carbon atoms and the vapor pressure.

$$H_v = \frac{2128\ N^{2/3}}{1+0.00512\ N^{2/3}+(.0930)(\log P)} \qquad (9)$$

where: P = vapor pressure

H_v = heat of vaporization.

Kreglewski and Zwolinski (36) based their empirical equation (10) upon Kurata and Isida's determination that the effective chain length varied as the two-thirds power of the number of carbon atoms.

$$\log (H_{v\infty} - H_v) = a - bN^{2/3} \qquad (10)$$

where: H_v = heat of vaporization

$H_{v\infty}$ = heat of vaporization when $N^{2/3} = \infty$ and

N = number of carbon atoms.

AN INTRODUCTION TO SOME ASPECTS OF LIQUID STATE THEORY

The Correlation of Vapor Pressure Data

The Antoine equation. As mentioned in the literature survey, the Antoine equation was chosen because of its simplicity, accuracy, and wide acceptance as an equation for the correlation of vapor pressure as a function of temperature.

The equation, when originally proposed by Antoine (1), had no theoretical basis, thereby being completely empirical in nature. It would be desirable to be able to obtain this equation from theoretical considerations. One might then be able to judge the reliability of experimental data on the basis of how well it fits the Antoine equation.

It was shown by Gutmann and Simmons (28) that the equation is derivable from the van der Waals equation of state which can be written

$$(P + a/V^2)(V - b) = RT. \qquad (11)$$

RT may be considered to represent the thermal energy of a liquid. This term was expressed by Tetrode (61) in terms of γ, the frequency of a possible mode of molecular

vibration, γ_m, the highest value thereof, and Planck's constant h'. Thus, according to Tetrode,

$$\left[P + \frac{a}{V^2}\right](V - b) = \frac{3N_o}{\gamma_m^3}\int_0^{\gamma_m} \frac{h'\gamma}{e^{h'\gamma/kT}-1}\gamma^2 d\gamma \quad . \qquad (12)$$

Tetrode obtained this equation by assuming that the system could be considered as a set of molecules which could vibrate about stationary points. The vibrations per molecule were quantized as was proposed by Einstein, but a continuous range of frequencies for the total system was assumed as was done by Debye (12). The equation may be applied to a liquid if it is assumed to be quasi-crystalline in nature, a model that has been proposed by Steward (59), Frenkel (23) and others. This view is also consistent with the hole theory.

The integral of equation (12) cannot be solved in a closed form, but Debye (12) presents a series solution. Equating the energy of the highest possible frequency, $h'\gamma_m$ to $k\theta_o$, where θ_o is the Debye temperature, and solving the integration in equation (12) one obtains,

$$(P + a/V^2)(V - b) = RT - \frac{3}{8} R\theta_o + \frac{RT\theta_o^{\,2}}{20T^2} - \frac{RT\theta_o^{\,4}}{1680T^4} + \ldots \qquad (13)$$

Wall (67) has shown that,

$$\ln f = \frac{b}{V-b} - \frac{2a}{V\phi(T)} + \ln \frac{\phi(T)}{V-b} \tag{14}$$

where $\phi(T)$ in this case is the right side of equation (13) and f is the fugacity.

If V could now be expressed in terms of temperature, and assuming that the fugacity is equal to the vapor pressure, one would have an expression for the vapor pressure in terms of temperature. Wall has shown that the volume of liquid may be approximated by solving for the linear V term in the van der Waals equation, assuming the quadratic and cubic terms negligible. Thus,

$$V = b + \left[\frac{bP+RT-PV}{a}\right] V^2 \approx b \ . \tag{15}$$

If the value of V obtained is substituted back into the right-hand portion of the van der Waals equation (15) and again solved for V, a first approximation is obtained. This operation may be repeated for successively better approximations. The result of this method if applied to equation (13) is

$$V = b + \left[b^2\phi(T)/a\right] + \left\{\left[2b^3\phi^2(T)/a^2\right] - \left[b^4\phi(T)P/a^2\right]\right\} + \ldots \tag{16}$$

If only pressures below one atmosphere are considered, the effect of pressure upon the volume of a liquid can be neglected and only the first two terms in equation (16) are required. Also the fugacity may be assumed equal to the vapor pressure and substituting (16) into (14) the result is of the form,

$$\ln P = A - B/\phi(T) \ . \tag{17}$$

By retaining the first two terms for $\phi(T)$ and substituting into (17) an equation is obtained which is identical in form to the Antoine equation

$$\ln P = A - \frac{B}{C+t} \tag{18}$$

where the constant C is identified with $273.16 - \frac{3}{8}\,\theta_o$.

Thus one should be able to calculate C from the knowledge of θ_o which is directly related to γ_m. Gutmann and Simmons (28) have used the values of γ_m calculated by Waring and Becker (68) to obtain C for a number of organic liquids. The values so calculated lie between 234 and 254.5. These values are of the proper magnitude, thereby giving increased credence to the previous development.

Liquid Models

In order to inter-relate the physical properties of a liquid by relations derivable from theoretical considerations, it is convenient to assume a model for the liquid state. Several lattice models are available (31) such as the cell, hole, and tunnel models. Because of the relative simplicity, the hole model of the liquid state seemed to be more amenable in describing a system of large regular molecules than any of the other models.

Kurata and Isida (37) applied this model to normal paraffin liquids in order to derive relationships which relate the number of carbon atoms in a molecular chain with the normal boiling point, the critical properties and the heat of vaporization at atmospheric pressure. It is their development which is used as a basis for an equation which relates liquid density with the vapor pressure and the number of carbon atoms in a chain. It also leads to another equation which relates the heat of vaporization with the vapor pressure and the number of carbon atoms.

A Hole Theory of Liquids

The present hole theory of liquids requires that a liquid system be divided into an array of cells, whose size is constant and is invariant with temperature and pressure. It is further assumed that the size of the cell is such that simultaneous entry of two molecules into one

cell can be entirely neglected because of the repulsive forces between molecules. The liquid state, therefore, consists of a system of cells, some of which are full, i.e. they contain a molecule, and others which are empty. As the temperature of such a liquid is raised, the number of empty cells increases, inducing an increase in volume and a corresponding decrease in density.

In considering a long chain molecule such as a normal paraffin, a cell volume, $\mathcal{V}$, may be chosen which is independent of the chain length and which occupies a volume somewhat larger than a methane molecule. A paraffin molecule containing n carbon atoms would thus occupy a certain number of consecutive cells, denoted by x.

Free Energy of the System

The liquid system proposed may be regarded as a type of "solution" containing hole "solvent" and the randomly distributed molecular "solute". The Helmholtz free energy of the system, F, can therefore be described in terms of the intramolecular free energy, F_I, the ideal free energy of mixing, F_{MIX}^{IDEAL}, and the excess free energy of mixing, F_{MIX}^{E}, so that,

$$F = F_I + F_{MIX}^{IDEAL} + F_{MIX}^{E} \quad . \tag{19}$$

The intramolecular free energy may be expressed as a function of the number of molecules in the system, N, and the free energy, f, related to the intramolecular degrees of freedom. Thus one may write,

$$F_I = Nf \quad . \tag{20}$$

The ideal free energy of mixing might be described if the Flory approximation is adopted in calculating the configurational entropy of mixing. Flory (19) developed an expression for the configurational entropy of mixing for a solution of rod-like polymers and single-site solvent molecules. Kurata and Isida proposed that this expression was mathematically identical with a "solution" of long chain paraffin molecules and holes as described above. In order to more fully appreciate the development of this theory, Flory's derivation will be presented, keeping in mind that the polymer molecule is replaced by a paraffin molecule, and that the single-site solvent molecules are now holes.

The Configurational Entropy of Flory

Throughout the derivation it is understood that only molecules which consist of a single linear sequence of structural units are considered, and that a hole theory of liquids is assumed. The following assumptions are also made:

1. All molecules are assumed to be of the same size.
2. The average concentration of molecular segments in cells adjacent to empty cells, i.e. holes, is equal to the overall average concentration of molecular segments in the liquid.

Let n_o equal the total number of cells in the lattice, and N_o equal the total number of molecules, each composed of x segments, any one of which may move into a vacant site. Let z equal the coordination number, otherwise known as the number of nearest neighbor cells. In order to determine the total possible number of non-identical configurations, it is suggested that successive additions of molecules be made to the empty lattice containing n_o cells.

After N_o molecules have been added, there will be available $n_o - xN_o$ cells which may be occupied by the terminal segment of the next molecule to enter the lattice. If the assumption of uniform distribution of holes is valid, then the number of unoccupied cells immediately adjacent to the terminal segment will be given by $z(n_o - xN_o)/n_o$. Since this last segment eliminates one of the neighboring cells, the number of cells available for the next segment would be

$$\alpha = (z - 1)(n_o - xN_o)/n_o \quad . \tag{21}$$

This relationship is not completely rigorous since it

does not exclude impossible configurations in which two segments belonging to the same chain but separated by two or more segments, occupy the same cell. Equation (21) will lead to the computation of too many configurations, but will be used as an approximation.

The number of configurations that a chain containing x segments may have without shifting a terminal group may therefore be expressed as

$$\left[\frac{z(n_o - xN_o)}{n_o}\right]\left[\frac{(z-1)(n_o - xN_o)}{n_o}\right]^{x-2} \quad . \tag{22}$$

If α is defined as

$$(z - 1)(n_o - xN_o)/n_o \quad , \tag{23}$$

then expression (22) becomes

$$\left[z/(z - 1)\right]\alpha^{x-1} \quad . \tag{24}$$

Since the terminal group can enter any one of $(n_o - xN_o)$ cells, the total number of configurations, Γ, that the $N_o + 1$ molecular chain may have in the entire lattice is written as

$$V_{N_o+1} = \tfrac{1}{2}\,(n_o - xN_o)\left[z/(z-1)\right]\alpha^{x-1} \quad . \tag{25}$$

The factor $\frac{1}{2}$ is introduced to avoid redundance of configurations resulting from the indistinguishability of the ends of a molecular chain.

Remembering the definition of α by expression (23) one may write equation (25) as,

$$V_{N_o+1} = \tfrac{1}{2}\,(n_o - xN_o)^x \left[\frac{(z)(z-1)}{(z-1)}\right]^{x-1} \left[\frac{1}{n_o}\right]^{x-1} . \tag{26}$$

If as an approximation z - 1 is considered equal to z, equation (26) becomes

$$V_{N_o+1} \approx \tfrac{1}{2}\,(n_o - xN_o)^x\,(z-1)^{x-1}(n_o)^{1-x} \quad . \tag{27}$$

Again, equation (27) may be rewritten as

$$V_{N_o+1} = \tfrac{1}{2}x^x\left[\frac{n_o}{x} - N_o\right]^x\left[\frac{z-1}{n_o}\right]^{x-1} \quad . \tag{28}$$

The total number of configurational combinations, W, for the system consisting of N_o molecules can be expressed by

$$W = (1/N_o!)\prod_{N_o=1}^{N_o} V_{N_o} \quad , \tag{29}$$

where the factor $1/N_o!$ eliminates redundant configurations obtained only by an interchange of one or more pairs of molecules. The term

$$\prod_{N_o=1}^{N_o} V_{N_o}$$

represents the products of the total possible number of configurations which each succeeding molecular chain may have as it enters the lattice.

The general equation (28) for the number of configurations which the N_o+1 molecule may assume as it enters the lattice may now be substituted into equation (29) such that,

$$W = \left[\frac{z-1}{n_o}\right]^{(x-1)N_o} \left[\frac{x^{xN_o}}{2^{N_o}N_o!}\right] \prod_{N_o=1}^{N_o} \left[\frac{n_o}{x} - N_o\right]^x \quad . \qquad (30)$$

It should be remembered that the term N_o within the product bracket is equal to the number of molecules within the lattice just before an additional molecule is added. Thus N_o will be equal to zero when the initial molecule is placed in the lattice. The product term within the bracket is therefore equal to the series shown in expression (31).

$$\left[\frac{n_o}{x} - 0\right]\left[\frac{n_o}{x} - 1\right]\left[\frac{n_o}{x} - 2\right] \cdots\cdots \left[\frac{n_o}{x} - N_o+1\right] \qquad (31)$$

Series (31) may be written as the ratio of two series as shown below.

$$\frac{\left[\frac{n_o}{x}\right]!}{\left[\frac{n_o}{x}-N_o\right]!} = \frac{\left[\frac{n_o}{x}\right]\left[\frac{n_o}{x}-1\right]\ldots\left[\frac{n_o}{x}-N_o+1\right]\left[\frac{n_o}{x}-N_o\right]\left[\frac{n_o}{x}-N_o-1\right]\ldots(1)}{\left[\frac{n_o}{x}-N_o\right]\left[\frac{n_o}{x}-N_o-1\right]\ \ldots\ldots\ (1)} \qquad (32)$$

By canceling terms on the right-hand side of equation (32) expression (31) is easily obtained. Equation (30) may then be written as

$$W = \left[\frac{z-1}{n_o}\right]^{(x-1)N_o}\left[\frac{x^{xN_o}}{2^{N_o}N_o!}\right]\left[\frac{(n_o/x)!}{(n_o/x-N_o)!}\right]^{x} \quad . \qquad (33)$$

Since N_o is a sufficiently large number, $N_o!$ may be replaced by $(N_o/e)^{N_o}$ using Stirling's approximation. The resultant equation is

$$W = \left[\frac{z-1}{e}\right]^{(x-1)N_o}\ (\tfrac{1}{2})^{N_o}\ \frac{(h+xN_o)}{h^h N_o^{N_o}}^{\ h+N_o} \qquad (34)$$

where H, the number of holes, equals $n_o - xN_o$.

The change in entropy when introducing holes into a perfectly arranged crystalline solid may be expressed by the Planck-Boltzmann equation given by Lewis and Randall (41) as,

$$S = k \ln W \quad . \qquad (35)$$

Here W is known as the thermodynamic multiplicity. It may be expressed as

$$W = \frac{W_{MIX}}{W_H W_M} \tag{36}$$

where W_{MIX} is the number of configurations possible in the mixture and W_H and W_M are the number of configurations possible for the "pure" holes and the perfectly arranged crystalline solid respectively. W_H and W_M are both equal to one since only one configuration is possible. Therefore, $W = W_{MIX}$. Thus equation (34) may be substituted into equation (35) resulting in

$$\Delta S_{MIX} = - k \ln \left[\frac{h^h N_o^{N_o}}{(h+xN_o)^{h+N_o}} \right]$$

$$+ k(x-1)(N_o)\left[\ln (z-1)-1\right] - kN_o \ln 2 \quad . \tag{37}$$

Equation (37) may be rearranged to give,

$$\Delta S_{MIX} = - k \ln \left[\left(\frac{h}{h+xN_o}\right)^h \left(\frac{N_o}{h+xN_o}\right)^{N_o} \right]$$

$$+ k(x-1)(N_o)\left[\ln (z-1)-1\right] - kN_o \ln 2 \quad . \tag{38}$$

Equation (38) can again be rearranged to give

$$\Delta S_{MIX} = - k\left[h \ln\left(\frac{h}{h+xN_o}\right) + N_o \ln\left(\frac{N_o}{h+xN_o}\right)\right.$$

$$\left. + k\,(x-1)N_o\left[\ln\,(z-1) - 1\right] - kN_o \ln 2\right] . \qquad (39)$$

When a perfectly arranged crystalline solid reverts to a disordered solid, the change in entropy may be found by setting h in equation (39) equal to zero. This is equivalent to assuming that no holes exist in a solid. Thus the entropy of disordering a perfectly arranged solid, ΔS^*, is

$$\Delta S^* = kN_o \ln\,(x/2) + kN_o\,(x - 1)\left[\ln\,(z - 1) - 1\right] . \qquad (40)$$

Therefore, to find the change in entropy when holes are introduced into a randomly arranged solid one subtracts (40) from (39) resulting in

$$\Delta S'_{MIX} = - k\left[h \ln\left(\frac{h}{h+xN_o}\right) + \ln\left(\frac{xN_o}{h+xN_o}\right)\right] . \qquad (41)$$

Since no forces of attraction or repulsion between molecules were considered, $\Delta S'_{MIX}$ may be thought of as the ideal entropy of mixing. If the free energy reference state for this system is chosen as "pure" holes plus a random lattice of molecules at temperature T, then the ideal

free energy of mixing may be expressed as

$$F_{MIX}^{IDEAL} = - T\Delta S_{MIX} \cdot \tag{42}$$

If one considers a system of volume V, then,

$$h = (V/\tau) - xN_o \tag{43}$$

and F_{MIX}^{IDEAL} may be expressed as

$$F_{MIX}^{IDEAL} = kT\left[\left((V/\tau) - xN_o\right)\ln\left(1 - (\tau xN_o/V)\right) + N_o \ln (\tau xN_o/V)\right] \cdot \tag{44}$$

Since the actual system is not ideal, one must determine the increase of free energy during mixing resulting from intermolecular forces. The term ψ may be defined as the increase in free energy occurring with the following rearrangement

where  represents a full cell and the blanks represent holes. Thus there is an interaction energy of $\frac{\psi}{2}$

per cellular interaction. The excess free energy of mixing, F^E_{MIX}, can then be expressed as

$$F^E_{MIX} = \left[1/2zn_o\right]\left[\frac{\Psi}{2}\right]\left[2\right]\left[\frac{h}{n_o}\right]\left[\frac{xN_o}{n_o}\right] \quad . \tag{45}$$

Here $\left[2\right]\left[\frac{h}{n_o}\right]\left[\frac{xN_o}{n_o}\right]$ represents the probability of finding a full cell — empty cell interaction, where the factor 2 arises because both hole-full and full-hole cell interactions are considered. Every such interaction requires a rearrangement, resulting in an increase of free energy, $\frac{\Psi}{2}$, upon mixing holes with full cells. The factor $1/2zn_o$ is the total number of cellular interactions in the system. If V is the volume of the lattice then

$$\frac{V}{\tau} - xN_o = h \ , \quad \text{and} \tag{46}$$

$$n_o = \frac{V}{\tau} \quad . \tag{47}$$

Substituting these equations into equation (45) and rearranging, one obtains

$$F^E_{MIX} = \tfrac{1}{2}z\Psi\left[(V - \tau xN_o)\left(\frac{xN_o}{V}\right)\right] \quad . \tag{48}$$

At this point the total free energy may be defined by combining equations (20), (44) and (48) resulting in

$$F = N_o f + kT\left\{\left[V/\tau - xN_o\right] \ln\left[1 - (\tau xN_o/V)\right]\right.$$

$$\left. + N_o \ln (\tau xN_o/V)\right\} + (z\Psi/2)(V - \tau xN_o)(xN_o/V) \ . \quad (49)$$

This is equivalent to equation (1) in the paper presented by Kurata and Isida (37). Their derivation continues below.

The Kurata-Isida Vapor Pressure Equation

The pressure P, and the chemical potential, μ , of a system may be described as,

$$P = -\left(\frac{\delta F}{\delta V}\right)_{T,N} \quad (50)$$

$$\mu = \left(\frac{\delta F}{\delta N_o}\right)_{T,V} \ . \quad (51)$$

Thus, by differentiating equation (49) as per equations (50) and (51) one obtains

$$P = -\left(\frac{\delta F}{\delta V}\right)_{T,N} = -\frac{kT}{\tau}\left\{\ln\left[1 - \frac{\tau xN_o}{V}\right]\right.$$

$$\left. + \left[V - xN_o\tau\right]\left[\frac{\tau xN_o}{V^2}\right]\left[\frac{V}{V-\tau xN_o}\right] + \left[\frac{-\tau N_o}{V}\right]\right\} - \left[\frac{z\Psi}{2\tau}\right]\left[\frac{\tau xN_o}{V}\right]^2 \quad (52)$$

and,

$$\mu = \left(\frac{\delta F}{\delta N_o}\right)_{T,V} = f + kT\left\{\left[\frac{V}{\tau} - xN_o\right]\left[\frac{-\tau x}{V-\tau xN_o}\right] - x \ln\left[1 - \frac{\tau xN_o}{V} + 1\right]\right.$$

$$\left. + \ln\left[\tau x\frac{N}{V}\right]\right\} + \frac{xz\psi}{2}\left[1 - \frac{2\tau xN_o}{V}\right] \quad . \qquad (53)$$

Let v represent the volume per molecule, V/N_o. By rearranging equations (52) and (53) and substituting v, the volume per molecule, for V/N_o one arrives at,

$$P = -\frac{kT}{\tau}\left\{\ln\left[1 - \frac{x\tau}{v}\right] + (x - 1)\frac{\tau}{v}\right\} - \frac{z\psi}{2\tau}\left[\frac{x\tau}{v}\right]^2 \qquad (54)$$

$$\mu = f + kT\left\{\ln\left[\frac{x\tau}{v}\right] - x \ln\left[1 - \frac{x\tau}{v}\right] - (x-1)\right\} + \frac{zx\psi}{2}\left[1 - \frac{2x\tau}{v}\right]. \qquad (55)$$

When considering a two phase system at equilibrium it is necessary that the pressures and the chemical potentials of the two phases be equal so that

$$P_g = P_l \qquad (56)$$

and

$$\mu_g = \mu_l \quad . \qquad (57)$$

Note that the subscripts g and l are adopted to represent

the gaseous and liquid phases respectively. Thus from equations (54) and (55) one may write

$$\ln\left[1 - \frac{x\tau}{v_g}\right] + (x - 1)\frac{\tau}{v_g} + \frac{z\psi}{2kT}\left[\frac{x\tau}{v_g}\right]^2 = \ln\left[1 - \frac{x\tau}{v_1}\right]$$

$$+ (x-1)\frac{\tau}{v_1} + \frac{z\psi}{2kT}\left[\frac{x\tau}{v_1}\right]^2 \qquad (58)$$

and

$$\frac{1}{x}\ln\left[\frac{x\tau}{v_g}\right] - \ln\left[1 - \frac{x\tau}{v_g}\right] + \frac{z\psi}{2kT}\left[1 - \frac{2x\tau}{v_g}\right] = \frac{1}{x}\ln\left[\frac{x\tau}{v_1}\right]$$

$$- \ln\left[1 - \frac{x\tau}{v_1}\right] + \frac{z\psi}{2kT}\left[1 - \frac{2x\tau}{v_1}\right], \qquad (59)$$

assuming that $f_1 = f_g$.

Assume, for simplicity, that v_g is very large compared with v_1 or $x\tau$ at temperatures below the boiling point. Equation (54) then reduces to the ideal gas equation,

$$P = kT/v_g \quad . \qquad (60)$$

If equations (58) and (59) are combined with equation (60), assuming v_g much greater than v_1, one obtains the Kurata-Isida vapor pressure equation

$$\ln P = \ln\left[\frac{kT}{v_1}\right] + (x - 1)\left[\frac{x\tau}{v_1}\right] - \frac{xz\psi}{2kT}\left[\frac{x\tau}{v_1}\right]\left[2 - \frac{x\tau}{v_1}\right]. \qquad (61)$$

<u>The Kurata-Isida Heat of Vaporization Equation</u>

Starting with equation (61) and assuming that $x\tau = v_1$ and noting that $\psi = \epsilon - TS$, Kurata and Isida (<u>37</u>) obtained

$$\ln P = \ln (kT/x\tau) + x\left[1 + (zS/2k)\right] - 1 - x(z\epsilon/2kT). \qquad (62)$$

Here ϵ and S are the internal energy and entropy terms respectively, which are associated with the Helmholtz free energy change, ψ. It was assumed for simplicity that ϵ and S are independent of temperature, so that equation (62) could be simply differentiated. Realizing that $R = N_A k$ the following result was obtained:

$$\frac{dP}{dT} = \frac{P}{T} + \frac{P}{T^2}\left[\frac{N_A xz\epsilon}{2R}\right] = \frac{H_v}{T(v'_g - v'_l)} \qquad (63)$$

Making the usual simplifying assumptions that v'_l is negligible compared to v_g at low pressures and that the ideal gas law holds, one may write with some rearrangement

$$RT + \frac{N_A xz\epsilon}{2} = H_v = E_v + P\Delta V \qquad (64)$$

where E_v equals internal heat of vaporization.

Again, assuming the ideal gas law, equation (64) becomes

$$E_v = \frac{N_A xz\epsilon}{2} \quad . \tag{65}$$

EXPERIMENTAL WORK

Introduction

The purpose of this work was to accurately measure the vapor pressures of several series of normal chain homologous compounds containing from three to twenty carbon atoms. The proposed measurement range was from 5 to 760 mm Hg or from -40 to 350 degrees Centigrade, whichever condition was limiting. A precision of $\pm$0.1 degrees Centigrade was sought, this being equivalent to $\pm$0.1 mm Hg at an approximate vapor pressure of 5 mm Hg for most organic substances.

The dynamic, static, and gas-saturation methods were the general means available for the accurate determination of vapor pressures. The most reliable static method is that of Smith-Menzies (69) using an isoteniscope. It is claimed that the average pressure deviation is $\pm$2 mm Hg with maximum deviations as high as 6 mm Hg. The precision boiling point method of Willingham and co-workers (70) was the only applicable dynamic procedure, claiming an error of only 0.02 to 0.05 mm Hg. A precision of 0.05 to 3.5 mm Hg (69) was indicated for the gas-saturation method, but this method suffers from a heavy reliance on the assumption that there is no association in the vapor, a situation which is not

always true and is difficult to correct for.

Accuracy, sample size, experimental time, and measurement range were the factors that had to be taken into consideration in choosing a method. The pressure range is satisfied by each of the above-mentioned methods but several major disadvantages exist for each. Low temperature determinations would be difficult to handle unless cumbersome refrigeration equipment were introduced, thus possibly hindering very low temperature work. A small sample size was desirable since the higher molecular weight homologues are very difficult and costly to purify owing to isomeric impurities which have physical properties very similar to those of the desired material. Sample sizes from ten to fifty milliliters are required in each case, although some semi-micro boiling-point methods exist which utilize only forty to one hundred milligrams, but the accuracy of these is dubious. Each of the methods requires at least an hour to produce a single vapor pressure datum of sufficient accuracy, a factor which would be undesirable when many measurements have to be made and when the material is at such a temperature that it will easily suffer thermal decomposition. None of the common methods satisfied the requirements of a small sample size and a short experimental time. Only one, the precision boiling-point method of Willingham, provided the desired precision. It was thus obvious that a new method

had to be sought for the determination of vapor pressures.

Vassalo and Harden (64), Chiu (10), and Kemme (33) described a technique whereby boiling points were measured by differential thermal analysis, hereafter known as DTA. An obvious extension of these works was to measure boiling points at different pressures, thereby determining temperature vapor pressure functions. Krawitz and Tovrog (35) used the DTA method for determining the vapor pressure of toluene between 65 and 760 Torr but no precision was given. As this work was in progress, Barrall, Porter and Johnson (2) reported measuring vapor pressures between 30 and 760 Torr using differential thermal analysis. An accuracy of $\pm$0.2 degrees Centigrade was claimed.

Instrumentation

The method whereby temperature changes in a sample are measured in contrast with the temperature changes of an inert reference material is known as differential thermal analysis. Both the reference substance and the sample are in the same thermal environment which is being changed at a controlled rate. Thermocouples are usually employed to measure directly the temperature of the sample and the temperature of the inert reference substance as both undergo a linear temperature rise. The thermocouple in the sample is wired in opposition to the one in the inert reference substance in a potentiometric circuit so that at a given temperature the

net voltage output between the two thermocouples will register the difference in temperature between the sample and the inert. This voltage output is plotted against the voltage output of the sample thermocouple, producing a thermogram. In essence this thermogram shows the temperature difference between the sample and inert at any instant. A phase transition, such as boiling, which will absorb or release energy in the sample will render the sample temperature different from that of the inert reference substance so that a temperature difference is recorded. This plot is known as an endotherm if energy is absorbed by the sample or an exotherm if energy is released. In the case of boiling, the endotherm will start at the bubble point and will continue to increase until all the material is vaporized. Then the sample thermocouple will more or less slowly approach the temperature of the inert substance and the signal will return to zero. The magnitude of this difference in temperature will depend on the heat capacity, thermal conductivity, weight, amount of energy gained, and the heating rate of the sample. During this transition, the sample temperature should ideally remain constant and will be recorded as the boiling point.

Description of differential thermal analyzer (60). A modified DuPont 900 Differential Thermal Analyzer was employed to obtain all the experimental vapor pressure data.

The basic specifications and description of the system as supplied by E. I. DuPont de Nemours and Co. are presented in this section. A discussion and description of the modifications will follow:

General Specifications

Temperature Range:	-100 to 500°C with general purpose cell, higher and lower temperatures accessible with accessory cells.
Sensitivity, ΔT:	0.025°C or 10^{-3} cal
Precision, T:	0.2°C
Scale, ΔT:	0.004, 0.008, 0.02, 0.04, 0.08, 0.2, 0.4 mv/in 0.1, 0.2, 0.5, 1.0, 2, 5, 10°C/in
Scale, T:	0.4, 0.8, 2, 4, 8 mv/in 10, 20, 50, 100, 200°C/in
Presentation:	8-1/2" x 11" preprinted paper, millivolt or temperature scale
Heating/Cooling Rates:	0 to 30°C/minute, continuously variable
Operating Modes:	Heat, Cool, Hold, Cycle between preset limits
Program Starting Temperature:	Continuously variable
Sample Size:	0.1 to 50 mg with general purpose cells
Sample Atmosphere:	Vacuum, inert, or controlled composition
Size:	22-1/4" wide x 20-3/4" deep x 10-3/8" high, not including bell jar

Utilities:	115 v., 60 cycle; 220 v., 50 or 60 cycle - available on special order. 200 watts
Bench weight:	40 lbs

System description. (60) The heart of any apparatus for performing differential thermal analysis is the thermocouple system. In Figure 1, S and R represent the thermoelectric junctions of the system immersed in sample and reference respectively. The common sides of both thermocouples are joined at B. The difference in temperature between sample and reference, ΔT, is indicated by the electrical potential across the points A-C, while the temperature, T of the sample is indicated by the potential across points A-B. Accessory equipment necessary for practical experimental work is also shown schematically. This includes a block to distribute heat evenly to sample and reference materials, a programming device and heater to change the temperature of the block at a uniform and predetermined rate, a high gain, low noise amplifier to increase the sensitivity of ΔT measurement, and a variable sensitivity recorder to plot ΔT as a function of T.

Specimen and reference materials are placed either into 4 mm glass tubes, sealed at one end, or 2 mm thin-wall glass capillaries. These are symmetrically inserted into a cylinderical aluminum block, 7/8"D. x 1-1/2". The block is heated by a cartridge heater which is inserted vertically into the center of the block. The cell is designed and constructed in this way in order to insure perfectly matched thermal environments for both sample and inert.

Analytical chromel-alumel thermocouples with controlled-energy weld junctions are used to insure uniformity of

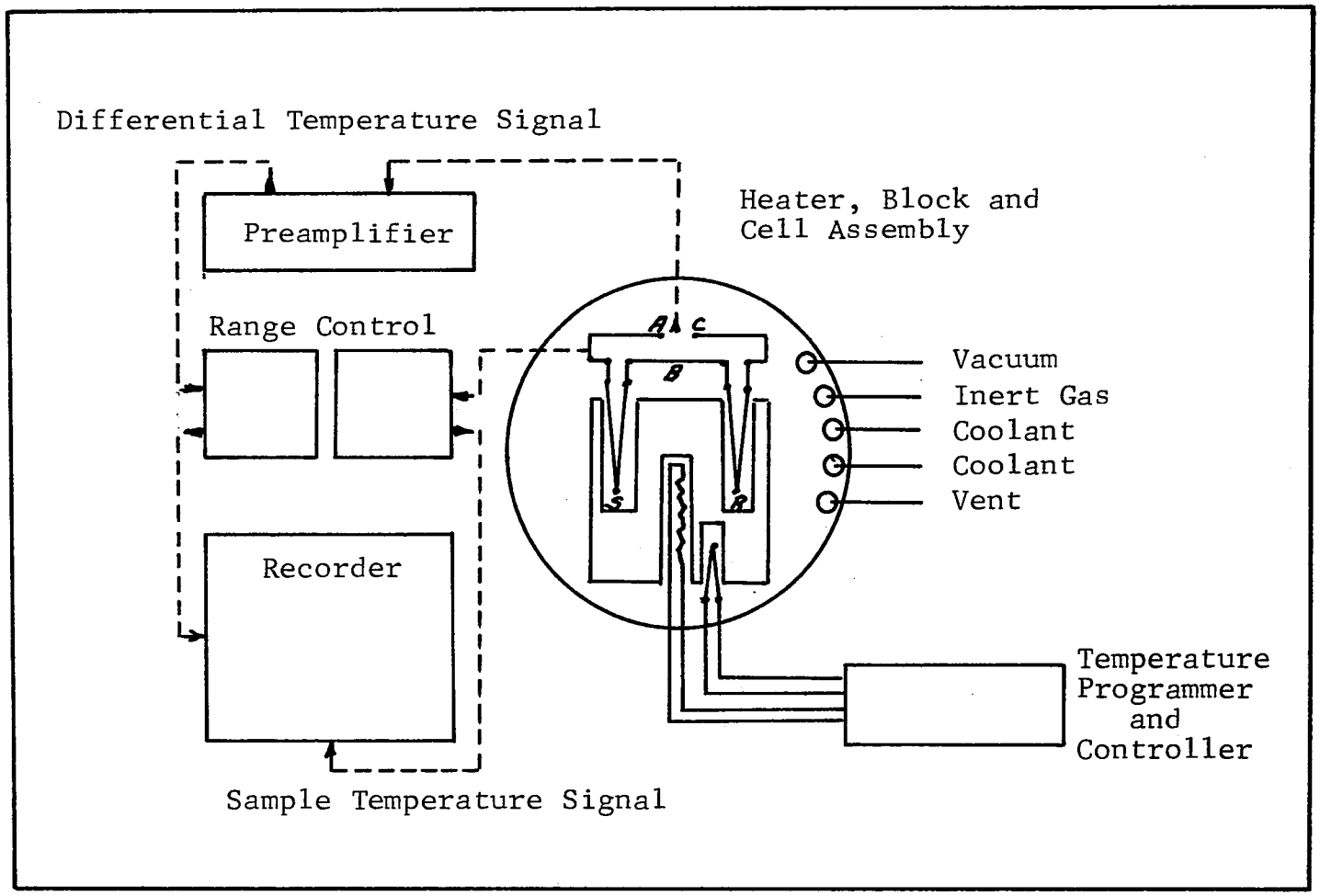

Figure 1: DTA SCHEMATIC

measurements. The thermocouples and heater and provided with plugs so that they may be removed with ease.

The entire cell assembly is hermetically isolated by a glass dome cover with an "O" ring seal. Five tubing connections pass into the assembly. A flow meter and a needle valve are provided with one of these for use as an inert gas purge. Another is provided with a vacuum gauge and valve for vacuum operation.

Instrument Modifications

In order to insure the most accurate and reliable results certain modifications and additions were made to the DuPont 900 Differential Thermal Analyzer.

Thermocouple circuit. Any reliable thermocouple measuring circuit must be designed in such a manner that only the reference and measuring junctions produce an EMF. This precludes the incorporation of any other dissimilar metal junctions which would produce an EMF dependent upon ambient temperatures. The DuPont 900 DTA incorporated the use of gold coated plugs to connect the individual thermocouples to the thermocouple circuit. The thermocouple scheme at these points was Chromel-gold-Chromel and Alumel-gold-Alumel which resulted in two sets of junctions, whose EMF's should cancel each other out if they were at the same temperature. Unfortunately this

was not the case especially if the cell was cooled or heated. By means of a standard Chromel-Alumel plug supplied by the Thermo-Electric Company of Saddle Brook, N. J., and a separate extension line to the ice reference junction, these plugs were by-passed. This spurious EMF which had a magnitude of $\pm$.04 mv was thereby avoided. A schematic of this change is shown in Figure 2.

Two ice point reference thermocouples are employed in the DuPont DTA. One serves as a reference for the furnace control circuit and the other for the sample thermocouple circuit. It was found that these must be placed in separate ice baths in order to avoid EMF interaction which produce erroneous results on the order of $\pm$.02 mv.

Potentiometer and recording system. The DuPont DTA employs a Mosely X-Y recorder to indicate the difference in temperature between the reference material and the sample as a function of sample temperature. The highest sample temperature recorder sensitivity is .4 millivolts per inch using Chromel-Alumel thermocouples. This is approximately equivalent to ten degrees Centigrade per inch or 0.01 inch per tenth of a degree. It can therefore be seen that the recorder was not sensitive enough to produce tracings which could be read with a precision

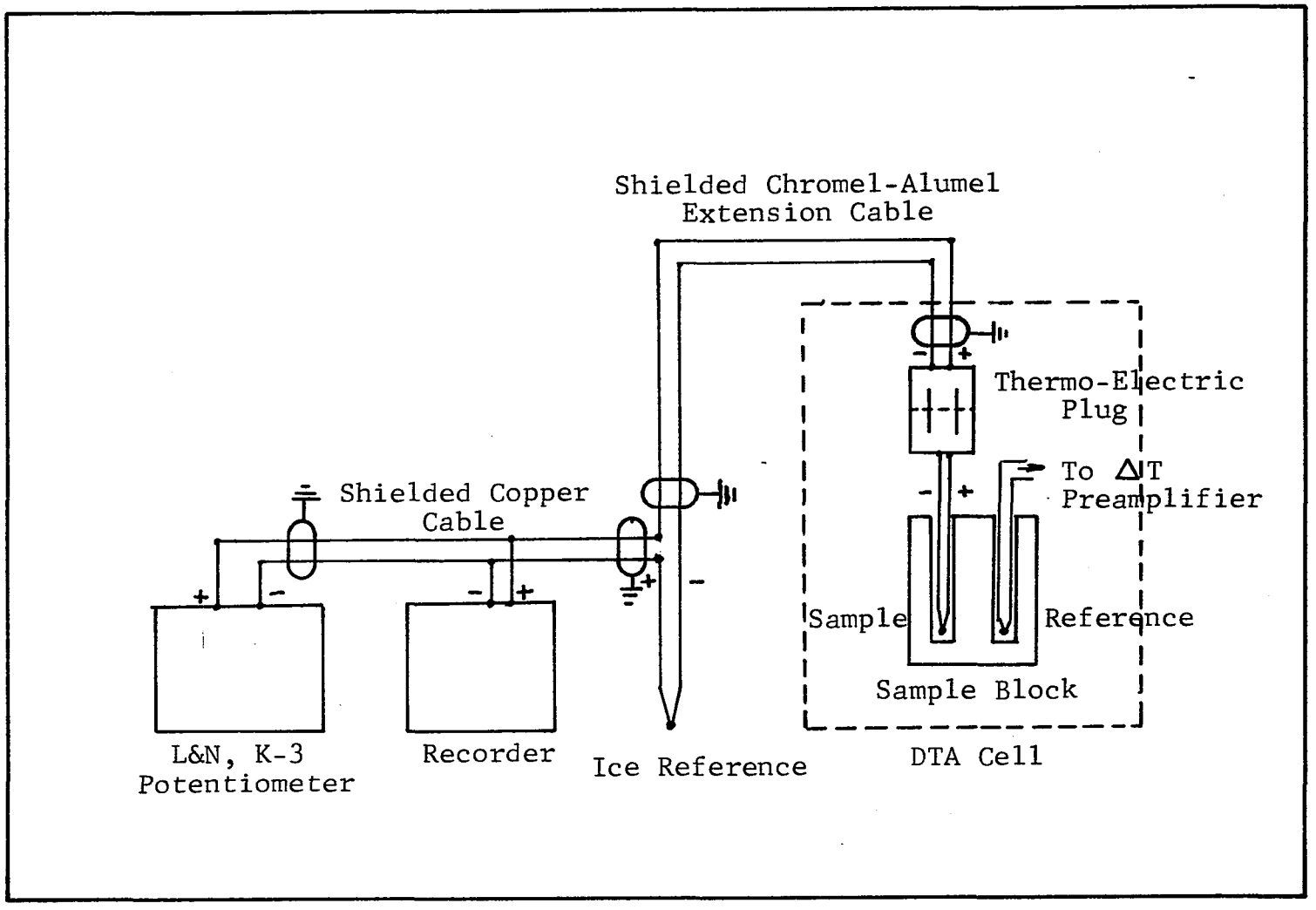

Figure 2: THERMOCOUPLE EXTENSION AND POTENTIOMETER CIRCUIT

of 0.1 degree Centigrade.

The recorder system also required daily calibration adjustments. These adjustments were tedious and time consuming. To avoid these difficulties, a Leeds and Northrop K-3 potentiometer with a 2430-D DC galvanometer was connected in parallel with the recorder circuit as shown in Figure 2. The recorder was then used only as a visual indicator to show when boiling took place and if the boiling point was constant. As the boiling point was approached the potentiometer was connected to the system and was approximately balanced. When boiling took place, at a constant temperature, the potentiometer was accurately balanced, resulting in an EMF reading of ± 0.001 mv, or $\pm .025^{\circ}$ Centigrade well within the desired precision, between -40 and 320° Centigrade.

Vacuum input. In order to obtain an accurate boiling point, a constant pressure at the point where boiling takes place is necessary. Shown in Figure 3 is an enlarged drawing of the 4 mm thin-wall glass capillary tube which was used to obtain boiling point data. The sample, a mixture of glass beads and liquid, lies in the bottom portion of the capillary with the thermocouple imbedded completely in the sample. Figure 3A shows the thermocouple-capillary arrangement before modification. The

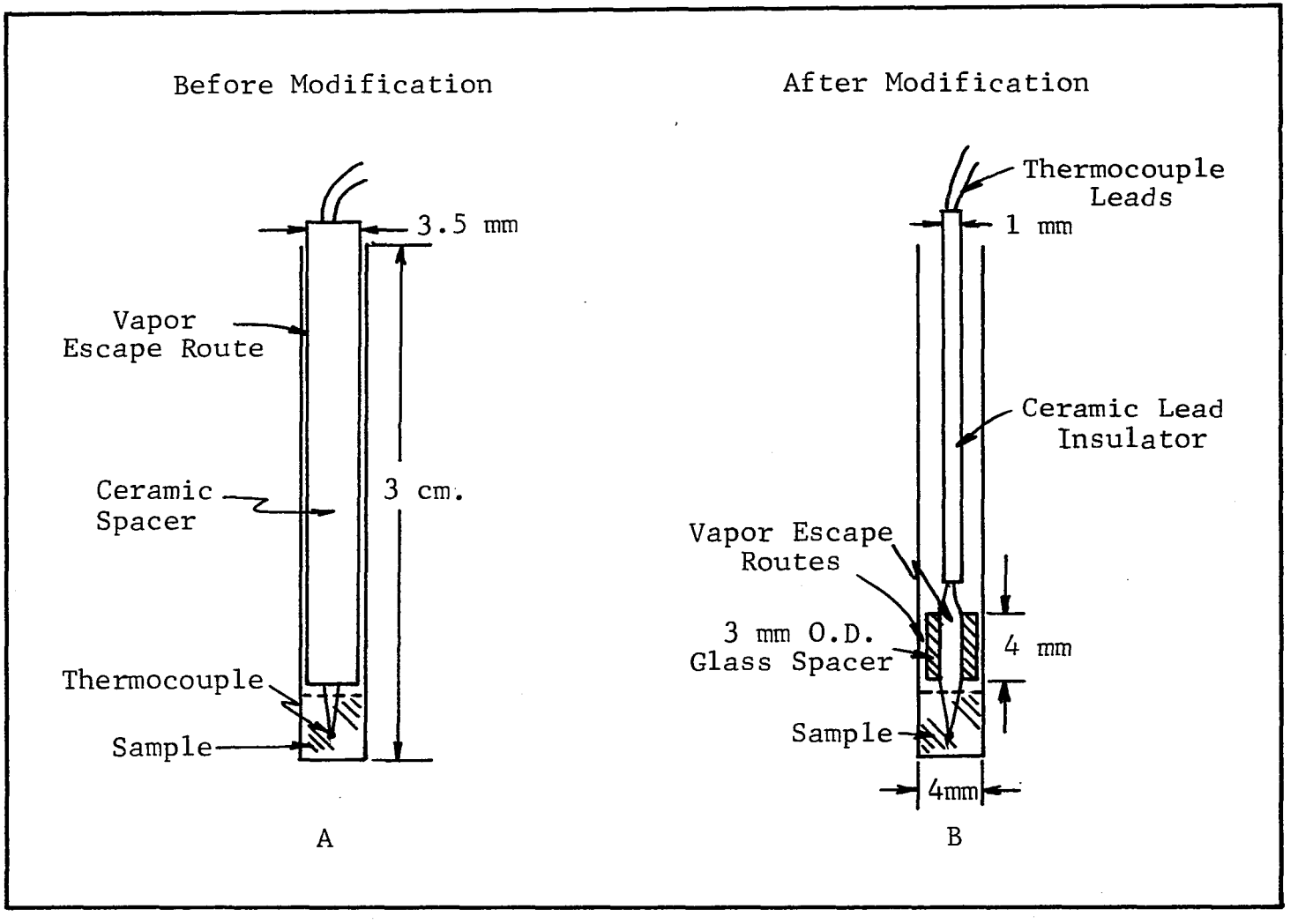

Figure 3: THERMOCOUPLE MODIFICATION

ceramic spacer served two purposes: it insulated the thermocouple lead wires from each other and also centered the thermocouple in the sample. As a result of this design the annulus between the spacer and the capillary was only on the order of .025 mm for a distance of 2.5 cm. At pressures greater than 50 mm Hg the annulus presents a negligible barrier to the escaping vapors, but below this pressure the mean free path of the escaping molecules approaches the annulus size. The calculations for the mean free path at low pressures are found in Appendix A. Thus a barrier is presented to the escape of the vapor which results in an increase of pressure and in turn produces an erroneous boiling point reading.

In order to avoid this difficulty the design was modified as in Figure 3B. The ceramic lead insulator has been decreased to 1 mm. In order to center the thermocouple a short piece of glass tubing, 3 mm O.D. x 4 mm x 1 mm I.D., was placed over the bare lead wires close to the thermocouple. This resulted in two vapor escape routes, one through the center of the glass spacer, the other through the annulus between spacer and capillary tube. Although the annulus space did not increase in size the length of the annulus decreased from 3 cm to 4 mm thus offering less resistance. This route plus the addition of one extra comparatively large escape route

resulted in a system of negligible pressure drop.

As the vapors escape from the capillary they emerge in the glass dome covering the cell system. In order that there would be a negligible pressure increase at this time, especially at low pressure conditions, the volume of the dome was doubled over that of the original design. In conjunction with these modifications the vacuum inlet line was increased to 6 mm I.D. so that any pressure increase could be more rapidly dissipated.

Cell cooling. In order to determine boiling points below room temperature it is necessary to be able to cool the cell as rapidly as possible so that the time per run is short. Several alternatives are suggested by DuPont using their specially designed cooling jacket. Coolant, such as nitrogen vapor obtained from liquid nitrogen, or cold CO_2 gas is recommended. Liquid nitrogen proved to be very difficult to handle and would flash violently in the cooling jacket. Even under these conditions the cooling rate was only about $5^{o}C/min$. Cold CO_2 gas, obtained by expanding compressed CO_2, was more convenient but still provided a very slow cooling rate because of the small overall heat transfer coefficient between the gas and the aluminum cell.

The best cooling method was obtained by permanently

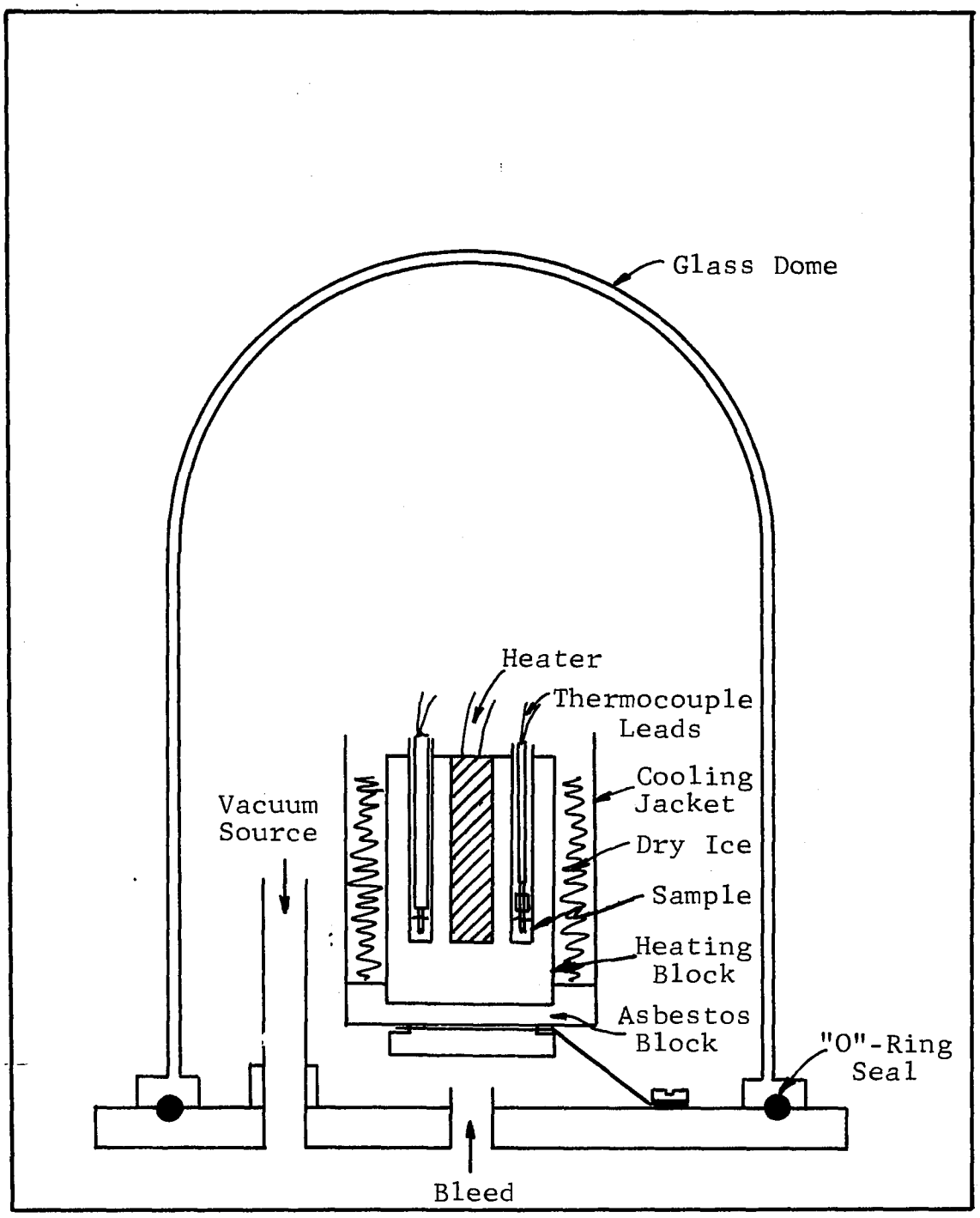

Figure 4: CELL ASSEMBLY

removing the cooling jacket cover as shown in Figure 4 and introducing finely powdered solid carbon dioxide into the annulus between cooling jacket and cell block. Cooling rates of from ten to fifteen degrees Centigrade per minute were easily achieved down to -40 to -50 degrees Centigrade. As soon as the desired temperature was obtained, the powdered CO_2 was blown out by means of dry compressed nitrogen expelled from a fine nozzle.

Heating rate control. The heating rate controller was designed to produce a rapid response to error in order to insure a linear temperature increase as a function of time. The design was acceptable as long as there was a relatively high heat loss from the heating block, thereby requiring a sufficiently high current demand by the heater. At low cell pressures and temperatures there was very little heat loss and in turn very little current was required. This resulted in an under-damped control situation where current was first excessively and then insufficiently supplied. In order to overcome this situation Mr. Parkell of DuPont Instruments (51) suggested the modification to the heater control circuit shown in the schematic in Figure 5. The new components are listed in Table 1.

As can be seen, if compared to the original schematic

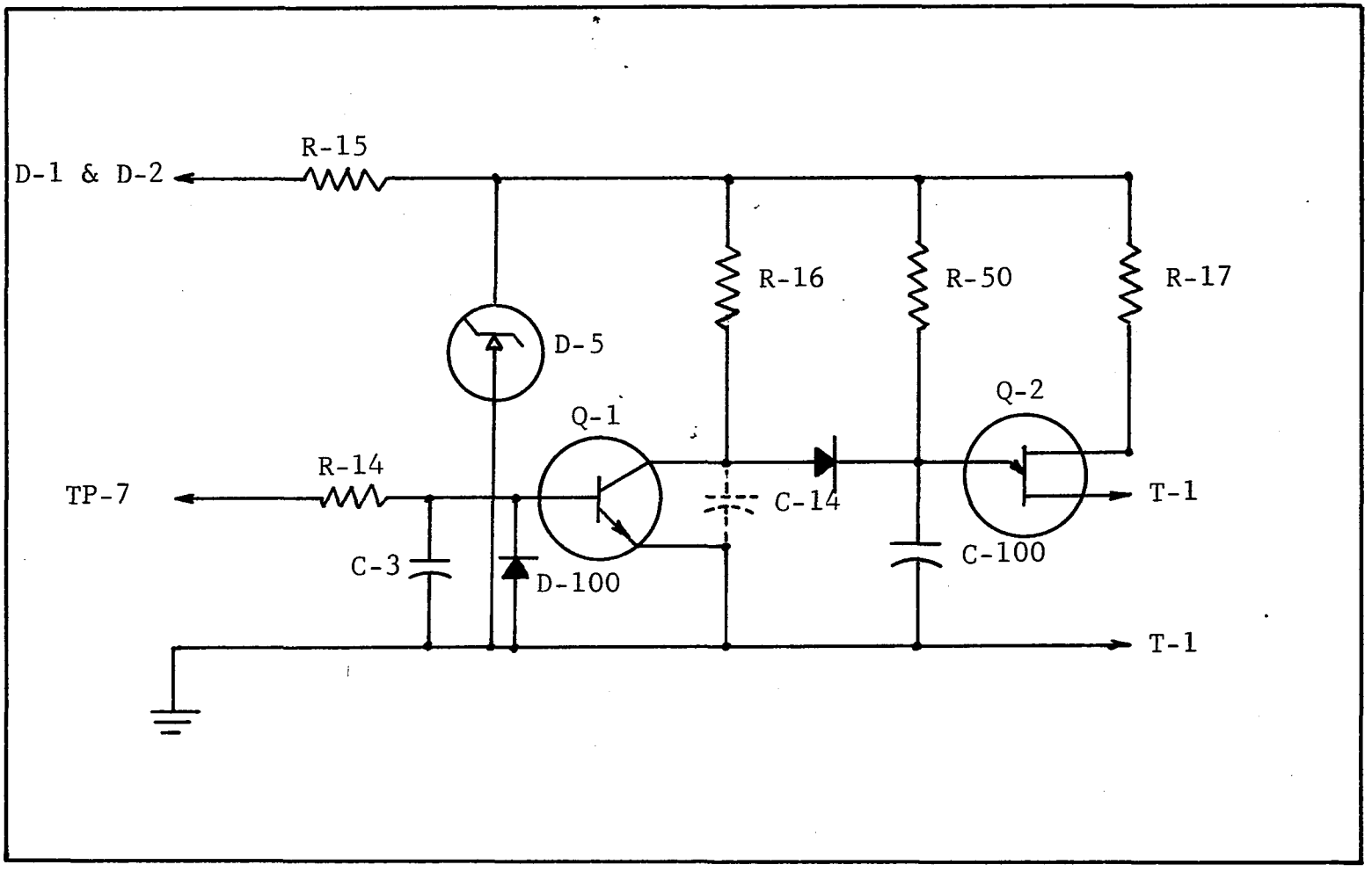

Figure 5: HEATER CONTROL MODIFICATIONS

Table 1: New Components

Part No.	Description	Rating
D 100	DIODE IN538	---
D 101	DIODE IN538	---
R 50	RESISTOR	100 KΩ
C 100	CAPACITOR	22 MFD, 200 v

diagram supplied by DuPont, capacitor C4 is removed, transistors D100 and 101, resistor R50, and capacitor C100 are added. This results in a circuit in which the necessary current demand for a linear temperature rate is gradually approached. This system proved to be effective down to 3 mm Hg, and still contained sufficient response at higher pressures and temperatures. At low temperatures, where very little heat input was required, the control system proved especially effective. A linear rise in temperature was achieved even at -40 degrees Centigrade.

Boiling Conditions

The sample was placed in a 2 mm capillary tube which in turn was inserted in an aluminum heating block as shown in Figure 4. Placed directly into the sample was a calibrated 28 gauge Chromel-Alumel thermocouple. It was here at the thermocouple junction that the boiling temperature was to be measured. Environmental conditions at this point had to insure that superheating was avoided, that there was a negligible pressure change, that the proper amount of heat was supplied, and that the sample quantity was sufficient to achieve a dynamic equilibrium between liquid and vapor. In an earlier section it was shown how a constant pressure over the sample was insured and will not bear repeating here.

Heating rate. Several experiments were performed to determine the effect of different heating rates. A 10 micro-liter sample of water on 50 mg of 100 micron glass beads was consistently employed, and the cell pressure was held constant at one atmosphere. Heating rates between .5 and 20 degrees Centigrade were tried. The data are shown in Table 2.

Considering that .004 milli-volts is equal to approximately .1 degrees Centigrade it can be seen that the boiling point is constant at heating rates between 2 and 20 degrees Centigrade per minute. At lower heating rates consistently low values are obtained. It was concluded that at heating rates lower than 1 degree Centigrade per minute not enough heat was supplied to promote boiling, rather only rapid vaporization. The endotherms at these low heating rates do show that an equilibrium has been achieved by virtue of a constant temperature during vaporization. This equilibrium is not that of the vapor pressure of the sample being equal to the vapor pressure of the surroundings, but rather an equilibrium between the heat input equal to the heat dissipation.

It can therefore be concluded that the heating rate should be at least 2 degrees Centigrade per minute in order to promote boiling. A median value of 5 to 10 degrees

Table 2: Heating Rate Effect

Heating Rate °C/min.	Thermocouple EMF	Temperature °C
.5	4.0536	101.34
1.0	4.0698	101.75
2.0	4.0773	101.93
5.0	4.0806	102.02
10.0	4.0819	102.05
15.0	4.0780	101.95
20.0	4.0776	101.94

Centigrade per minute was used in obtaining the vapor pressure data in this work.

A heating rate higher than 20 degrees Centigrade per minute was not attempted, but superheating would result at a heating rate where the system could not dissipate all the heat energy it received.

Liquid placement. In every experiment which measures vapor pressure by a dynamic method, superheating is a problem which must be overcome. This is usually accomplished by employing rough surfaces which supply active sites where boiling might be initiated. In this case 100 micron glass beads were employed to alleviate any noticeable superheat. From 4 to 10 micro-liters of sample was mixed with about 40 mg of glass beads. This produced a dry mixture when intimately mixed. Each bead was thus surrounded by a thin film of liquid. This resulted in a negligible increase in pressure due to liquid head and supplied the liquid with many active boiling sites. Within this liquid film a boiling equilibrium was set up between the liquid and its vapor.

Several sizes of glass beads were used to try to determine which size would be most effective. Since the amount of liquid sample that could be utilized is directly proportional to the surface area, smaller beads would be

able to handle more material, thus extending the boiling period. On the other hand, the smaller the beads the smaller were the voids from which the vapors could escape, thus more probably producing non-equilibrium conditions and bumping. Large beads would overcome this problem but a smaller sample size was required. One hundred micron glass beads are a compromise which produce very good results.

The effect of a curved surface upon the boiling point might be questioned. Calculations performed, as shown in Appendix A, showed this effect to be negligible.

Sample size. As mentioned in the last section, the sample is mixed with glass beads so that each bead is covered with a thin film of liquid sample. It is important that the amount of liquid surrounding each bead be of the proper magnitude. From 4 to 6 $x10^{-5}$ moles of total sample (4-12 micro-liters) is approximately correct for 40 mg of 100 micron glass beads. If not enough sample is supplied, a thermogram such as that shown in Figure 6A is obtained. The curve usually proceeds in a comparatively gentle downgrade slope which continues until recovery. Sometimes it even slopes slightly backwards as is seen when a sample superheats, although, in this case, the maximum endothermic temperature might be several

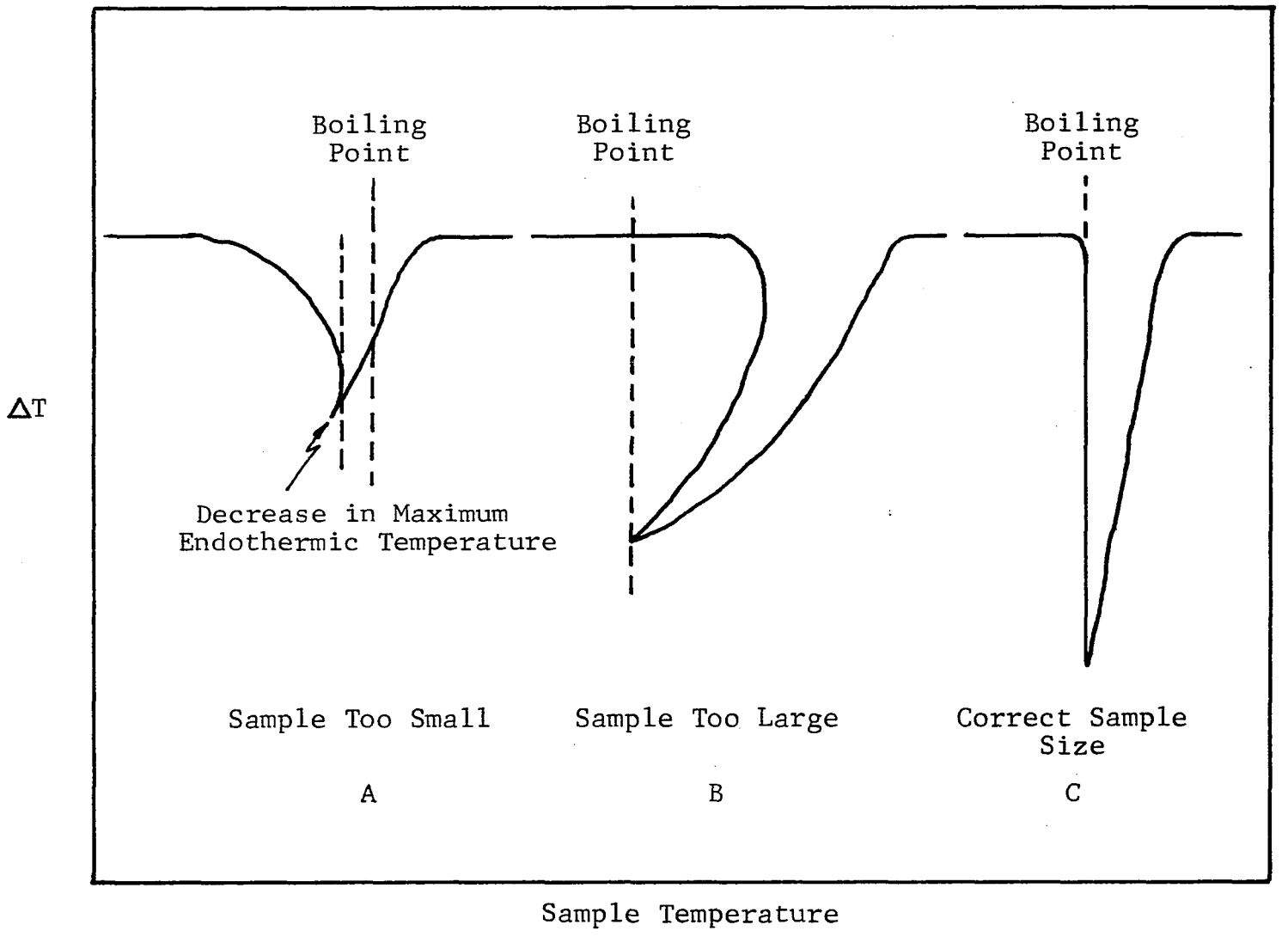

Figure 6: BOILING ENDOTHERMS

degrees below the true boiling point. A comparatively small ΔT is also characteristic of this phenomenon showing that a small amount of heat was required to vaporize the sample, and that the sample temperature was increasing. It can therefore be concluded that too small a sample size will produce a condition which is not conducive to true equilibrium. The required sample size also seems to depend upon the amount of energy required to vaporize the sample. The greater the amount of energy required per unit volume, the smaller the sample required. Therefore, at low pressures where the heat of vaporization is greater than at higher pressures, less sample is required. As the pressure is increased, it is preferable that the sample size also be increased. It should be stressed at this point that the sample size is important but not overly critical. A good deal of latitude in sample quantity exists. For most materials a ratio of 5 - 10 micro-liters per 40 mg of glass beads will almost always suffice. Conditions exist, however, where either a smaller or larger sample is required but these conditions are immediately evident as discussed herein. Too large a sample results in superheating; this is brought about because each bead does not have its own film of liquid but rather that the liquid is now filling all the voids between the beads. In these voids, super-

heating takes place since there are no active boiling sites available. A thermogram as shown in Figure 6B is obtained. The maximum endothermic temperature shown is above the boiling point, sometimes by as much as 10 degrees Centigrade. It is felt that when the liquid in the voids has boiled away the system attempts to return to a true boiling equilibrium and the curve slants back, but equilibrium is rarely achieved.

A true boiling point endotherm is shown in Figure 6C. Note that the curve breaks quite rapidly and is perfectly vertical from that point until recovery. This is a perfect indication that all conditions are correct and that the material's purity is of such quality that no boiling point range can be detected.

Sample purity. An extremely pure sample is of utmost importance when performing vapor pressure determinations. As was pointed out previously, DTA is an inherently strong tool in determining whether a sample is sufficiently pure to obtain accurate data. In general, it was found that a sample had to have a purity level greater than 99.5 mole per cent to show a constant boiling point by DTA. Usually the remaining .5 per cent impurity consisted of a close boiling isomer, thus showing the sensitivity of DTA.

By observing the DTA curve several things could be ascertained about the sample purity. Figure 7A shows a typical thermogram of a sample which contains a volatile impurity. What takes place in the sample tube might be considered a simple distillation. Finally all the volatile impurity is vaporized and a constant boiling endotherm ensues. A slight variation of this thermogram is shown in Figure 7B. In this case the sample contains not only a more volatile but also a less volatile impurity demonstrated by the increase in boiling temperature toward the bottom of the endotherm. In some cases, as shown in Figure 7C the amount of impurity is so great that there is a continual boiling point increase as the sample is vaporized. In some cases where there are many different impurities several vertical portions on the endotherm are observed which indicate that either several pure components are vaporizing at different times or that an azeotrope has been achieved in the last vertical portion. A thermogram of a pure sample is shown in Figure 7D.

The DTA vapor pressure system has proved to be a very valuable tool in determining purity. It should be understood that DTA does not indicate the amount of impurity but rather it can indicate if a sample is of such purity that it has a boiling point range less than .1 degree Centigrade. If a sample passes this test it will not

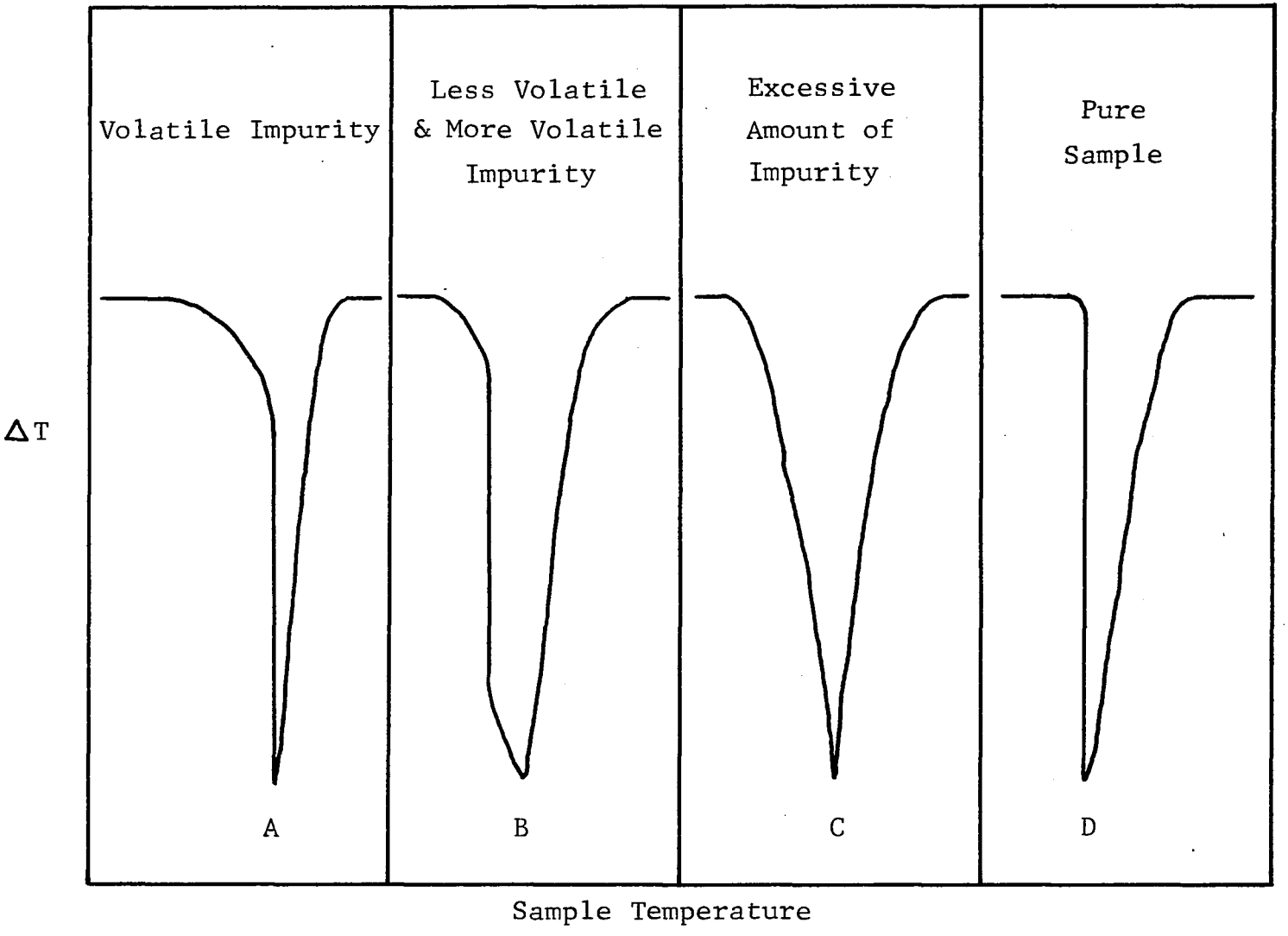

Figure 7: PURITY CHECK THERMOGRAMS

limit the accuracy of the instrumentation.

This property of DTA was used extensively in determining the relative purity of several cuts obtained from a spinning band distillation column. Each cut was sampled on the DTA to see which produced a constant boiling endotherm. The sample which did was then tested under pressures from 5 mm to 760 mm Hg to determine whether any azeotrope existed. This was the only means available for determining the purity of several high boiling alcohols. Even gas chromatography could not be utilized in these cases because the alcohols were so polar and had such high boiling points that they would not pass through the column very readily without decomposition. Separation of the lower alcohols into their components by gas chromatography also proved very difficult.

Vacuum System

In general, the vacuum system which was connected to the furnace of the DTA consisted of a high capacity vacuum pump with a 30 liter ballast. Control was achieved by use of a mercury-filled Cartesian manostat. A vacuum manifold was placed in the system so that several takeoffs from the system were available. The following section presents a more detailed description of the system. A schematic diagram is shown in Figure 8.

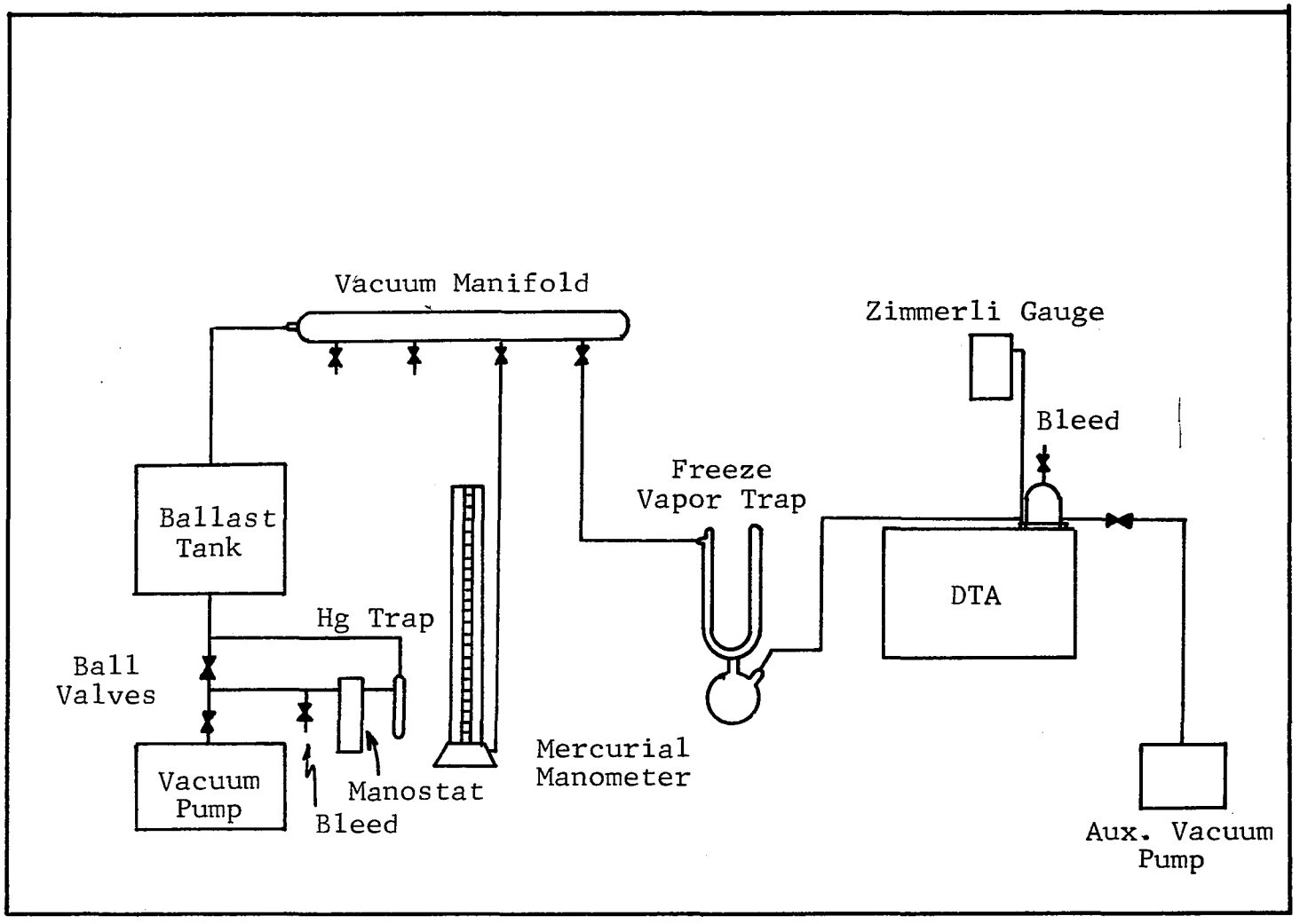

Figure 8: VACUUM SYSTEM SCHEMATIC

Vacuum pump. A Welch Model #1397 Duo-Seal vacuum pump was employed as the major pump in the system. This pump was supplied with vented exhaust valves which prevented the condensation of vapors in the pump. A #1417B exhaust filter was added to the pump so that it could handle high gas flow rates without throwing oil. This pump was chosen because of its relatively high pumping capacity of 420 liters per minute at atmospheric pressure.

Ballast. A 30-liter 3-neck round bottom glass vessel was used as the ballast tank. All connections to the flask were O-Ring-sealed Ball joints (Scientific Glass HVS joints) so that a good vacuum seal was assured. The ballast was incorporated in order to supply the system with sufficient reserve volume. In this way the effect of any small changes in the system pressure would be kept to a minimum. The ballast also acted as a calming chamber to damp out any disturbances caused by the pump. This tank was found to be very important at low pressures where a very small imbalance in the system can cause poor results in vapor pressure measurements. The ballast also made pressure regulation easier for the Cartesian manostat since the larger system required longer on and off cycle periods. This proved to be particularly advantageous as shown from Table 3.

Table 3: Pressure of System as a Function of Time

Time Hrs:Min.	Pressure mm Hg
0:00	3.6
0:07	3.6
0:13	3.4
0:17	3.2
0:35	3.2
1:00	3.4
1:07	3.2
1:35	3.3
1:38	3.4

It can be seen that there is a slight pressure variation as a function of time. If a ballast were not used the total range of variation would be the same but the frequency of change would be greater. The result is that there is less of a pressure change during the short duration of boiling with the ballast than without it. Considering that at 5 mm Hg a tenth of a millimeter pressure change is equivalent to a boiling point change of one-tenth degree Centigrade, the incorporation of a ballast is very important.

Manostat. A model #8 Cartesian manostat was purchased from the Manostat Corporation. This is a maximum sensitivity instrument which claims a precision of .05% or 0.1 mm Hg, whichever is greater. It was fitted with a 4 mm orifice which allowed a flow rate of 130 liters per minute at atmospheric pressure. Flexible connections were attached to the manostat so that the seal under the float could be broken at low pressures by shaking the instrument, conveniently producing a different set point when desired. A precautionary mercury trap was placed after the manostat.

Pressure measuring gauges. Two basic measuring devices were employed: a Wallace and Tiernan Precision Mercurial Manometer and a Scientific Glass Precision

Model Zimmerli gauge. The Wallace and Tiernan gauge was used from 100 to 760 mm Hg with an accuracy of $\pm$.033% of full scale range and a sensitivity of $\pm$.004% of the same. The Zimmerli gauge was employed from 5 to 100 mm Hg with an accuracy of $\pm$.05 mm Hg. The Precision Zimmerli gauge was connected directly under the DTA dome to avoid any error in measurement. It was found that there was a pressure difference of about .15 mm Hg between the dome and the manifold at low pressures; this error disappeared above 50 mm Hg. The absolute accuracy of the Zimmerli gauge was checked by first exposing it to .001 mm Hg vacuum and then adjusting for zero pressure. The Zimmerli gauge then checked within the prescribed accuracy at 85 mm Hg with the Wallace and Tiernan gauge, which was considered a primary standard.

Miscellaneous equipment. A large capacity dry ice-acetone vapor trap was employed to trap condensables in order to avoid contamination of the pump oil and pressure increase due to condensables entering the system during boiling.

A 1½-inch diameter by 2-foot vacuum manifold with six inlet connections, each equipped with a 6 mm Scientific Glass HVS stopcock was used. One inlet went directly to the DTA via a vapor trap while the others were used for

pressure measurements and vents to the atmosphere. High vacuum Dow Corning Silicone grease was used as the lubricant.

A small capacity vacuum pump was connected into the system in such a way as to bring the work chamber to a predetermined pressure before opening the DTA to the rest of the system which was maintained at a preset pressure. This was done so that the set point of the manostat would not be disturbed and thereby avoided constant readjustment. This method also significantly reduced the time a sample was exposed to near boiling conditions, a factor very important when considering heat degradable materials.

Two Lunkenheimer 3/4" top entry ball valves were placed just past the major vacuum pump. The first valve was used as a shut off between the system and the pump. The other valve served as a means to by-pass the manostat controller. This was necessary if the system was to be taken down to a low pressure in a short time since the line to the manostat was comparatively small.

A needle valve in the line just before the manostat served as a bleed if further control was sought. Usually it was used to upset the system very slightly to insure that the manostat functioned in bringing the system back

to the set point pressure. In order to keep any dust from entering the system through this bleed valve, a drying tube packed with glass wool was connected to the valve outlet to atmosphere.

Piping. Three-quarter inch galvanized iron pipe was used to connect the vacuum pump with the ballast tank. Tygon tubing of the same inside diameter served as the glass to metal connector at this point. The ballast tank and the manifold were also connected by three-quarter inch I.D. Tygon tubing. The by-pass line leading to and from the manostat consisted of one-half inch galvanized iron pipe with Tygon tubing of the same inside dimension serving as a flexible connector. Five-eights inch Tygon tubing served as the connection between the manifold, trap and DTA. All pipe to tubing connections were secured with metal band clamps to insure a tight fit. A low vapor pressure silicone based pipe dope was liberally applied to all threaded connections to insure leak free operation.

Preparation and Purification of Materials

Two straight chain homologous series were studied, the primary alkyl chlorides and the primary alcohols between C_3 and C_{16}, although not all members of the series could be obtained. All of the materials were obtained from sources shown in Tables 4 and 5, pages 74 and 75.

Table 4: Source of Normal Alcohols

Compound	Supplier	Purity Level Before Purification
n-propanol	Union Carbide	---
n-butanol	Union Carbide	---
n-pentanol	Union Carbide	---
n-hexanol [1.]	Poly Science Corp.	98%
n-heptanol	K & K Laboratories	---
n-octanol [1.]	Poly Science Corp.	99+%
n-nonanol	K & K Laboratories	99-95%
n-decanol [1.]	Poly Science Corp.	99+%
n-dodecanol [1.]	Poly Science Corp.	99+%
n-tetradecanol	Conoco Corp.	97%
n-hexadecanol	Conoco Corp.	95%

[1.] Did not require further purification.

Table 5: Source of Alkyl Chlorides

Compound	Supplier	Purity Level Before Purif.
1-chloropropane	Matheson, Coleman & Bell	---
1-chlorobutane	Matheson, Coleman & Bell	---
1-chlorohexane	Matheson, Coleman & Bell	---
1-chloroheptane	Matheson, Coleman & Bell	---
1-chloro-octane	Matheson, Coleman & Bell	---
1-chlorononane	K & K Laboratories	95-99%
1-chlorodecane	K & K Laboratories	95-99%
1-chloroundecane	K & K Laboratories	95-99%
1-chlorododecane	K & K Laboratories	95-99%
1-chlorotetradecane	Matheson, Coleman & Bell	---
1-chlorohexadecane	Matheson, Coleman & Bell	---

The following section will discuss the preparation and purification of each compound under the heading of the required purification method.

It should be pointed out that the final criterion of satisfactory purity was a straight vertical boiling point endotherm, indicating that there was no detectable boiling point range. Gas chromatography was employed as a tool for purification and also as a purity indicator.

It is possible to detect very small impurity levels by use of gas chromatography but it is very difficult to obtain quantitative data. At best, gas chromatographic results are good to ± 2 per cent and only after the instrument and column have been calibrated. In this instance, of course, calibration was impossible so that only a rough estimate of sample purity would be given by gas chromatography by assuming internal normalization. Where only one peak could be observed, the material was said to be 99+ per cent pure.

Preparative Vapor Phase Chromatography

The alkyl chlorides were purified by the use of preparative gas chromatography, though much care had to be exercised with the higher members of the series in order to avoid decomposition of the chloride. A Wilkens

Model 700A Preparative Gas Chromatograph was employed. This instrument was set up so that it would automatically inject material into the chromatographic column, collect the specified eluted fractions and reinitiate the cycle.

Table 6 lists the chromatographic conditions under which the alkyl chlorides were purified. In all cases aluminum chromatographic columns were used with helium as the carrier gas and thermal conductivity as the means of detection.

The only alcohol purified by chromatography was heptanol. A Carbowax 20M on Chromosorb P, 20' x 3/8" aluminum column was used. The following conditions were employed:

Detector temperature	190 degrees Centigrade
Injector temperature	180 degrees Centigrade
Column temperature	170 degrees Centigrade
Helium flow rate	100 cc/min.

A purity of 99+ per cent was obtained with this method.

<u>Material collection using gas chromatography</u>. Generally a cooled collection bottle as supplied by Wilkens Instrument was sufficient to capture upwards of 70 per

Table 6: n-Alkyl Chlorides
Purification by Gas Chromatography

Compound No.	Column Packing Liquid Phase	Substrate	Column[1] Length	Inj. Volume	Det. Temp. °C	Inj. Temp. °C	Col. Temp. °C	Helium Flow cc/min.	Purity[2] Check %
3	QF-1	W[3]	20'	50	90	115	65	70	99+
4	Apiezon L	W	15'	250	195	110	95	150	99+
6	Apiezon L	W	15'	150	140	160	140	70	99+
7	Apiezon L	W	15'	100	200	200	155	70	99+
8	Apiezon L	W	15'	80	295	273	195	65	99+
9	Apiezon L	W	15'	80	260	310	185	55	99+
10	Apiezon L	W	15'	50	280	322	227	70	99+
11	Carbowax 20M	P[4]	20'	150	230	240	200	300	99+
12	Carbowax 20M	P	20'	150	260	260	210	300	99+
14	Carbowax 20M	P	20'	100	240	240	240	300	99
16	Carbowax 20M	P	20'	100	240	240	240	300	99

1 Aluminum Column - 3/8" I.D.
2 See page 76.
3 Chromosorb W
4 Chromosorb P

cent of the eluted material at flow rates under 150 milliliters per minute. Above these flow rates, the vapor was dispersed as a fog, making capture most difficult. This was especially true of the high molecular weight alkyl chlorides where the column temperature had to be low in order to avoid decomposition and the flow rate high enough to achieve elution in a reasonable amount of time. The problem was overcome by the use of an apparatus which is shown in Figure 9. The collection device was filled with 25 micron glass beads so that the dispersed fog would impinge upon the beads and coalesce. After about two collection cycles the beads became wet and the collection efficiency increased to about 80 per cent. A total of .5 milliliters could be collected in this fashion at which time the receiver had to be emptied into a sample bottle. The product was vacuum distilled in order to separate the liquid from the beads with as little loss as possible. The distillation receiver is shown in Figure 9. The liquid sample was heated with a heat gun under high vacuum so that no decomposition would take place. Gentle heating would prevent beads from bumping out. The vapor was condensed using a bath of dry ice and acetone.

Spinning Band Distillation

A Nester-Faust teflon spinning band column was used

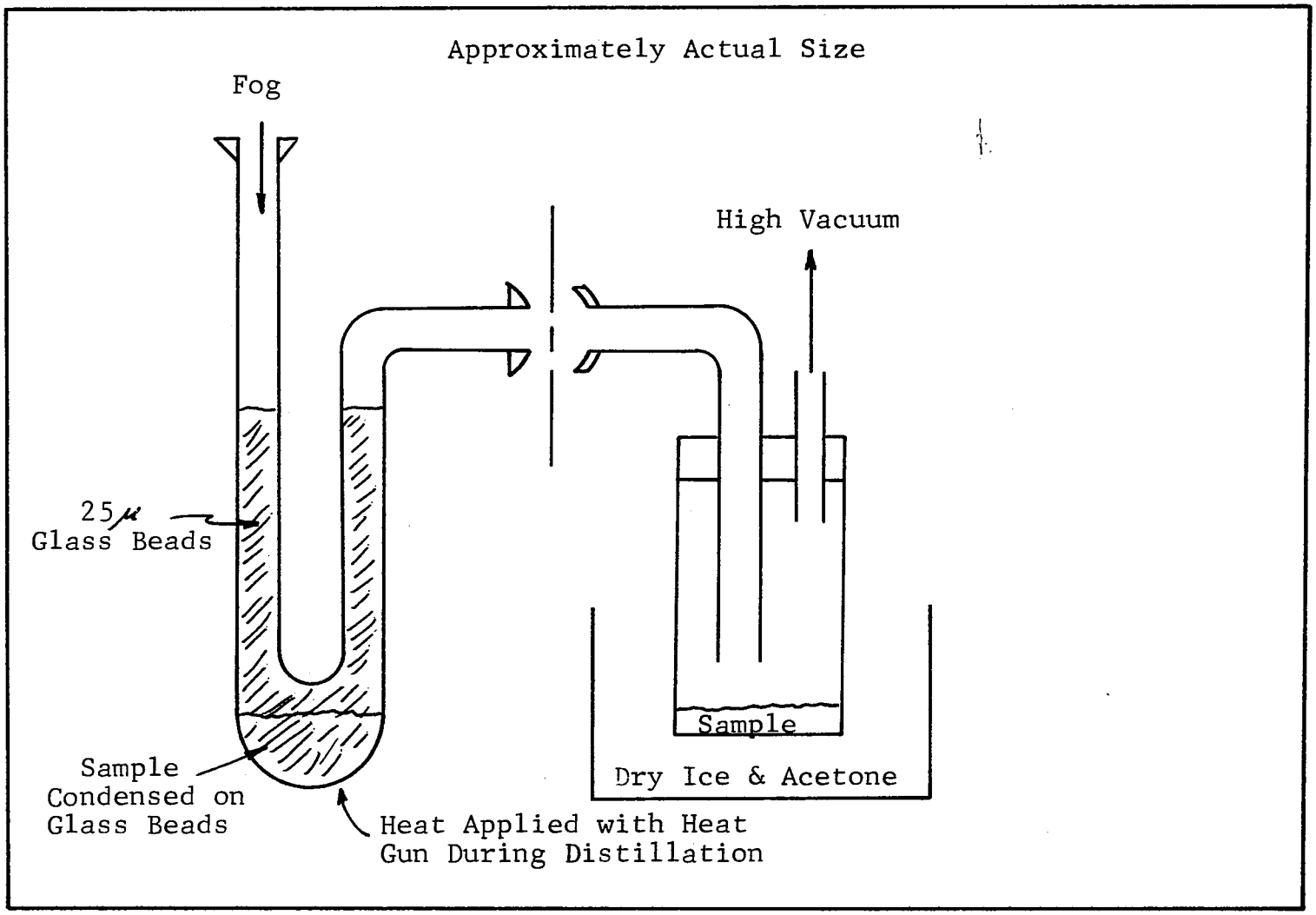

Figure 9: CHROMATOGRAPHIC COLLECTION DEVICE

to purify the higher alcohols because of the difficulty in making chromatographic separations. These difficulties were mainly due to the low vapor pressure and high polarity of the alcohols. Long retention times, high column temperatures, excessive peak tailing, and poor resolution were the results of decomposition of the compounds on the column.

The spinning band column proved to be very effective in purifying these higher alcohols. One hundred milliliter batches were distilled, taking four equal cuts at 50:1 reflux ratios. Again, because of the alcohol properties, purity tests could not be performed by gas chromatography. The DTA was employed to test the boiling point range of each cut at a constant pressure. Those cuts which showed no detectable boiling point range were then tested between 5 mm and atmospheric pressure to make certain that no azeotrope existed. Purity was thus determined by virtue of a constant boiling point, that which is of primary concern when making vapor pressure studies. Nonanol, tetradecanol, and hexadecanol were purified in this fashion.

Todd Column

Table 7 lists the materials that were purified using a Todd distillation column at atmospheric pressure. A 15 mm I.D. x 80 cm glass column packed with 1/8" glass

Table 7: Materials Purified on the Todd Column and Analyzed by Gas Chromatography

Compound	[1] Column Packing Liquid Phase	Substrate	Det. Temp. °C	Col. Temp. °C	Inj. Temp. °C	Helium Flow cc/min.	Purity Level %
n-propanol	10% Carbowax 4000	Fluoropak + TPA	190	130	180	120	99+
n-butanol	10% Carbowax 4000	Fluoropak + TPA	190	130	180	120	99+
n-pentanol	10% Carbowax 4000	Fluoropak + TPA	190	130	180	120	99+

[1] 10' x ¼" column

helices was employed at a reflux ratio of 20:1. During the distillation the low boiling fraction was discarded. When a constant head temperature was achieved several equal volume cuts were taken and analyzed on a gas chromatograph under the conditions shown in Table 7. In this way the pure cuts could be identified and used for vapor pressure determinations.

Experimental Procedures

Thermocouple calibration. The temperature sensing device incorporated in the DTA was a 28 gauge analytical Chromel-Alumel thermocouple. In order to obtain accurate data it was imperative to know the thermo-electric characteristics of the thermocouple in comparison with the ice point reference couple.

The procedure for calibrating the thermocouple was simply to determine the boiling point EMF's of pure materials whose vapor pressure data was accurately known, thus determining the EMF corresponding to a definite temperature. A calibration was made every 10 to 20 degrees Centigrade from -40 degrees Centigrade up to 305 degrees Centigrade with a variety of materials. Wherever possible the materials were used in overlapping temperature ranges to insure that the results were independent of the material. Table 8 lists the materials used, their useful temperature ranges, the reference from which the

Table 8: Calibration Standards

Material	Data Accuracy °C	Calibration Temp. Range °C	Data Ref.	Purity[1] Mole %	Source
n-pentane	±.1	-40 to 35	(57)	99	Phillips Petroleum Co.
n-hexane	±.1	2 to 63	(57)	99	Matheson, Coleman & Bell
water	±.1	60 to 90	(30)	99.9	--------
m-xylene	±.01	110 to 132	(49)	99	Matheson, Coleman & Bell
n-octanol	±.01	140 to 195	(49)	99	Poly Science Corp.
benzophenone	±.01	200 to 305	(49)	99	Matheson, Coleman & Bell

[1] All materials except water were of chromatographic purity.

primary data were obtained, and the data accuracy. All materials were spectroscopically and chromatographically pure, and showed no visible boiling point range on the DTA.

Water, which could not be tested on the gas chromatograph because of its extreme polarity, was purified as follows: To one liter of tap water was added .2 gm potassium permanganate and .5 gm sodium hydroxide. This solution was slowly distilled through a distilling column. The middle third was redistilled and the center cut was taken for the sample.

Duplicate or triplicate determinations were made at each calibration point in order to reduce random error. The mean was then chosen as the calibration value.

A very interesting result was noted when the absolute calibration temperature was plotted against the difference between the observed EMF and the EMF calculated by assuming a .04 millivolt per degree Centigrade linear thermocouple response. This is shown in Figure 10. There was not a continuous positive or negative deviation but rather an extremely non-linear, irregular difference function. Many works in which temperature is measured by the use of thermocouples do not seem to be aware of this since calibrations are performed usually at 100 to

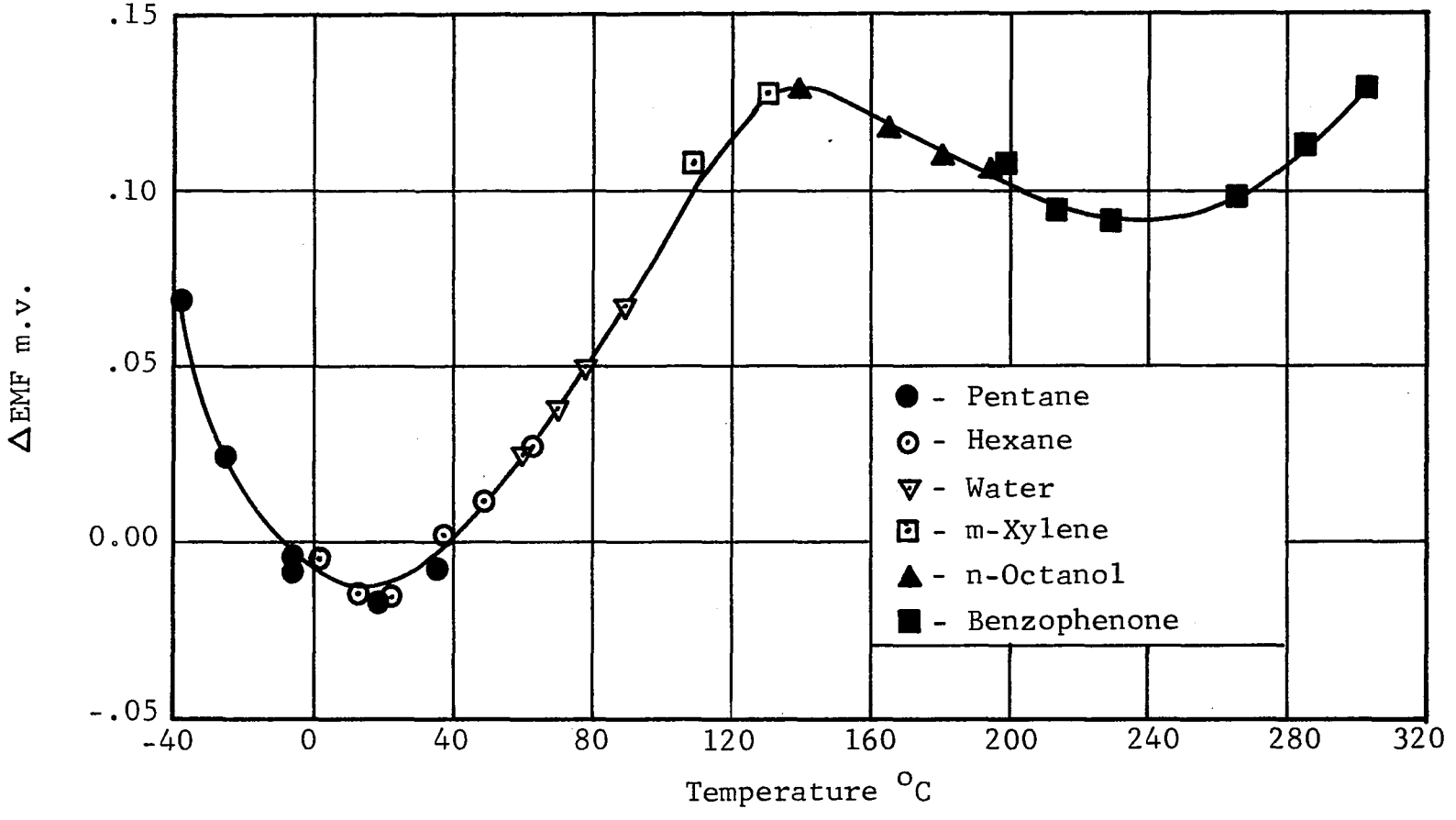

Figure 10: THERMOCOUPLE CALIBRATION

200 degrees Centigrade intervals. Errors of several degrees would not be uncommon in such cases.

The EMF-temperature function was assumed to be linear between calibration points. As can be seen from Figure 10, this approximation is good within .004 millivolts or .1 degree Centigrade since the curvature between points is no greater than that value. The calibration temperatures and the thermo-electric response values are listed in Appendix B.

Vapor pressure measuring procedure. The following stepwise procedure is the one typically followed in measuring vapor pressures by DTA:

1. Adjust to the desired pressure in the major system. In determining a complete vapor pressure curve between 5 mm and atmospheric pressure, it is advisable to start at the lowest pressure and work up, thereby beginning at a low heating block temperature and increasing for successive runs. This saves a good deal of time otherwise spent in cooling the block before proceeding to the next run.

In order to adjust the pressure, open both ball valves shown in Figure 8, page 67 and allow the system to reach a pressure slightly higher than the desired pressure, at

which time both valves are closed. Tip the manostat and shake it well so that the mercury seal is broken and a new set point is achieved, after which the manostat is set upright again. Open the ball valve to the pump, whereupon the pressure will decrease slightly. Minor adjustments may be made using the adjusting knob on the manostat. In order to test the set point, open the bleed needle valve slightly to upset the system and close it again. The pressure should return to the original set point.

2. Prepare the sample by placing 40 mg of 100 micron glass beads in a 4 mm glass capillary. Using a ten micro-liter syringe, inject 4 to 10 micro-liters onto the beads, the amount depending upon the factors discussed under the heading of "Boiling Conditions", page 56. Using a fine wire, mix the beads and the liquid intimately. If the sample is a solid, heat the beads and the capillary, then inject the molten sample.

3. Raise or lower the temperature of the block until it is about 20 to 30 degrees Centigrade below the expected boiling point. The temperature may be lowered by spooning powdered dry ice into the annulus around the block. In order to obtain rapid cooling the dry ice must be kept in contact with the block by lightly tapping the cooling jacket so that the ice will pack. Excess ice is then

easily removed by blowing it out with nitrogen expelled through a fine nozzle. The temperature is rapidly raised by manually controlling the voltage to the heater.

4. When the cell block is below ambient temperature, insert the thermocouple into the capillary first, as shown in Figure 3B, page 49, then insert the entire assembly into the sample block making sure that the thermocouple junction is completely immersed in the sample. The thermocouple wire can be bent in such a way as to force the junction downward under tension. The capillary is inserted last so that as little condensation as possible will form near the sample.

If the cell block is above room temperature, the capillary may be placed into the block first if desired. This is necessary if the sample is a solid so that it will melt and allow the thermocouple to be inserted.

5. Place the glass dome over the cell and start the auxiliary vacuum pump. Open the valve to the cell until the desired pressure is obtained, then close the valve. At this time the cell is opened to the main vacuum system. See Figure 8, page 67.

6. Set the heating rate controller at 10 degrees Centigrade per minute and set the starting temperature so

that the heater voltage is about 5 to 20 volts. At low starting temperatures, lower the starting voltage to insure a gradual approach to the proper heating rate.

7. Adjust the recorder to the proper temperature range and set the mode switch on record.

8. Stir the reference temperature ice bath to insure equilibrium.

9. Observe the thermogram until a vertical endotherm appears, at which time the K-3 Potentiometer is placed in the circuit and balanced.

10. Measure the system pressure.

11. Using the thermocouple calibration table, convert the recorded EMF to degrees Centigrade using linear interpolation.

The result is a vapor pressure-temperature point which can be obtained in about fifteen minutes. In case the material is heat sensitive, one can place the sample into the heating block at a temperature a few degrees below the boiling point, rapidly obtaining the desired pressure while starting to heat to the boiling point. This procedure, although somewhat difficult to control, will insure the least time of exposure to high temperature.

This procedure was used successfully in determining the vapor pressures of the high molecular weight alkyl chlorides.

EXPERIMENTAL RESULTS

About thirteen experimental vapor pressure determinations were made for each compound. These points were evenly spaced about five to fifteen degrees Centigrade apart. This was necessary in order that each point should carry equal weight in the subsequent regression analysis. The original data can be found in Appendix C.

Tables 9 and 10, pages 93 and 94, list the range of vapor pressure measurement, the total number of data points and the maximum boiling point variation for each compound. The maximum boiling point variation was obtained from the recorded boiling endotherm by measuring the amount of variation from a vertical axis.

Table 11, page 95, shows the goodness of fit of the experimental data to the Antoine equation via some statistical parameters and absolute deviations from the actual data. A theoretical discussion of the Antoine equation can be found in the "Theory" section of this work. Table 12, page 96, lists the Antoine constants and the C.I. (95%) associated with them. Tables 13 and 14,

Table 9: Experimental Data Range - The n-Alkyl Chlorides

Carbon Number	No. of Data Points	Pressure Range mm Hg	Temp. Range °C	Maximum Boiling[1,2] Point Range °C
3	9	28.8 - 776.0	-25.1 - 47.1	N.D.[3]
4	12	10.1 - 758.8	-16.7 - 78.5	N.D.
5	13	5.0 - 774.0	15.0 - 135.6	N.D.
7	13	5.1 - 753.4	34.4 - 160.1	N.D.
8	13	5.6 - 773.2	54.1 - 184.1	N.D.
9	14	5.1 - 752.8	69.1 - 204.8	N.D.
10	13	5.5 - 754.7	86.2 - 225.6	N.D.
11	14	5.5 - 763.0	101.4 - 245.4	N.D.
12	14	5.5 - 764.0	116.0 - 263.6	N.D.
14	13	5.2 - 764.2	141.7 - 297.0	N.D., -.2 200 mm
16	15	5.1 - 766.5	165.6 - 326.8	N.D., -.2 120 mm

1 $\pm .05^{o}C$ is the smallest detectable boiling point range.

2 These data represent the maximum boiling point range for every pressure except where indicated.

3 N.D. - no boiling point range detected.

Table 10: Experimental Data Range - The n-Alcohols

Carbon Number	No. of Data Points	Pressure Range mm Hg	Temp. Range °C	Maximum Boiling Point Range[1,2] °C
3	14	14.9 - 758.5	19.8 - 97.3	N.D.[3]
4	13	5.5 - 766.0	22.6 - 117.8	N.D.
5	13	4.3 - 502.1	33.9 - 125.8	N.D.
6	13	5.7 - 757.3	52.2 - 157.3	N.D.
7	13	4.7 - 760.8	63.6 - 176.4	N.D.
8	12	5.3 - 760.0	78.9 - 195.3	N.D.
9	13	5.6 - 763.9	91.7 - 213.6	N.D.
10	13	5.6 - 757.6	105.0 - 231.0	N.D.
12	14	5.3 - 766.0	126.5 - 265.3	N.D.
14	12	5.7 - 755.2	151.6 - 295.9	N.D., $\pm$.1 120 mm
16	13	5.9 - 759.2	172.1 - 325.1	N.D., $\pm$.4 80 mm

1 $\pm$.05°C is the smallest detectable boiling point range.

2 These data represent the maximum boiling point range for every pressure except where indicated.

3 N.D. - no boiling point range detected.

Table 11: Goodness of Fit to the Antoine Equation

Carbon Number	No. of Data Points	Sum of Squares of Regression	Correlation Coefficient	Variance of Estimate x 10^4	Error Analysis Pressure Estimate Avg.Abs. %	Max.Abs. %
			n-Alcohols			
3	14	4.1789	.99944	4.227	.397	.880
4	13	5.3562	.99960	4.233	.667	1.525
5	13	5.6086	.99974	2.908	.447	2.243
6	13	5.2915	.99991	.970	.540	1.307
7	13	5.4169	.99990	.995	.619	1.565
8	12	5.1125	.99993	.831	.714	1.334
9	13	5.2734	.99999	.129	.338	.674
10	13	5.3077	.99989	1.132	1.004	2.189
12	14	6.7135	.99997	.363	.535	1.973
14	12	5.2036	.99996	.472	.793	1.665
16	13	5.2433	.99984	.166	1.180	3.569
			n-Alkyl Chlorides			
3	9	1.9840	.99729	17.955	.418	1.251
4	12	4.0562	.99321	61.825	.677	1.230
6	13	5.4274	.99966	3.716	.738	1.646
7	13	5.3620	.99992	.901	.402	.983
8	13	5.3246	.99991	.923	.548	1.161
9	14	6.5356	.99995	.536	.361	1.194
10	13	5.2804	.99999	.136	.212	.820
11	14	6.0781	.99999	.095	.270	.544
12	14	6.3766	.99998	.256	.431	.889
14	13	5.4233	.99995	.549	.659	2.050
16	15	6.7743	.99997	.331	.638	1.466

Table 12: Antoine Constants - Pressure Range 5 - 760 mm Hg

Carbon Number	Antoine Constants					
	A	± C.I. (95%)	B	± C.I. (95%)	C	± C.I. (95%)
			n-Alcohols			
3	8.18894	.86293	1690.864	325.533	221.346	13.968
4	7.42117	.34030	1351.555	396.336	179.810	9.808
5	7.55787	.24240	1492.549	119.999	181.529	9.656
6	7.28781	.17268	1422.031	88.077	165.444	7.715
7	6.85450	.16624	1256.783	80.417	139.663	7.754
8	6.62354	.16908	1196.639	84.438	124.107	8.445
9	6.83667	.07376	1373.417	41.593	133.968	3.915
10	6.39379	.21350	1180.306	113.401	104.321	11.779
12	6.68662	.11792	1454.635	70.995	117.235	7.295
14	6.48407	.17456	1412.907	108.373	95.368	11.275
16	7.04183	.36732	1880.126	273.437	127.123	25.198
			n-Alkyl Chlorides			
3	6.96655	5.93060	1126.383	1617.020	229.370	17.001
4	6.87098	6.65052	1182.903	1738.518	218.265	19.425
6	6.76886	.28820	1304.968	109.018	200.058	7.282
7	6.83820	.13028	1410.064	138.333	195.639	5.529
8	6.84310	.14358	1469.829	81.119	187.157	7.572
9	6.94063	.10906	1586.937	63.468	185.505	6.061
10	6.99172	.06904	1676.793	44.963	182.017	4.145
11	6.97249	.05863	1713.225	37.097	173.366	3.707
12	6.96976	.09977	1754.079	64.095	165.632	6.295
14	6.88717	.17188	1776.491	120.120	146.180	11.633
16	7.00109	.13187	1924.969	67.799	140.341	9.106

Table 13: Vapor Pressures of the Normal Straight Chain Alcohols

Pressure	Propanol	Butanol	Pentanol	Hexanol	Heptanol	Octanol
mm Hg			Temperature °C			
5	---	21.2	36.1	50.4	64.5	77.9
10	---	30.7	46.1	60.7	75.0	88.7
15	19.8	36.6	52.4	67.2	81.7	95.6
20	24.1	41.0	57.0	72.1	86.6	100.7
30	30.6	47.6	63.9	79.3	94.1	108.4
40	35.4	52.5	69.1	84.7	99.6	114.2
55	40.9	58.1	75.0	90.9	106.1	121.0
80	47.7	65.1	82.4	98.6	114.2	129.4
120	55.4	73.2	90.9	107.6	123.5	139.2
200	65.8	84.2	102.4	119.7	136.3	152.7
300	74.7	93.6	112.2	130.2	147.4	164.5
500	86.6	106.4	125.7	144.4	162.8	180.8
760	97.2	117.9	137.6	157.2	176.6	195.6
A	8.18894	7.42117	7.55787	7.28781	6.85450	6.62354
B	1690.864	1351.555	1492.549	1422.031	1256.783	1196.639
C	221.346	179.810	181.529	165.444	139.663	124.107

The values above are calculated from the given Antoine Constants and the equation $\log P = A - \frac{B}{C+t}$.

Table 13: Continued

Pressure	Nonanol	Decanol	Dodecanol	Tetradecanol	Hexadecanol
mm Hg			Temperature °C		
5	89.8	102.9	125.7	148.9	169.2
10	101.3	114.5	138.6	162.3	184.0
15	108.7	121.9	146.7	170.8	193.3
20	114.1	127.4	152.9	177.2	200.3
30	122.3	135.7	162.0	186.8	210.6
40	128.4	142.0	168.9	194.0	218.4
55	135.5	149.3	176.9	202.5	227.4
80	144.4	158.5	186.9	213.1	238.6
120	154.7	169.2	198.5	225.4	251.6
200	168.8	184.1	214.5	242.4	269.4
300	181.1	197.0	228.3	257.2	284.7
500	198.0	215.1	247.6	277.9	305.7
760	213.2	231.7	265.0	296.8	324.6
A	6.83667	6.39379	6.68662	6.48407	7.04183
B	1373.417	1180.306	1454.635	1412.907	1880.126
C	133.968	104.321	117.235	95.368	127.123

The values above are calculated from the given Antoine Constants and the equation $\log P = A - \frac{B}{C+t}$.

Table 14: Vapor Pressures of the Normal Straight Chain Alkyl Chlorides

Pressure	Chloro-propane	Chloro-butane	Chloro-hexane	Chloro-heptane	Chloro-octane	Chloro-nonane
mm Hg			Temperature °C			
5	-49.7	-26.6	14.9	34.0	52.1	68.7
10	-40.6	-16.8	26.2	45.9	64.4	81.6
15	-34.9	-10.6	33.3	53.4	72.2	89.8
20	-30.6	- 5.9	38.6	59.0	78.1	95.9
30	-24.2	1.0	46.6	67.4	86.8	105.0
40	-19.4	6.2	52.5	73.7	93.3	111.8
55	-13.8	12.3	59.5	81.0	100.9	119.7
80	- 6.9	19.8	68.1	90.1	110.4	129.5
120	1.1	28.6	78.2	100.7	121.4	140.9
200	12.1	40.6	92.0	115.1	136.4	156.5
300	21.5	51.0	104.0	127.7	149.5	170.0
500	34.6	65.3	120.6	145.0	167.5	188.6
760	46.3	78.2	135.6	160.7	183.8	205.4
A	6.96655	6.87098	6.76886	6.83820	6.84310	6.94063
B	1126.383	1182.903	1304.968	1410.064	1469.828	1586.937
C	229.370	218.265	200.058	195.639	187.157	185.505

The values above are calculated from the given Antoine Constants and the equation $\log P = A - \frac{B}{C+t}$.

Table 14: Continued

Pressure	Chloro-decane	Chloro-undecane	Chloro-dodecane	Chloro-tetradecane	Chloro-hexadecane
mm Hg			Temperature °C		
5	84.5	99.7	114.1	140.9	165.1
10	97.8	113.5	128.2	155.6	180.4
15	106.3	122.2	137.1	164.9	190.1
20	112.6	128.7	143.8	171.8	197.4
30	122.1	138.4	153.7	182.2	208.1
40	129.1	145.6	161.1	190.0	216.2
55	137.3	154.1	169.8	199.0	225.6
80	147.5	164.6	180.6	210.3	237.3
120	159.3	176.8	193.0	223.3	250.8
200	175.5	193.4	210.1	241.2	269.2
300	189.4	207.7	224.8	256.6	285.2
500	208.6	227.5	245.1	278.0	307.1
760	225.9	245.3	263.4	297.2	326.9
A	6.99172	6.97249	6.96976	6.88717	7.00109
B	1676.793	1713.225	1754.079	1776.491	1924.969
C	182.017	173.366	165.632	146.180	140.341

The values above are calculated from the given Antoine Constants and the equation $\log P = A - \frac{B}{C+t}$.

pages 97 and 99 present vapor pressure-temperature data at set conditions for the n-alcohols and the n-alkyl chlorides.

THEORETICAL DERIVATIONS

Liquid Density as a Function of Vapor Pressure

The following derivation is based upon Kurata and Isida's equation (61) and will present a newly developed relationship between liquid density, vapor pressure and the number of carbon atoms in a straight chain molecule.

It may be recalled that the liquid volume is equal to the sum of the volume of full cells plus holes. At low temperatures, i.e., below the normal boiling point, one may assume that the number of empty cells in a liquid is negligible compared to the number of full cells. Thus one may write that the liquid volume per molecule, v_1, is equal to $x\tau$, the volume of a molecule. The molal liquid density, ρ_1, may then be described as

$$\rho_1 = 1/N_A v_1 \tag{66}$$

where N_A is Avagadro's number. Substituting (66) into (61) and realizing that $R = N_A k$ one obtains

$$\ln P = \ln (RT\rho_1) + x - 1 - \frac{N_A z x \psi}{2TR} . \tag{67}$$

Equation (67) may be rewritten into the following more useful form

$$\ln (T\rho_1) = \left[\ln \frac{P}{R} + 1\right] + \left[\frac{N_A z \psi}{2RT} - 1\right] x \quad . \qquad (68)$$

It is of interest to consider equation (68) at constant pressure. It can be seen that the term $\left[\ln \frac{P}{R} + 1\right]$ would be a constant and for simplicity the term $\left[\frac{N_A z \psi}{2RT} - 1\right]$ was also arbitrarily considered constant. The resultant equation shows $\ln (T\rho_1)$ linear in x. Thus a plot of $\ln (\rho_1 T)$ vs. x should produce a straight line for each pressure considered. By definition, x is a function of the effective chain length of a molecule, which in turn should be related to the number of carbon atoms in a chain. It has been shown (37) that the function is sufficiently well represented by

$$x = N^{2/3} \qquad (69)$$

where N equals the number of carbon atoms in a chain. Thus a plot of $\ln (\rho_1 T)$ vs. $N^{2/3}$ should also produce linear isobars. Figure 11, page 104 shows that this is actually the case for the normal alkanes. Thus one may justifiably write

$$\ln (T\rho_1) = A + Bx \qquad (70)$$

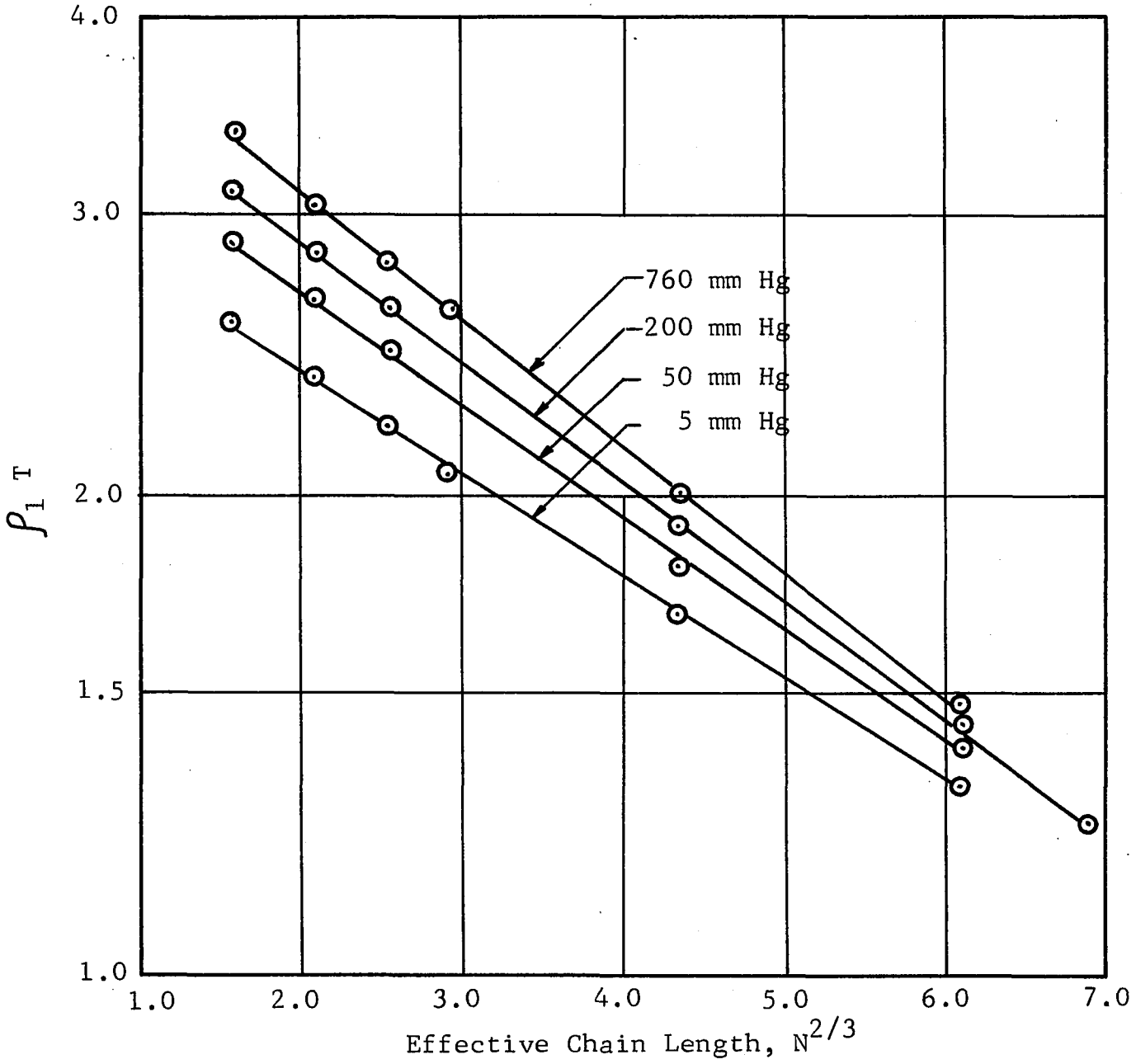

Figure 11: DENSITY, N-ALKANES

where $$A = \left[\ln \frac{P}{R} + 1\right] , \tag{71}$$

and $$B = \left[\frac{N_A z \psi}{2RT} - 1\right] . \tag{72}$$

Equation (71) shows that A is some linear function of ln P. By setting x in equation (70) equal to zero, one may solve for A at different pressures. A plot of A vs. ln P demonstrates the expected linear function for the normal alkanes, as shown in Figure 12, page 106. It was shown similarly that B too is a linear function of ln P as demonstrated in Figure 13, page 107. Substituting these linear functions for A and B in terms of ln P into equation (68) one obtains

$$\ln (T\rho_1) = C + D \ln P + Ex + Fx \ln P . \tag{73}$$

Thus an equation has been developed which relates the liquid density of any compound in a straight chain homologous series with the effective chain length of the compound and its vapor pressure at a corresponding temperature. Application of this equation to the n-alkenes, n-alkyl chlorides and the n-alcohols reveals that these series also conform. The results of this application are fully discussed in a later section.

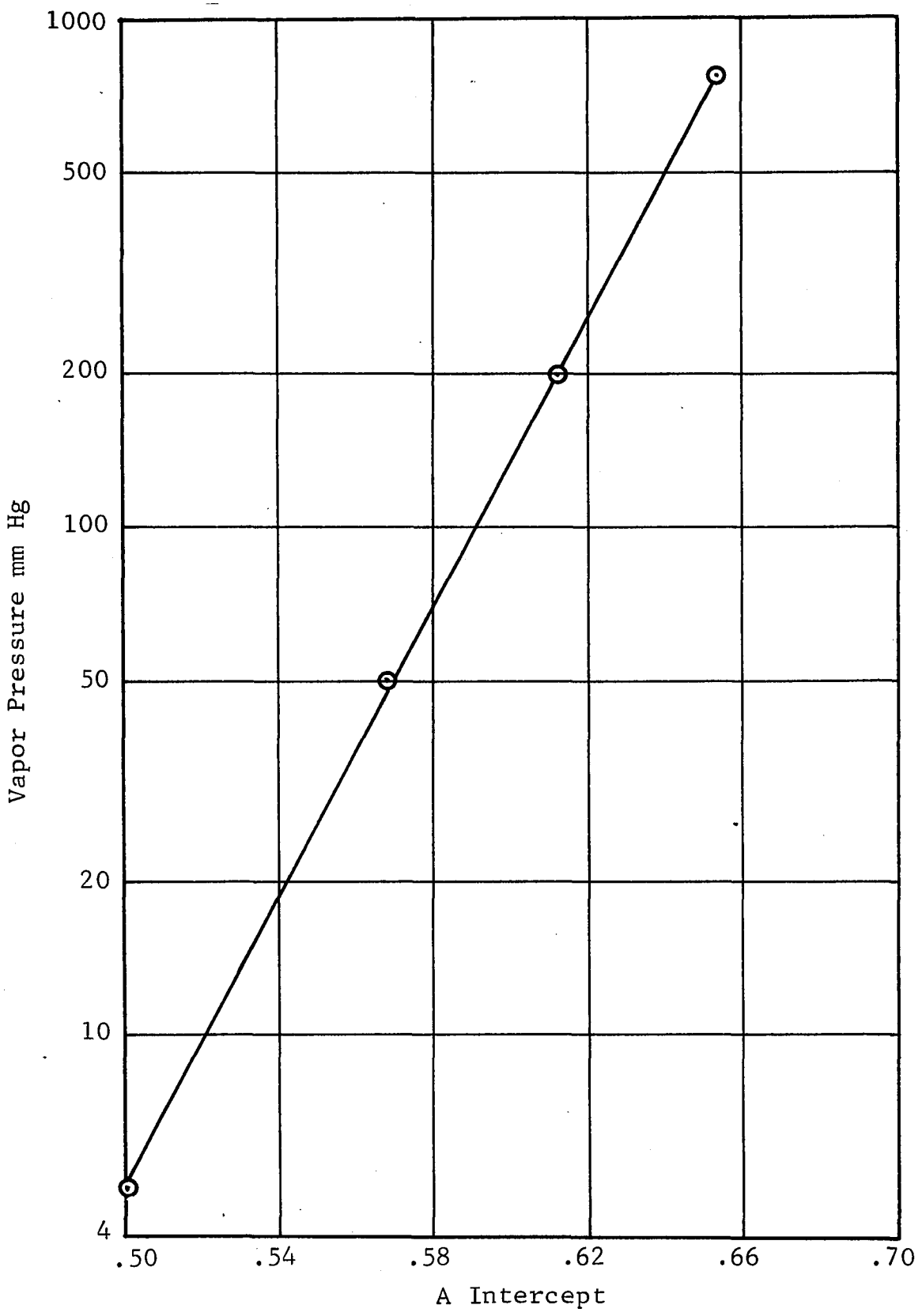

Figure 12: N-ALKANES, DENSITY INTERCEPT

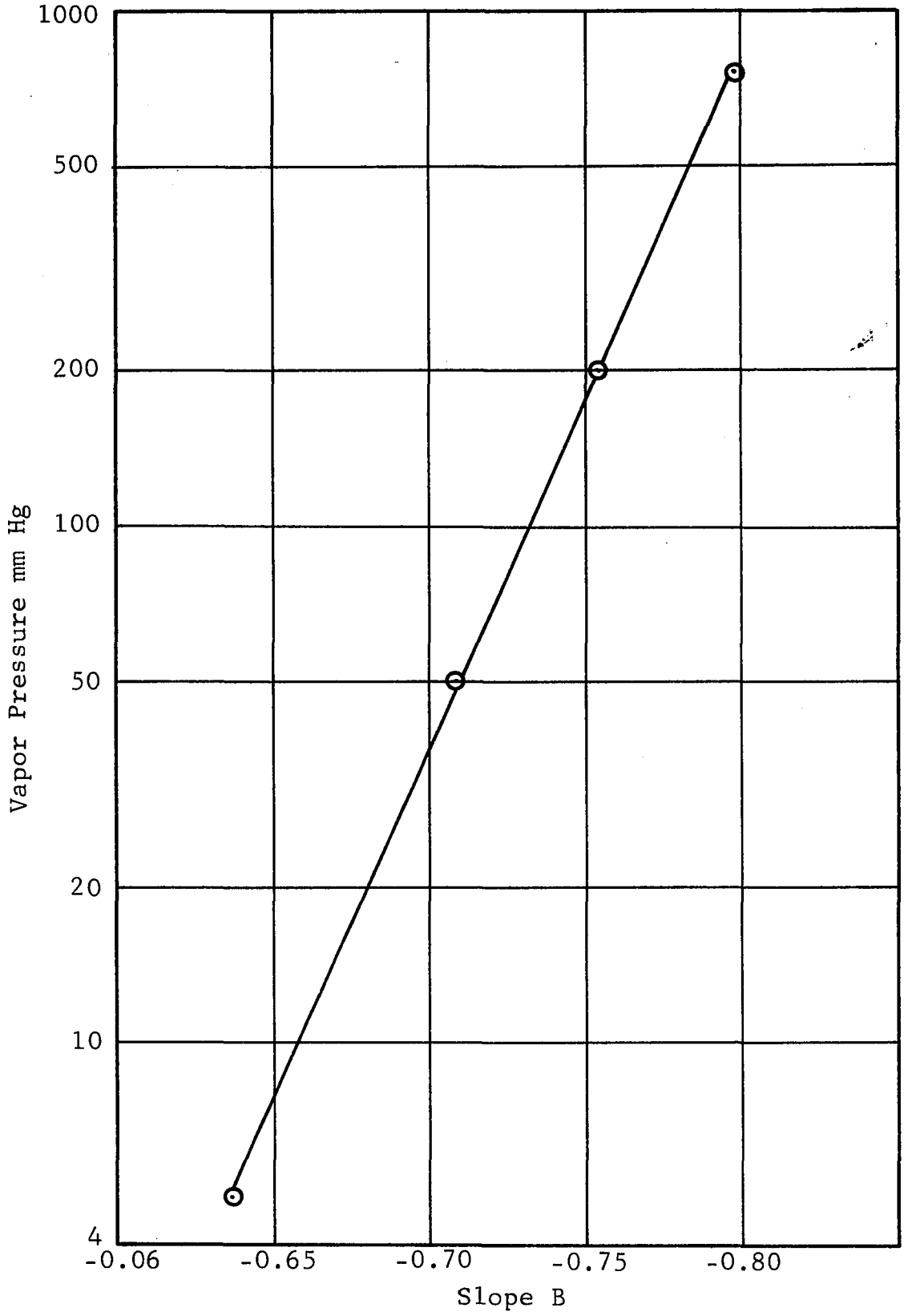

Figure 13: N-ALKANES, SLOPE B

A Modified Kurata-Isida Heat of Vaporization Equation

One may recall equation (65) as

$$E_v = \frac{N_A x z \epsilon}{2} \quad . \tag{65}$$

Since all the terms, except x, on the right side of equation (65) are constants, a plot of E_v as a function of x should be linear. A plot of E_v as a function of x where x equals $N^{2/3}$ shows a linear relation between E_v and x; but contrary to equation (65), this linear relation is a function of vapor pressure as seen in Figure 14, page 109. Note that there is a common intercept at x = 0 and E_v = 0 for the normal alkanes. Similar plots for the n-alkyl chlorides and the n-alcohols, Figures 16 and 17, pages 111 and 112, show the same linear functions but different common intercepts at x = 0. Plots of the slopes of these curves as a function of pressure show them to be linear in ln P. This plot may be seen in Figure 15, page 110.

Thus at constant pressure one may write

$$E_v = A + Bx \tag{74}$$

where B equals $\frac{N_A z \epsilon}{2}$ and A is a constant characteristic of the series.

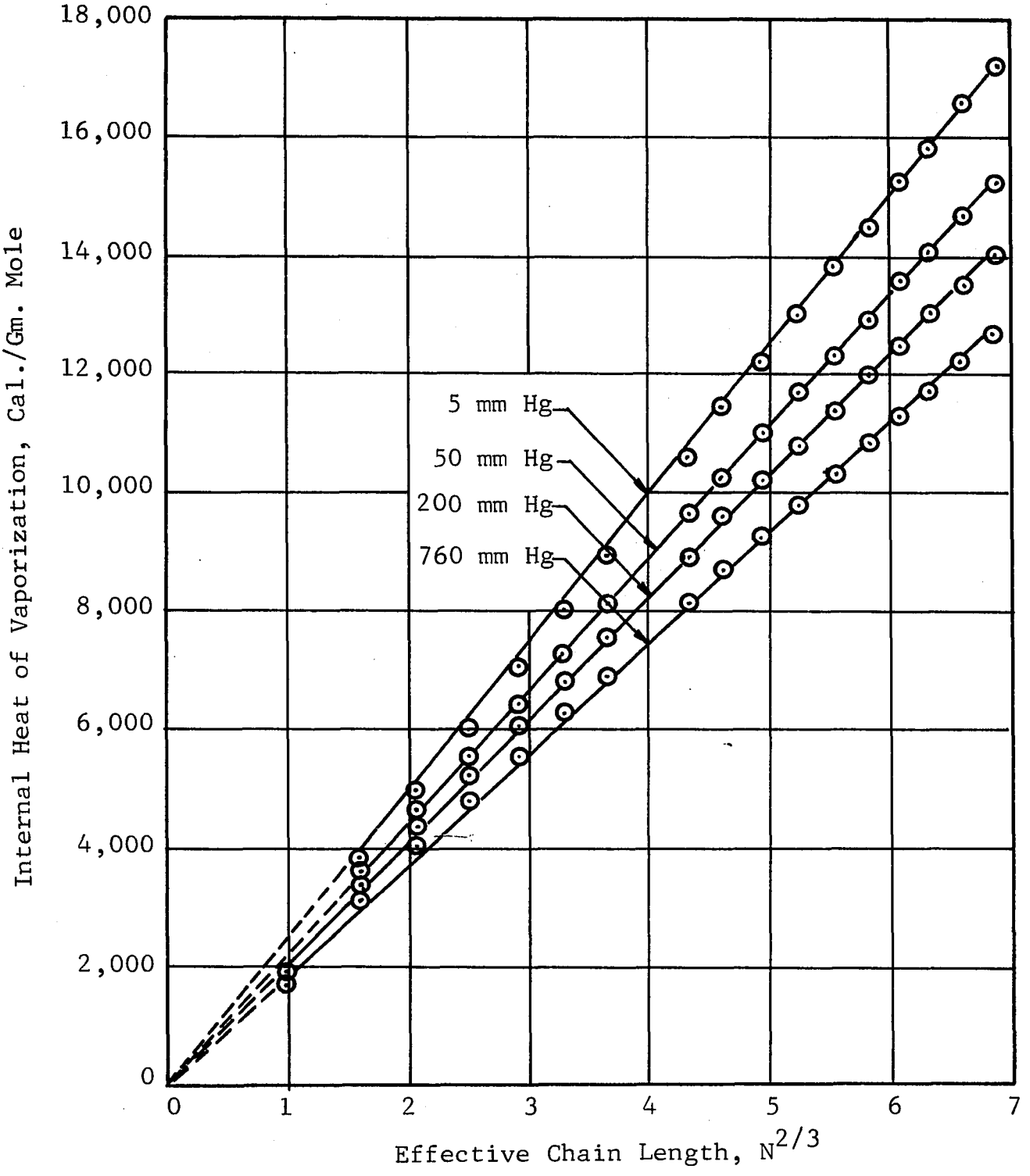

Figure 14: HEAT OF VAPORIZATION - N-ALKANES

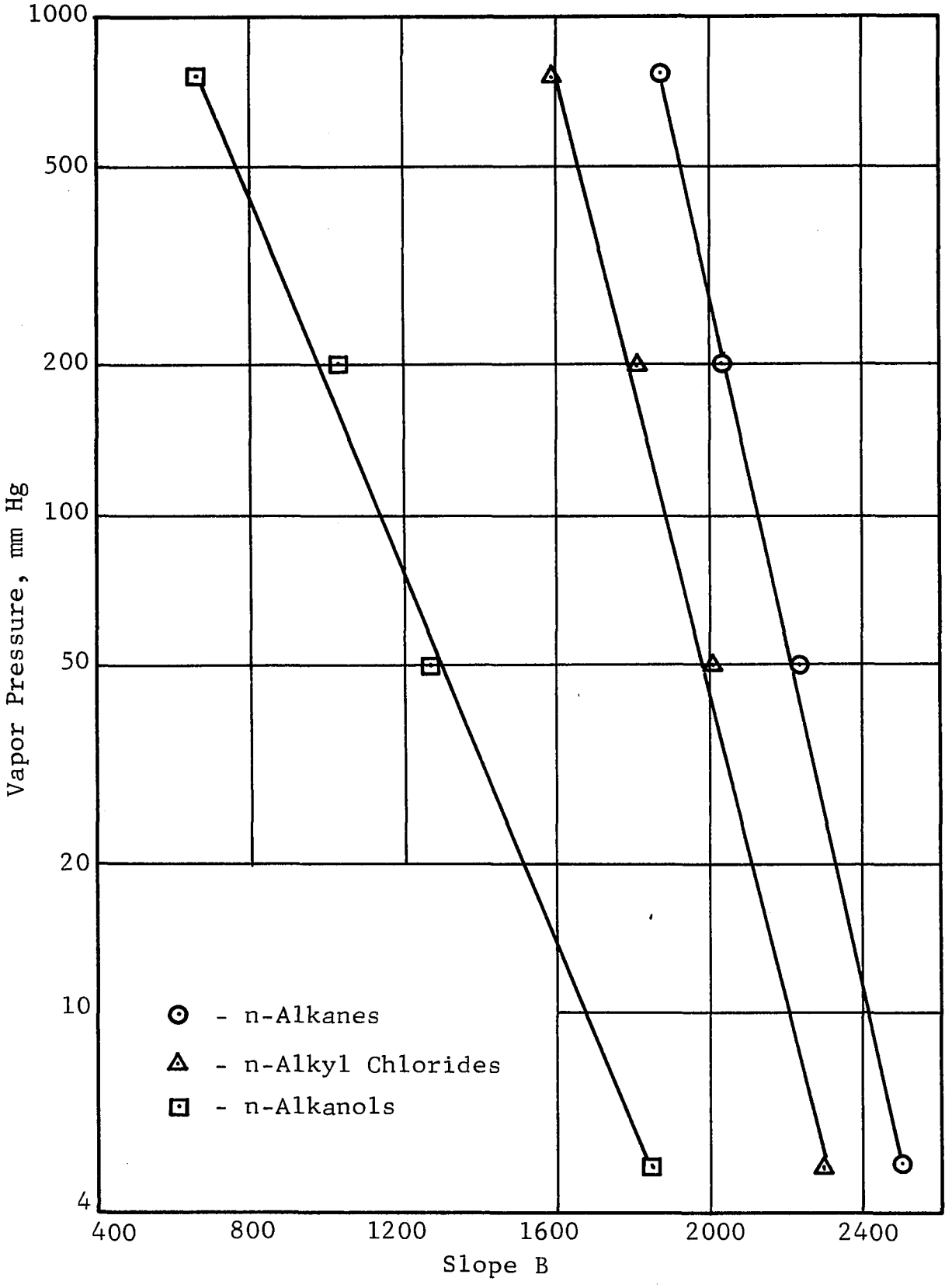

Figure 15: HEAT OF VAPORIZATION, SLOPE B

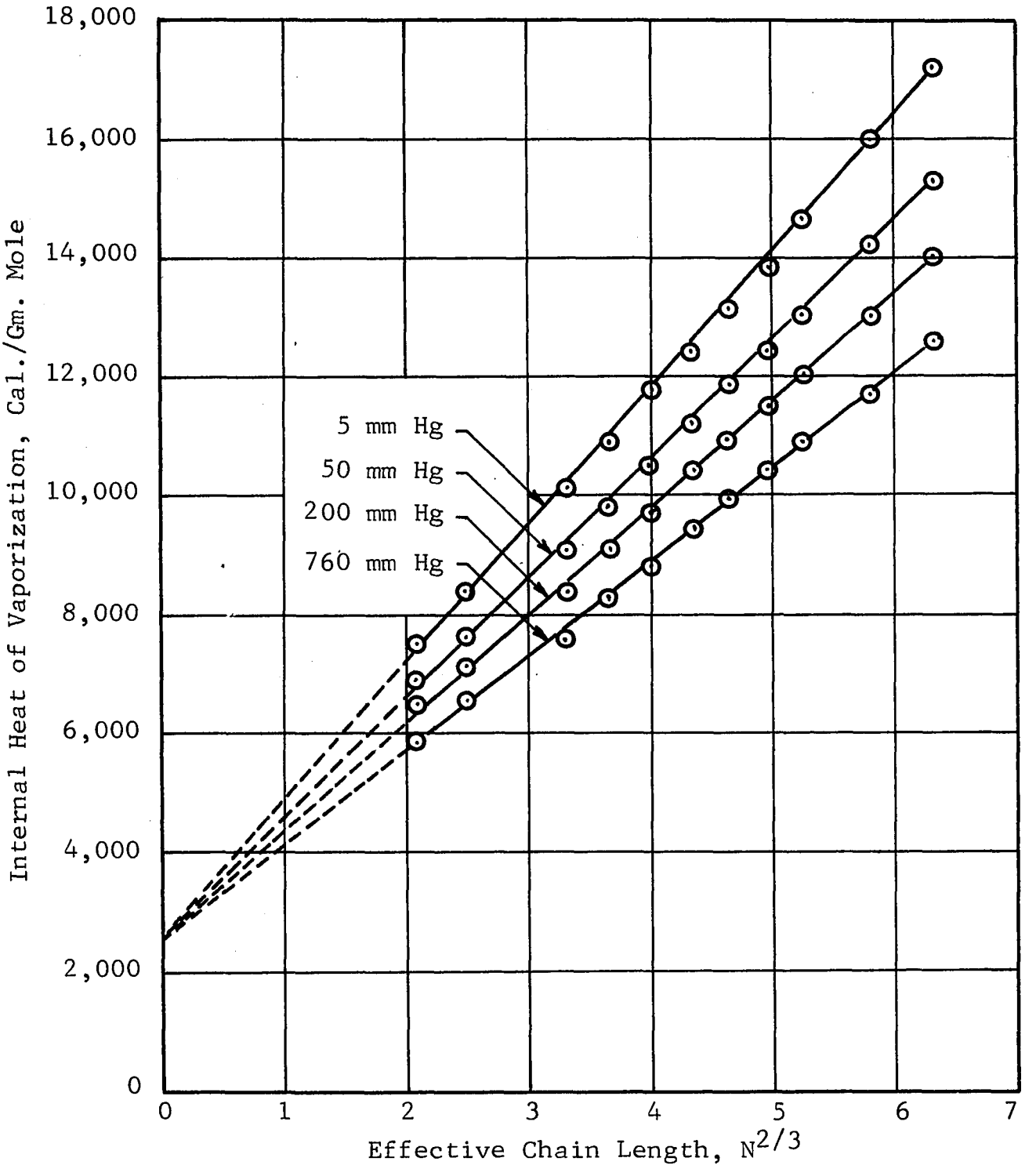

Figure 16: HEAT OF VAPORIZATION, N-ALKYL CHLORIDES

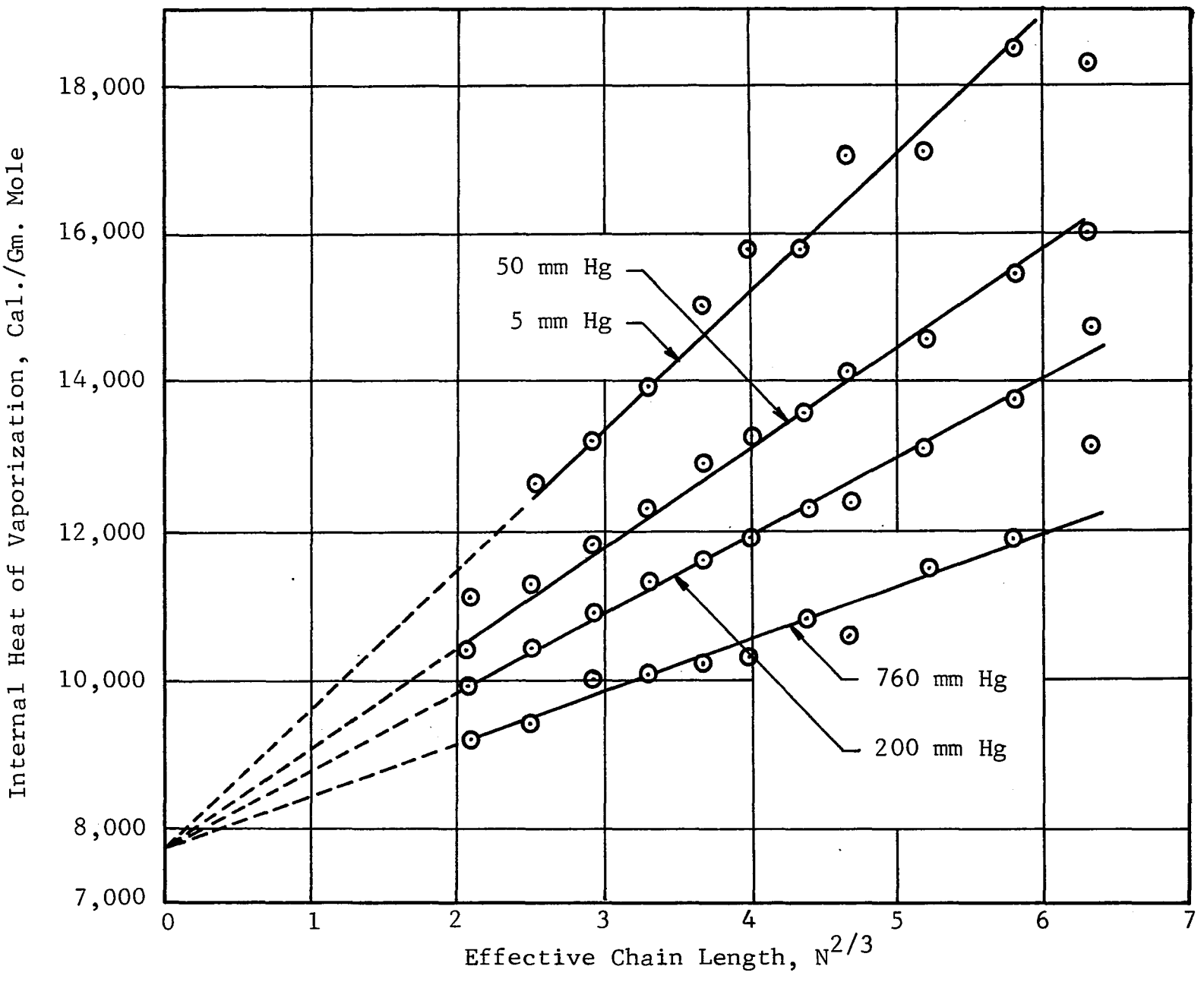

Figure 17: HEATS OF VAPORIZATION, N-ALKANOLS

From the foregoing discussion one is justified in writing

$$B = C + D \ln P \quad . \tag{75}$$

By combining equations (74) and (75) an equation is obtained which describes the internal energy of vaporization as a function of vapor pressure and effective chain length for an homologous series. Thus

$$E_v = A + Cx + Dx \ln P \quad . \tag{76}$$

ANALYSIS AND APPLICATION OF CORRELATIONS

Computational Methods of Data Correlation

The Antoine equation. The Antoine equation possesses several advantages over other types of vapor pressure equations. In every case it fits the data better than the equations of the simple Clausius-Clapeyron type, except where C is equal to 273, at which point it corresponds. The values of the constants are readily determined and the equation may be rearranged easily so that it is explicit for either variable. The Antoine equation reproduces the value of moderately precise data within an error of 0.1 to 2 per cent in P, more precisely than many more complex equations. On the negative side, the Antoine equation cannot be extrapolated above a reduced temperature of .8 to .85 although two sets of equations can be used, one up to T_R = .8 and the other from T_R = .8 to and including the critical point (62).

The three Antoine constants were determined by the method of multi-linear regression analysis. A regression analysis is based upon three assumptions (62). The given equation shall be a true representation of the data, the experimental data shall contain only random errors, and

these errors are normally distributed. The latter two requirements were assumed true based upon a study of the instrumental precision. The first assumption was justifiable because the Antoine equation has been shown to fit the vapor pressure data of many compounds of all types well, and because a theoretical basis for the equation was deduced for the relationship.

Application of a least squares curve fitting technique requires that the equation in question must be of the linear form

$$y = a + bx_1 + cx_2 \quad \ldots \quad . \tag{77}$$

Winslow (71) has shown that the Antoine equation may be expressed as

$$\log P = a + (b/t) + (c \log P/t) \ , \tag{78}$$

where the Antoine A, B and C constants are expressed as

$$A = a$$
$$B = -(ac + b)$$
$$C = -c$$

Thus if the following substitutions are made one obtains

the equivalent of equation (77):

$$1/t = x_1$$
$$\frac{\log P}{t} = x_2$$
$$\log P = y \quad .$$

The computational work was programmed for an IBM 1620-II computer. The complete Fortran program is shown in Appendix D.

<u>The density correlation</u>. The derived density correlation was presented as

$$\ln (T\rho_1) = C + D \ln P + Ex + Fx \ln P \quad . \qquad (73)$$

In order to test the validity of the equation it would be necessary to determine the constants and then compare the calculated density values obtained with this function with the experimental values. The constants for the equation were evaluated using the technique of least squares multiple linear regression analysis (<u>66</u>). In order for this technique to be used, the equation had to be linearized. The following substitutions were made

$$\ln (T\rho_1) = y$$
$$\ln P = x_1$$
$$x \ln P = x_2$$

and the resulting linear equation becomes

$$y = C + Dx_1 + Ex + Fx_2 \quad . \tag{79}$$

The computational work in obtaining the least squares coefficients was done by an IBM 1620-II computer with disc storage. The complete program may be found in Appendix D. It should be pointed out that a Fortran IID compiler with a format of fourteen significant figures was used in order to insure an ample degree of significance. This was found necessary since two large numbers are subtracted to find a small difference when solving for the individual partial regression coefficients, as can be seen in the program.

The program was arranged so that temperature-density data points for an entire homologous series were read directly into core storage along with the Antoine constants for each compound. Thus at any temperature-density point the vapor pressure could be determined. With this information the least squares analysis was carried out and the constants were generated along with a statistical analysis of the correlation. The analysis produced information for the total correlation coefficient, the sum of squares of regression, the residual sum of squares, and the variance of estimate for the line. The program then generated density data at the original input temperatures so that a point

by point comparison could be made between the experimental density and the calculated density. The comparison produced a density difference and per cent error for each point as well as average and maximum absolute per cent errors for the total data set. The results of this analysis will be presented in a following section.

In order to use the correlation to predict unknown densities from vapor pressure data, a program was written which predicts densities at every ten degrees Centigrade from corresponding vapor pressure data ranging from 5 to 760 mm Hg, using the derived density equation. The program is shown in Appendix D.

Heat of vaporization correlation. The modified Kurata-Isida heat of vaporization equation was given on page 113 as

$$E_v = A + Cx + Dx \ln P \quad . \tag{76}$$

As with the density correlation, an equation was fitted to the data using the technique of multi-linear regression analysis. The following substitutions were made in order to linearize the equation:

$$E_v = y$$
$$x \ln P = x_1 \quad .$$

After substitution the equation presents itself in the multi-linear form

$$y = A + Cx + Dx_1 \quad . \tag{80}$$

The multi-linear regression analysis was carried out according to Volk (66). The computational work was done by an IBM 1620-II computer using a Kingston Fortran compiler. The program was designed so that only the Antoine constants for each compound in a series had to be supplied. The heat of vaporization data were self-generating in the program. The method of generation will be discussed in the following section. The entire program is found in Appendix D. The program output presented a statistical analysis of the correlation and a point by point comparison of the experimental with the correlation value. A summary of the output values is given in the section headed "Results".

Variation of Effective Chain Length Parameter

It may be recalled that x, the effective chain length, was assumed to be the two-thirds power of the number of carbon atoms. In order to determine whether this was the optimum power, a generalized function was set up as

$$x = N^y \tag{81}$$

where N equals the number of carbon atoms in the chain. In order to find the optimum y the density correlation was carried out with different powers of N. The variance of estimate of the least squares line obtained for each power was plotted against the power. The power which produced the minimum variance of estimate was chosen as the optimum. Examples of these plots are presented in Figures 18 and 19, pages 124 and 130.

Data Sources

Density. Density data for the investigated homologous series were obtained from the American Petroleum Institute, Project 44 (57) wherever possible, since it was felt that this was the most reliable source. Missing data were obtained wherever possible.

A complete listing of density data and references is given in Appendix E. A listing of the Antoine constants used to determine the vapor pressure for compounds, other than those which were determined experimentally, is also given in the Appendix, together with their sources.

Heat of vaporization. The internal heats of vaporization were calculated from vapor pressure data using the Haggenmacher method (29), and Fishtine's method (18) for obtaining the delta compressibility factor, ΔZ. The

Haggenmacher equation uses as its basis the Clapeyron equation in the form

$$\frac{d \log P}{d(1/T)} = - \frac{H_v}{2.303R(Z_g - Z_l)} \quad . \tag{82}$$

Differentiating the Antoine equation with respect to 1/T yields,

$$\frac{d \log P}{d(1/T)} = \frac{T^2 B}{(t+C)^2} \quad . \tag{83}$$

Subtracting equation (83) from (82) and rearranging results in

$$H_v = \frac{2.303RT^2 B \Delta Z}{(t+C)^2} \tag{84}$$

where ΔZ equals $Z_g - Z_l$.

Since,

$$H_v = E_v + P\Delta V \tag{85}$$

and,

$$V = \frac{RT}{P}\Delta Z \tag{86}$$

one obtains by proper substitution

$$E_v = \frac{2.303RT^2 B \Delta Z}{(t+C)^2} - RT\Delta Z \quad . \tag{87}$$

Fishtine gives different values of ΔZ as a function of $\frac{T}{T_b}$ where T_b is the normal boiling temperature. He claims an accuracy of ± 1.5 per cent for most substances, which is sufficient for the purpose in this dissertation.

Equation (87) was used in the heat of vaporization correlation program to generate internal heats of vaporization.

Results

The Kemme-Kreps density equation and the modified Kurata-Isida heat of vaporization equation were tested by applying them to the four homologous series: n-alkanes, n-olefins, n-primary alkyl chlorides and the n-primary alcohols. The following discussion will consider each equation separately.

The density correlation. A summary of the results for the n-alkanes is shown in Table 15, page 123. The plot to obtain the optimum power for the chain length parameter, y, is shown in Figure 18, page 124. It should be noted that a large error was obtained in correlating the density for the series between C_1 and C_{18}. This large discrepancy was found only when methane was included in the correlation. Because of this result, the first member of any series which contained only one carbon atom was not included in this and

Table 15: Density Correlation - n-Alkanes

Type of Correlation	All Data	Neglect C_1	Limited Data	Prediction with Limited Data Constants
Range of Series	C_1 - C_{18}	C_2 - C_{18}	C_5 - C_8	C_2 - C_{18}
No. of Density Data Pts.	186	183	8	183
Optimum y	.80	.57	.57*	.57*
C constant	1.0517	1.1382	1.1602	1.1602 *
D constant	.051381	.068721	.069374	.069374*
E constant	-.12549	-.19568	-.20286	-.20286*
F constant	-.0034700	-.0090056	-.0091401	-.0091401*
Sum of Squares of Regression	12.09	11.61	.1308	---
Correlation Coefficient	.9947	.9999	.9999	---
Var. of Est. of ln ($T\rho_1$)	7.0×10^{-3}	1.3×10^{-5}	8.0×10^{-8}	---
Avg. Absolute Error, %	1.25	.282	.019	.699
Max. Absolute Error, %	21.57	1.50	.042	2.380

*Assumed values

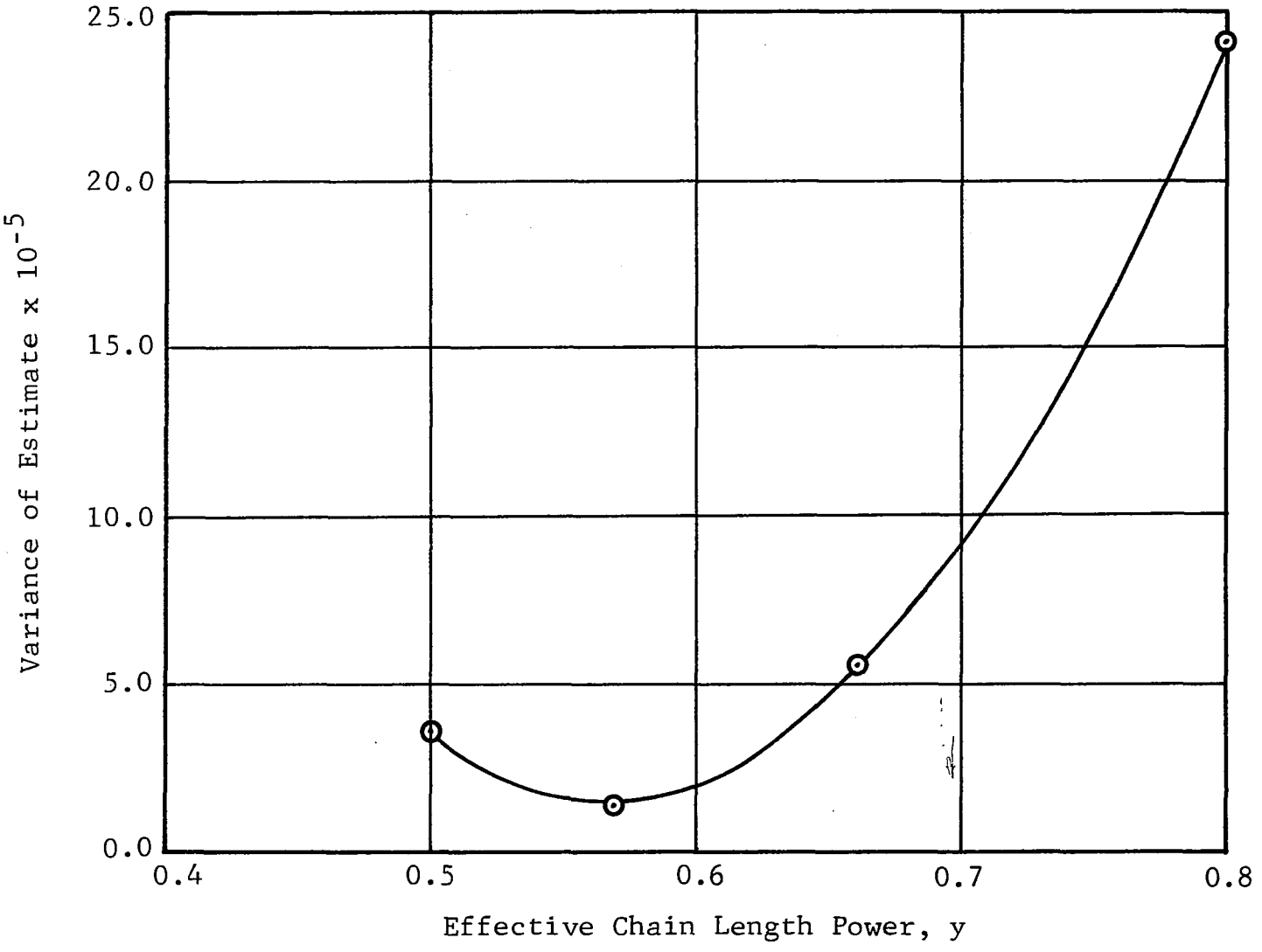

Figure 18: LINEAR REGRESSION OF DENSITY CORRELATION, N-ALKANES C_2 - C_{18}

other correlation analyses.

The API density data (57) are given only up to 260 degrees Centigrade. By using the correlated equation (73) for the series between C_2 and C_{18}, density data are produced for each compound at 10 degrees Centigrade intervals between the temperature at which its vapor pressure is about 10 mm Hg and its saturation temperature. The highest temperature, at 310 degrees Centigrade, is given for octadecane. Thus any density points above 260 degrees Centigrade have been predicted. The results are given in Appendix F.

It was also of interest to determine how well the density could be predicted if only a few data points are known for the lower members of an homologous series. Thus the densities at 20 and 30 degrees Centigrade for C_5 to C_8 n-alkanes were chosen as typical data that might be available for the less common series. By using these data the correlation constants were determined as shown under the heading of "Limited Data" in Table 15, page 123. Density data were then generated using the determined constants and compared with known data. The average and maximum per cent error is shown under the heading of "Prediction with Limited Data Constants".

Table 16, page 126 presents the results obtained in

Table 16: Density Correlation - n-Alkenes

Type of Correlation	All Data	Limited Data	Prediction with Limited Data Constants
Range of Series	C_2 - C_{14}	C_5 - C_9	C_2 - C_{14}
No. of Density Points	93	8	93
Optimum y	.68	.68*	.68*
C constant	1.1146	1.1913	1.1913*
D constant	.066227	.076455	.076455*
E constant	-.14185	-.20496	-.20496*
F constant	-.0064619	-.011011	-.011011*
Sum of Squares of Regression	4.592	.1473	---
Correlation Coefficient	.9989	.9999	---
Var. of Est. of ln (ρ_1T)	1.1×10^{-4}	1.4×10^{-7}	---
Avg. Absolute Error, %	.752	.025	.721
Max. Absolute Error, %	2.69	.058	5.27

*Assumed values

correlating the densities for the n-alkenes. The same format is presented as for the n-alkanes. Again, using the correlation constants from known data, a complete set of density data were computed between C_2 and C_{18} for temperature corresponding to vapor pressure between 10 and 760 mm Hg. These data are given in Appendix F.

Very few density data were available for the n-alkyl chlorides. All available data were used to compute the correlation constants and the optimum y shown in Table 17, page 128. The missing data were then predicted using these constants. These results are summarized in Appendix F.

A limited number of density data for the n-alcohols were found for homologues between C_2 and C_{18}. This entire set of data was used in determining the correlation constants and the optimum y. This information is given in Table 18, page 129 and Figure 19, page 130. Again, all missing data in the temperature range corresponding to vapor pressures between 10 and 760 mm Hg were predicted with the determined constants.

Some low temperature vapor pressure-density data (63) were obtained for a few of the higher alcohols. It was of interest to see how well the correlation would perform over an area of extremely low vapor pressure with constants obtained from the previously mentioned higher vapor

Table 17: Density Correlations - n-Alkyl Chlorides

Type of Correlation	All Data
Range of Series	C_3 - C_6
No. of Density Points	17
Optimum y	.55
C constant	1.3960
D constant	.080328
E constant	-.26550
F constant	-.015683
Sum of Squares of Regression	.3270
Correlation Coefficient	.9999
Variance of Est. of ln ($T\rho_1$)	8.1×10^{-7}
Avg. Absolute Error, %	.059
Max. Absolute Error, %	.209

Table 18: Density Correlation - n-Alcohols

Type of Correlation	All Data
Range of Series	C_2 - C_{18}
No. of Density Points	60
Optimum y	.2
C constant	3.8072
D constant	.069556
E constant	-2.0470
F constant	-.026009
Sum of Sq. of Regression	8.499
Correlation Coefficient	.9999
Var. of Est. of ln (ρ_1T)	2.0×10^{-5}
Avg. Absolute Error, %	.369
Max. Absolute Error, %	.839

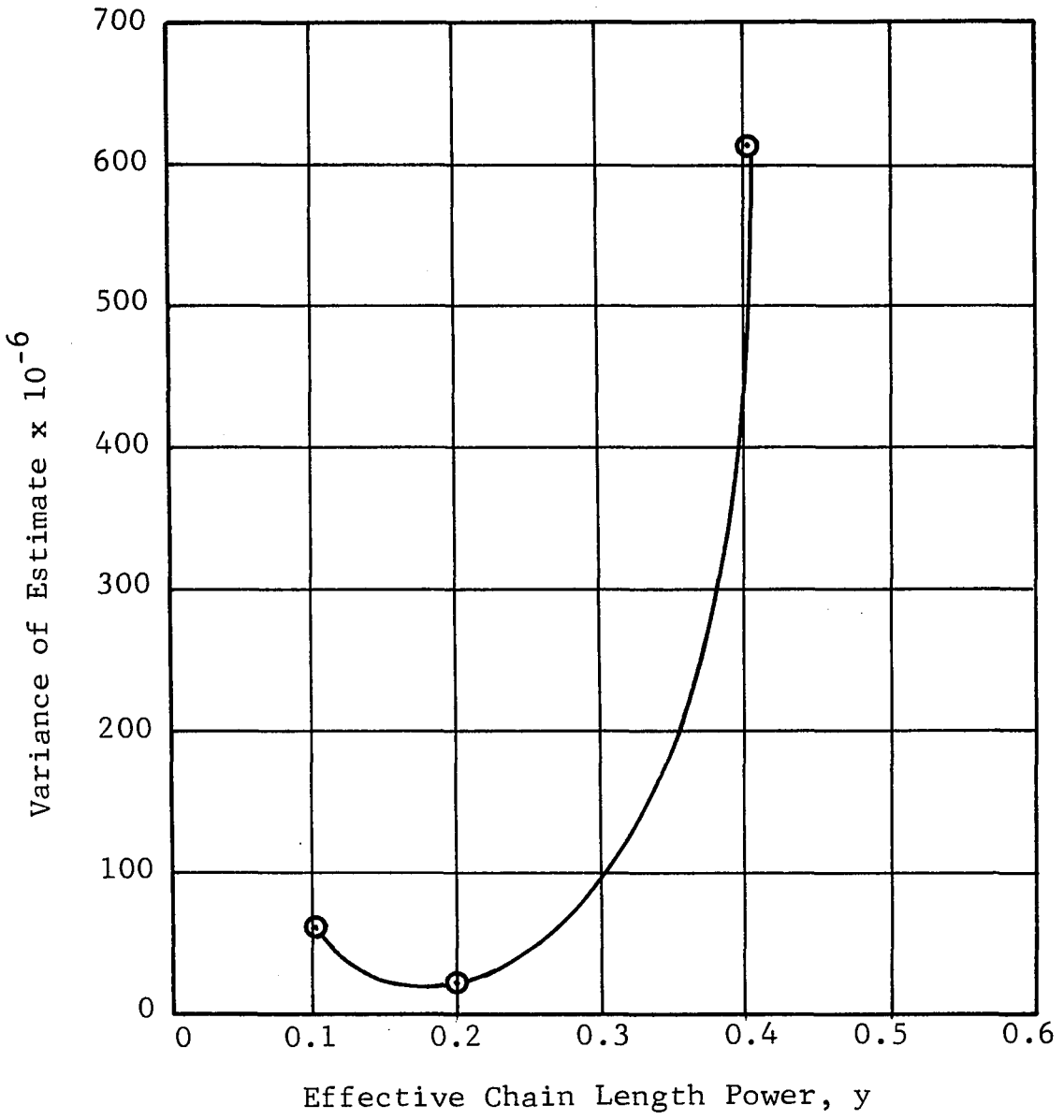

Figure 19: LINEAR REGRESSION OF DENSITY CORRELATION N-ALKANOLS

pressure density data. The results are shown in Table 19, page 132.

The heat of vaporization correlation. As in the density correlation, x is equal to the carbon number raised to some power, y. The optimum power was determined by substituting various powers in the regression analysis and obtaining the respective variance of estimate of the internal heat of vaporization. These values were then cross plotted and the optimum power was taken at the minimum variance of estimate as with the density correlation.

Table 20, page 133, presents a compilation of results when the heat of vaporization correlation was applied to the four series considered. E_v is expressed in calories/gm. mole. The correlation is not extremely sensitive to y so that the average value of .675 for all four series might well be used without any apparent increase in error.

Table 19: Predicting Densities at Low Vapor Pressure with Constants Obtained at High Vapor Pressure

Carbon No.	Temperature °C	Vapor Pressure mm Hg	% Error in Density Estimate
10	20.0	.00535	-1.48
10	25.0	.00912	-1.25
12	30.1	.00161	-2.37
12	25.0	.000846	-3.01
14	38.0	.000597	-2.99
16	50.0	.000363	-3.44
18	59.0	.000027	-7.96

Table 20: Results of Heat of Vaporization Correlation

Series	n-Alkanes	n-Alkenes	n-Alkyl Chlorides	n-Alcohols
Range of Series	C_1 - C_{18}	C_2 - C_{14}	C_1 - C_{18}	C_1 - C_{18}
No. of Data Points	157	117	162	162
Optimum y	.65	.70	.70	.65
A constant	-304.91	125.43	3228.6	7341.2
C constant	2870.5	2407.3	2159.7	2463.1
D constant	-125.89	-103.83	-115.9	-246.4
Sum of Squares of Regression	2.542×10^9	1.032×10^9	1.890×10^9	1.418×10^9
Correlation Coefficient	.9996	.9996	.9983	.9976
Variance of Estimate of E_v at a Point	86.4	65.5	247.8	267.1
Avg. Absolute Error, %	1.18	1.00	1.53	1.30
Max. Absolute Error, %	7.41	6.09	8.18	4.14

DISCUSSION OF RESULTS

Experimental

Instrumental precision. It was necessary to determine the precision of the instrument in order to ascertain what magnitude of errors could be ascribed to the DTA method. Any other errors would necessarily be due to faulty calibration or poor sample purity. It was felt that the method of calibration insured against any error greater than the instrument precision. Sample purity, of course, could be checked by a variation in boiling point.

In order to determine the instrument precision, the boiling point of doubly distilled water was determined at a pressure of 233.9 mm Hg over a period of about eight months. Between August 25, 1965 and September 22, 1965 eight runs were made. The data are shown in Appendix A. On April 11, 1966 another check was made to determine if the thermocouple characteristics remained the same after obtaining all the necessary data. After repeated exposure to thermal cycling, no noticeable change in the thermocouple characteristics could be observed.

The instrument precision was evaluated and is shown by the following statistics:

Range	.0053 milli-volts $\approx$ .13° Centigrade
Standard Deviation	$\pm$.0018 milli-volts $\approx$ $\pm$.05° Centigrade
C.I. (95%)	$\pm$.00407 milli-volts $\approx$ .10° Centigrade

The range is the difference between the highest and lowest values of the series of measurements. The calculations are shown in Appendix A.

Experimental data. In some instances, especially for the lower members of an homologous series, there are some reliable experimental data in the literature. This was especially true for the alcohols and much less so for the alkyl chlorides. Table 21, page 136 presents a comparison between the experimental data generated from Antoine constants based on this author's experimental results, and the literature values for the alcohols and alkyl chlorides. The source of literature data is indicated in the tables. It should be noticed that for any one compound some discrepancy exists among several literature sources. As stated in the "Introduction", this was one of the reasons why original data were sought for this work. These chosen literature values were characterized by experimental techniques of seemingly good quality.

Sample purity. It is felt that sample purity is one of the major factors leading to the observed discrepancies. The most common method to test for purity is to record

Table 21: Alcohol and Alkyl Chlorides: Comparison of Experimental and Literature Vapor Pressures

Compound	No. of Data Points	Pressure Range mm Hg	% Diff.[1] Max.	% Diff.[1] Avg.	Avg. % Diff.	Lit. Ref.
Propanol	1	--- 760.0	-.02	---		(8)
"	12	199.4 - 751.0	-.81	.576		(3)
"	1	--- 760.0	-.02	---	-.50	(4)
Butanol	9	6.78 - 578.6	18.86	2.68		(5)
"	1	--- 760.0	-.55	---		(4)
"	10	247.9 - 697.5	.69	.032		(3)
"	3	125.5 - 506.5	1.37	-.93	.91	(15)
Pentanol	8	26.0 - 611.9	-7.97	-4.84	-4.84	(5)
Hexanol	10	9.75 - 659.8	16.39	1.95		(5)
"	11	7.80 - 714.0	-11.90	5.11		(32)
"	1	--- 763.1	.75	---		(65)
"	5	10.3 - 124.0	2.16	.95	-1.21	(56)

[1] The difference is calculated by subtracting the author's experimental value from the literature value for vapor pressures.

Table 21: Continued

Compound	No. of Data Points	Pressure Range mm Hg	% Diff.[1] Max.	% Diff.[1] Avg.	Avg. % Diff.	Lit. Ref.
Heptanol	9	7.48 - 364.5	-1.90	-1.38		(5)
"	1	--- 7.0	-8.85	---	-2.13	(65)
Octanol	8	6.68 - 201.5	-10.18	-2.75		(5)
"	6	57.0 - 507.5	1.54	.808		(15)
"	2	7.50 - 11.80	-8.40	-8.04		(65)
"	7	12.20 - 211.0	1.42	1.08	-1.17	(55)
Nonanol	1	--- 7.50	-4.95	---	-4.95	(65)
Decanol	10	5.40 - 225.6	3.21	2.37	2.37	(55)
Dodecanol	8	9.90 - 199.9	4.15	1.07	1.07	(55)
n-Butyl Chlor.	3	123.5 - 506.5	.74	.616		(15)
"	6	82.3 - 591.4	-2.20	-1.63	-.88	(58)

[1] The difference is calculated by subtracting the author's experimental value from the literature value for vapor pressures.

the boiling point range of the collected material upon fractional distillation (5, 58, 32, 4, 8). This is not per se a guarantee of purity unless one knows the boiling point of the pure material. A truer test would be to perform a simple distillation on the collected material and notice its boiling point range. If a material is sufficiently pure, its boiling point will not vary by more than the sensitivity of the temperature measuring device employed in the vapor pressure measurement apparatus. This test is exactly what is performed during a boiling point measurement by DTA as explained in the "Experimental" section of this thesis. Thus it is felt that the major problem in obtaining accurate data has been overcome by the use of DTA.

Measurements of the refractive index were used by one investigator (55) to test purity, but this is good only if data are available for the pure components. Gas chromatography has proved to be a very useful tool in checking for purity and was successfully used (3). Freezing point determinations were employed (15, 3) to check purity but it was pointed out that the alcohols were difficult to test since they are apt to supercool before crystallization set in.

Temperature sensors. Temperature measuring devices

in many works were not chosen with adequate care. In two cases reported, thermocouples were employed. In one instance (8) the thermocouple had not been calibrated, in another (55) the thermocouple had been calibrated at 100 to 200 Centigrade degree intervals. It is shown in the "Experimental" section that thermocouple calibration at 20 to 30 Centigrade degree intervals, at the very least, is required in order to obtain data within .3 degrees Centigrade.

Of all the data considered, those of Biddiscombe et al (3) and Dreisbach et al (15) were considered of high quality. Good agreement with their data is shown in Table 21, page 136.

Correlations of data. Li and Rossini (42), using extrapolation techniques and empirical correlation methods, have tried to estimate the Antoine constants of several homologous series, using the limited amount of data available. One of these series was the 1-chloro-alkanes. Their estimated data were compared with this author's work. This was accomplished by generating vapor pressure-temperature data by the use of this author's Antoine constants, and those estimated by Li and Rossini. The points were chosen between 5 mm and 760 mm Hg so that they would be equally spaced on a plot showing the reciprocal tem-

perature as a function of the logarithm of pressure. Thus these points carried an equal weight upon comparison. A per cent difference based on this work's experimental data was then obtained at each point and averaged for each compound. The results are seen in Table 22, page 141 . It may be noticed that a rather definite trend exists rather than a random distribution of differences. As one goes toward higher molecular weights in the series, the difference between the experimental data and the Li and Rossini estimates becomes more pronounced. This might be expected in that over seventy per cent of the data available in making the estimates existed for only the first four members in the series. Thus one would expect the estimates to be good in the beginning and become less reliable as the extrapolation increased. Although much care was taken by Li and Rossini, it is felt that their estimates are in error and must be revised in the light of these present data.

A similar situation exists with data published for the 1-alkanols by the API (57). No source or method for obtaining these data was mentioned. The same method of comparison was used as with the alkyl chlorides. The results of the comparison are given in Table 23, page 142. It may only be surmised that a similar method of estimation was used, producing the same trend in differences.

Table 22: Alkyl Chlorides - Comparison of Experimental and Literature Vapor Pressures

Compound	Average % Difference[1] on Pressure Comparison
1-Chloropropane	- 2.00
1-Chlorobutane	- 1.51
1-Chloropentane	- 2.73
1-Chlorohexane	- 1.94
1-Chloroheptane	- 3.66
1-Chloro-octane	- 4.15
1-Chlorononane	- 4.46
1-Chlorodecane	- 4.79
1-Chloroundecane	- 5.90
1-Chlorododecane	- 7.03
1-Chlorotetradecane	-11.00
1-Chlorohexadecane	-10.85

[1] Vapor pressures were compared at thirteen points between 5 mm and 760 mm Hg pressure by subtracting the literature value (42) from the experimental. The per cent difference was averaged for each compound.

Table 23: Alcohols - Comparison of Experimental and API Vapor Pressures

Compound	Average % Difference[1] on Pressure Comparison
Propanol	.94
Butanol	1.47
Pentanol	- 1.38
Hexanol	- 4.33
Heptanol	- 4.94
Octanol	- 4.19
Nonanol	- 2.78
Decanol	- 6.74
Dodecanol	-13.17
Tetradecanol	-17.49
Hexadecanol	-18.67

[1] Vapor pressures were compared at thirteen points between 5 mm and 760 mm Hg pressure by subtracting the API value (57) from the experimental. The per cent difference was averaged for each compound.

The Antoine equation. In determining how well the experimental data was described by the Antoine equation one may refer to Table 11, page 95. It is seen that no trend existed between the average or maximum absolute error and the carbon number. This is true both for the n-alkyl chlorides and the n-alcohols. One would expect this to be the case since the instrument precision is not a function of boiling temperature, the only factor which varies.

Another aspect in analyzing the fit of the Antoine equation is how well it describes the data at any one of the two pressure extremes and whether there is a greater error of fit at any one extreme. This analysis was accomplished by averaging the absolute per cent error for the first three points of comparison, about 5, 10 and 15 mm Hg, and the last three points, about 300, 500 and 760 mm Hg. The results of this comparison are shown in Table 24, page 144. It may be noticed that there is no error trend at either high or low pressure with carbon number. There is, however, somewhat greater incidence of error at low pressures, as shown by comparison of the average error of the high and low pressure estimates. This might be expected since the pressure can be read to a higher degree of accuracy, on a per cent basis, at higher than at lower pressures.

Table 24: Antoine Equation - Error Analysis of Fit

Carbon No.	Pressure Estimate Average Absolute Error, % High	Low
	n-Alkyl Chlorides	
3	.30	.70
4	.67	.80
6	.87	.63
7	.37	.57
8	.53	.80
9	.37	.70
10	.13	.33
11	.27	.30
12	.07	.33
14	.57	.97
16	1.07	.77
Average	.47	.63
	n-Alcohols	
3	.30	.70
4	.70	.10
5	.30	.12
6	.50	.90
7	.33	1.23
8	.50	1.20
9	.43	.33
10	.63	1.83
12	.57	.33
14	.70	1.37
16	.40	2.03
Average	.54	.92

Decomposition of samples. Because some of the organic materials studied were exposed to relatively high temperatures it was necessary to consider the problems of molecular degradation.

In considering the alcohols the most common decomposition reaction should be the dehydration to the corresponding olefin. This reaction takes place over an aluminum oxide catalyst at 350 to 450 degrees Centigrade, higher than the boiling temperatures of any alcohol tested.

Since none of the liquid is exposed to a catalytic surface during a vapor pressure determination by DTA, it is felt that no significant degradation occurs. This is verified by the constancy of the boiling points obtained for the alcohols.

The alkyl chlorides would most likely decompose to the olefin plus hydrogen chloride. A piece of moist litmus paper placed near the sample tube opening verified the production of HCl above 240 degrees Centigrade. This was also indicated by the formation of a cloud of white vapors in the working chamber. Chlorides heavier than chlorodecane were exposed to temperatures greater than 240 degrees Centigrade; the highest temperature was the normal boiling point of chlorohexadecane at 326.8 degrees Centigrade. Nonetheless, no boiling point range could be de-

tected with any of these compounds except chlorotetradecane and chlorohexadecane which contained small amounts of impurities. Therefore, it is concluded that decomposition took place only in the vapor and had no effect upon the recorded boiling point. Products of decomposition formed in the vapor phase had no opportunity to condense and to contaminate the boiling liquid with the present technique.

Density Correlation

The effective chain length parameter. It may be remembered from the "Correlation of Results" section, page 119, that the effective chain length, x, was described as a function of the carbon number to some power, y, in equation (81). This section also presented the method whereby the optimum power, y, was obtained. The following are the optimum values of y:

n-Alkanes	.57
n-Alkenes	.68
n-Alkyl Chlorides	.55
n-Alcohols	.20

It is of interest at this point to know how sensitive y is in the density correlation. In order to determine this sensitivity, y was perturbed from its optimum value. Using the perturbated value of y, the correlation was analyzed by making a point by point comparison between

the calculated and observed density data and then computing a maximum and average per cent error. It was assumed for simplicity that the change in maximum and average per cent error would be linear functions of the change in y for small changes. Thus the terms $\left[\Delta \text{Avg. \% Error}/\Delta y\right]$ and $\left[\Delta \text{Max. \% Error}/\Delta y\right]$ should be constants indicative of the sensitivity of y. The values of these constants for a Δy of .1 are given in Table 25, page 148. It may be seen that the correlation is not very sensitive to y so that an average value for the alkanes, alkenes, and alkyl chlorides may be assumed. Table 26, page 149 presents the average and maximum estimated per cent error when employing an average y in the correlation.

At this time, one might ask why does the effective chain length vary as a function of the number of carbon atoms raised to a power rather than being a direct linear function. It must be remembered that the effective chain length, x, expresses the number of consecutive cells occupied by N carbon atoms. The cell size was defined as a volume slightly larger than that occupied by a methane molecule. Thus if each carbon group occupied an equal volume, a linear function would be in order. But this is not the case, since the end groups of a chain such as CH_3-, are larger than the center -CH_2- segments. As the chain becomes longer, the effect of these larger end

Table 25: Perturbation of y

Series	Opt. y	Correlation Error Avg.%	Correlation Error Max.%	$\frac{\Delta \text{Avg.\% Error}}{\Delta y}$ [1]	$\frac{\Delta \text{Max.\% Error}}{\Delta y}$ [1]	Range
Alkanes	.57	.282	1.50	.201	.961	C_2 - C_{18}
Alkenes	.68	.752	2.69	.038	.975	C_2 - C_{14}
Alkyl Chlorides	.55	.059	.209	.003	.0093	C_3 - C_6
Alcohols	.20	.369	.839	.304	.921	C_2 - C_{18}

[1] $\Delta y = .1$

Table 26: Estimated Error When Using a Mean y

Series	Opt. y	Avg.Error %	Max.Error %	Avg. y	Avg.Error %	Max.Error %
Alkanes	.57	.282	1.50	.60	.342	1.23
Alkenes	.68	.752	2.69	.60	.782	3.47
Alkyl Chlorides	.55	.059	.209	.60	.061	.214

groups upon the chain length diminishes. One might also visualize that as a chain becomes longer it acquires a greater number of degrees of freedom, thereby allowing it to seek a lesser volume per number of carbon atoms in the chain. This effect manifests itself only during the addition of the first few carbon atoms, further addition only results in a more or less linear increase in effective length. Therefore, the effective chain length is best described as a power of N.

Different terminal groups on a molecular chain do not seem to influence the effective chain length as indicated by the almost identical chain length parameter, y, for the alkanes, alkenes, and alkyl chlorides. This might be expected since the per cent increase in chain length due to the substitution of a chlorine atom for a hydrogen atom quickly diminishes as the chain grows. The same reasoning may be applied to the difference in chain lengths between an alkene and alkane except in this case there is a decrease in length due to a loss of two hydrogen atoms, thereby inducing a greater attraction between the two affected carbon atoms.

The alcohols, however, provide a glaring exception to this generalization. Instead of a y of about .6 they produce a y of .2. If this was consistently the case,

one could attribute the exception to hydrogen bonding present in the alcohols. The effect of this bonding is a greater attraction between the molecules resulting in a more compact molecular structure which would manifest itself in a shorter effective chain length. But when the effective chain length parameters for the heats of vaporization correlation are examined, one finds they are all of the same order of about .68, including the alcohols. No reasonable explanation for this inconsistency can be offered at present.

Significance of correlation terms. It is of importance to determine if each term in the correlation is significant in comparison to the whole. Thus, if one term is consistently very small compared to the others, it might be neglected resulting in a simpler correlation. An analysis was made of each term at average conditions of 100 mm Hg vapor pressure for a chain of nine carbon atoms. An average chain length power of .60 was used for each of the series except for the alcohols where .20 was chosen. The results are given in Table 27, page 152. Note that each term is significant and must be retained in the correlation.

Heat of Vaporization Correlation

The heat of vaporization expression is given in terms

Table 27: Significance of Terms

Series	C	D ln P	Ex	Fx ln P	y
n-Alkanes	1.1382	.3162	-.7335	-.1553	.60
n-Alkenes	1.1146	.3045	-.5322	-.1117	.60
n-Alkyl Chlorides	1.3960	.3832	-.9947	-.2706	.60
n-Alcohols	3.8072	.3200	-3.175	-.1860	.20

$P = 100$ mm Hg

$N = 9$

$x = N^y$

of three constants as

$$E_v = A + Cx + Dx \ln P \ . \qquad (76)$$

It was found that for four different straight chain homologous series the effective chain length, x, could be expressed as the carbon number to the 0.675 power. Thus a very concise equation is given which will correlate the internal heat of vaporization of an entire homologous series as a function of the vapor pressure and the number of carbon atoms. Such an equation could be very easily stored in a computer memory along with the constants for different series, and called for whenever these data are required. It also serves as a useful equation in concisely expressing heat of vaporization data of homologous series in terms of one equation rather than expressing the data in terms of an equation such as equation (87),page 121, where the Antoine constants B and C must be given for each member of the series and a ΔZ must be determined.

Effect of terminal groups. It is of interest to look at the effects of the different terminal groups on the constant A. It may be recalled that A is the "heat of vaporization" when the number of carbon atoms is zero. For the alkane series, where there is no terminal group, the value of A is -304.91 cal./gm. mole. This would be only

about 3 per cent less than zero if an average heat of vaporization of 10,000 cal./gm. mole is chosen. Thus it is not unreasonable to say that A is practically zero. This would be reasonable in the sense that the only end group to give rise to a heat of vaporization is a hydrogen atom. The alkene series shows a slightly higher A of 125.43 cal./gm. mole. Though the increase over the A for the alkane series is slight, it is felt that it is real. It could very well be attributed to the effect which the double bond has upon the increase of attraction between molecules. The increase in A for the alkyl chlorides is much more pronounced, the value being 3228.6 cal./gm. mole. Thus one might say that the Cl- group has an attractive energy equivalent to A. The alcohols again show a definite increase with an A value of 7341.2 cal./gm. mole. This increase should definitely reflect the effect of hydrogen bonding which exists between alcohol groups. Thus, from this correlation it is possible to obtain approximate additive values for the heat of vaporization for different organic groups. It is also of interest to note that as the chain length increases, the effect of a terminal group becomes smaller and smaller so that the heat of vaporization of higher members of different series approach the same value.

Comparison with Nakanishi et al (48) correlation. A correlation was presented by Nakanishi et al as shown below:

$$H_v = \frac{2128\ n^{2/3}}{1+0.00512\ n^{2/3}+(.0930)(\log P)} \quad . \qquad (9)$$

This equation is discussed in the "Literature Survey", page 16. Although the authors correlated the external, instead of the internal, heat of vaporization with carbon number and vapor pressure, it is still of interest to find how well the equation given in this thesis compares with equation (9) in correlating heat of vaporization. The comparison was so made that an absolute per cent difference between the observed heat of vaporization and the computed value for the normal alkanes at the normal boiling point was obtained for each correlation. The results are shown in Table 28, page 156. It can be seen that no significant difference exists between the two correlations, although the average per cent error is somewhat lower with the modified Kurata-Isida equation (76).

Nakanishi has applied his equation to only the first nine members of the alkane series. It has been shown that the modified Kurata-Isida equation could be applied

Table 28: Comparison Between Observed and Correlated Heats of Vaporization

Compound	Modified Kurata-Isida Equation (76) Abs. % Diff. E_v	Nakanishi et al Equation (9) Abs. % Diff. H_v
Methane	8.59	8.29
Ethane	3.51	4.73
Propane	1.45	2.39
Butane	.37	1.07
Pentane	.16	.49
Hexane	.04	.20
Heptane	.05	.90
Octane	.16	1.52
Nonane	.41	2.09
Average	1.64	2.19

successfully not only to the normal alkanes up to octadecane, but also to the normal alkenes, the normal primary alkyl chlorides and the normal primary alcohols. The average absolute error for all four series was 1.25 per cent.

A Corresponding State

It is of interest to note that in both the density and the heat of vaporization correlations, expressions presented themselves which were found to be constant, at a constant vapor pressure, for an homologous series. Both of these expressions, in general, included terms which are descriptive of the attractive energies between full cells.

The density equation (72) introduces ψ/T as a constant at constant vapor pressure. Here ψ represents the Helmholtz free energy change in separating two full cells by an empty cell. The temperature, T, may be considered as representative of the kinetic energy of the system. Thus, the ratio, $\psi/2T$, quantitatively describes an energy level per cell which is constant at constant vapor pressure. In this sense one might look at vapor pressure as a corresponding state within an homologous series.

A similar situation exists for the heat of vaporization equation (74) where ϵ , the energy required to separate two full cells, is constant at a constant vapor pressure. Again, vapor pressure presents itself as a corresponding state.

In summation, it may be said that within any one homologous series the energy level per cell is constant when the vapor pressures are equal.

CONCLUSIONS

1. The molal liquid density of a straight chain organic homologous series may be expressed as a function of the vapor pressure and the number of carbon atoms in a chain with a maximum error in density of 2.69 per cent. The equation given as

$$\ln (T\rho_1) = C + D \ln P + EN^y + FN^y \ln P \quad ,$$

where C, D, E, F and y are constants, was derived using the hole model of liquids. The constant y may be assumed as .60 except for highly associated series, such as the alcohols, where .20 must be used. The four other constants may be determined from a knowledge of a minimum of eight sets of data points for four members of a series and applying them in a multilinear regression analysis.

2. The internal heat of vaporization of a straight chain organic homologous series may be expressed as a function of the vapor pressure and the number of carbon atoms in a chain with a maximum error of 8.18 per cent and an average error of 1.25 per cent. The

equation given as

$$E_v = A + CN^y + DN^y \ln P$$

was obtained using the hole theory of liquids. The constant, y, is equal to .68 for the straight chain homologous series examined.

3. The boiling points of pure organic liquids may be determined by the method of DTA described in this thesis with an accuracy of $\pm$.1 degree Centigrade C.I. (95%). This can be done between 5 and 760 mm Hg pressure for a temperature range of -40 to 325 degrees Centigrade.

4. Each vapor pressure determination by DTA may be made in about ten minutes. A sample volume of less than 10 micro-liters is usually sufficient, making the method ideally suited for determining vapor pressures of small gas chromatographic samples.

5. The DTA technique provides a method whereby vapor pressures of thermally unstable materials may easily be determined, even at temperatures where the rates of decomposition are high.

6. The DTA method provides a way of checking on the

purity of substances so that accurate vapor pressure data is insured.

RECOMMENDATIONS

1. Vapor pressures of many different homologous series should be obtained with the existing equipment. These data should be applied to the developed equations to test for further validity. Some modifications may have to be made in order to express the number of cells a molecule will occupy.

2. The existing equipment may be modified so that high vapor pressure data may be obtained.

3. The possibility of obtaining the bubble points of mixtures using the DTA equipment should be investigated.

NOMENCLATURE

E_v = internal heat of vaporization, cal./gm. mole

f = free energy per molecule related to intramolecular freedoms

F = Helmholtz free energy

F_I = intramolecular free energy

F^E_{MIX} = excess free energy of mixing

F^{IDEAL}_{MIX} = ideal free energy of mixing

h = number of holes in a liquid

h' = Planck's constant

ΔH_v = external heat of vaporization, cal./gm. mole

k = Boltzmann constant

L_v = latent heat of unknown substance

L_{vR} = latent heat of reference substance

n_o = number of cells in a lattice

N = number of carbon atoms in a molecular chain

N_A = Avagadro's number

N_o = number of molecules in a system

P = vapor pressure mm Hg

R = gas constant

ΔS_{MIX} = ideal entropy of mixing holes with a perfectly arranged solid

ΔS^* = entropy of disordering a perfectly arranged solid

$\Delta S'_{MIX}$ = ideal entropy of mixing holes with a randomly arranged solid

t = temperature, ^{o}C

T = absolute temperature, ^{o}K

T_b = normal boiling point, ^{o}K

v_g = volume per gaseous molecule

v_l = volume per liquid molecule

v_g' = molal volume of the gaseous phase

v_l' = molal volume of the liquid phase

V = volume of the system or lattice

W = total number of configurational combinations

W_{MIX} = number of configurations possible in a mixture of empty and full cells

W_H = number of configurations possible for empty cells

W_M = number of configurations possible for a perfectly arranged crystalline solid lattice

x = number of consecutive cells

y = effective chain length power

z = coordination number

Z_g = gas compressibility factor

Z_l = liquid compressibility factor

ΔZ = difference between gas and liquid compressibility factors

α = number of cells available for each consecutive segment

γ = frequency of a mole of vibration

γ_M = the highest value of γ

ϵ = internal energy

θ_0 = Debye temperature

μ = the chemical potential

γ = total number of configurations of a molecular chain

ρ_ℓ = liquid density, gm. mole/ml.

τ = cell volume

ψ = an increase in free energy defined on page 31.

APPENDIX A

GENERAL COMPUTATIONS

CALCULATING INSTRUMENT PRECISION

Refer to data in Table 29, page 168.

Data Points m.v.	$m.v. - \overline{m.v.}$	$(m.v. - \overline{m.v.})^2 \times 10^8$
2.8384	.0003	9
2.8403	.0016	256
2.8368	.0019	361
2.8395	.0008	64
2.8398	.0011	121
2.8401	.0014	196
2.8395	.0008	64
2.8391	.0004	16
2.8350	.0037	1369

$\overline{m.v.} = 2.8387$

$$\underline{\text{variance}} = s^2 = \sqrt{\frac{\Sigma(m.v.-\overline{m.v.})^2}{n-1}} = \sqrt{\frac{2456\text{x}10^{-8}}{8}} = 17.521\text{x}10^{-4}$$

where n = number of data points

$$\underline{\text{standard deviation}} = s = \pm .0018 \text{ m.v.}$$

$$\underline{\text{C.I. (95\%)}} = \overline{m.v.} \pm ts = 2.8387 \pm (2.262)(.0018) = 2.8387 \pm .00407$$

where t is the Students T test factor from Volk (66).

Date	EMF m.v.	Pressure mm Hg
8/24/65	2.8384	233.8
8/26/65	2.8403	233.9
8/26/65	2.8368	233.9
8/27/65	2.8395	233.9
9/1/65	2.8398	233.8
9/7/65	2.8401	233.9
9/9/65	2.8395	233.7
9/22/65	2.8391	234.3
4/11/66	2.8350	233.9

Table 29: Boiling Points of Water

DETERMINING THE EFFECT OF A CURVED SURFACE UPON VAPOR PRESSURE (25)

The difference between the vapor pressure of a liquid on a curved surface and that on a flat surface may be determined by the following equation:

$$\ln\left[\frac{P}{P_o}\right] = \left[\frac{2\gamma}{r\rho}\right]\left[\frac{M}{RT}\right],$$

where: M = molecular weight
ρ = density
P_o = flat surface vapor pressure
P = curved surface vapor pressure
γ = surface tension
T = absolute temperature

Let us consider water at 30 degrees Centigrade and a .01 cm. radius bead. Then

$$\ln\left[\frac{P}{P_o}\right] = \left[\frac{(2)(71.18\ \text{dynes/cm.})}{(.01\ \text{cm})(1\ \text{gm/cm.}^3)}\right]\left[\frac{(18)}{(8.48\text{x}10^5\ \frac{\text{dynes-cm}}{\text{mole}^{\circ}\text{K}})(303^{\circ}\text{K})}\right]$$

$$\ln\left[\frac{P}{P_o}\right] = 2.3\text{x}10^{-5}$$

Thus one can readily see that there is no significant difference in vapor pressures between the curved and flat surface.

COMPUTING MEAN FREE PATH (39)

The mean free path is given by the equation

$$\lambda = \frac{.707}{\sigma n}$$

if a Maxwellian distribution of molecular velocities is assumed. For the purposes of this calculation, such an assumption is warranted.

σ = the collision cross section = $4\pi r^2$

n = number of molecules per unit volume

r = molecular radius

Assume an ideal gas of molecules with $r = 1.5 \times 10^{-7}$ mm at a pressure of 10 mm Hg and 25 degrees Centigrade.

$\sigma = (4)(\pi)(1.5 \times 10^{-7}\ \text{mm}) = 28.3 \times 10^{-14}\ \text{mm}^2$

$n = 3.95 \times 10^{14}$ molecules/mm^3

$\underline{\lambda = .006\text{mm} \approx .01\text{mm}}$

APPENDIX B

THERMOCOUPLE CALIBRATION

Temperature, °C	EMF, m.v.
-39.34	-1.4959
-25.03	- .9674
- 4.05	- .1715
+13.00	+ .5158
20.57	.8161
28.53	1.1363
38.29	1.5330
49.75	2.0015
62.77	2.5380
69.97	2.8362
78.49	3.1892
90.00	3.6660
110.04	4.4993
132.13	5.4031
140.27	5.7296
166.09	6.7496
181.17	7.3462
195.28	7.9067
215.50	8.7038
231.55	9.3420
266.90	10.7626
287.20	11.5885
305.90	12.3546
350.90	14.1978

Table 30: Thermocouple Calibration

Run No.	Thermocouple EMF at Boiling Point m.v.	Pressure mm Hg	Boiling Point °C
		Pentane	
221E	-1.4959	21.2	-39.34
220E	-.9674	51.1	-25.03
224E	-.1804	150.0	-4.33
219E	-.1715	152.0	-4.05
218E	.5781	346.2	14.85
223E	.7268	402.2	18.63
222E	1.4280	756.5	35.94
		Hexane	
225E	-.0989	40.0	-2.30
148E	.5198	88.0	13.00*
149E	.5140	87.3	
150E	.5135	87.5	
151E	.8155	124.3	20.57*
152E	.8158	124.5	
153E	.8170	124.4	
154E	1.1355	175.9	28.53*
155E	1.1365	175.9	
156E	1.1370	175.9	
157E	1.5330	261.6	38.29*
158E	1.5341	261.7	
159E	1.5320	261.3	
160E	2.0007	401.8	49.75*
161E	2.0002	401.3	
162E	2.0038	402.2	
163E	2.5350	627.1	62.77*
164E	2.5392	627.9	
165E	2.5398	628.2	
		Water	
166E	2.4204	149.0	60.02*
167E	2.4260	149.4	
168E	2.4294	150.0	
169E	2.8338	233.0	69.97*
170E	2.8363	233.5	
171E	2.8384	233.8	
181E	3.1892	334.0	78.49

*The boiling temperature is given at an average pressure for a set of runs. The corresponding EMF used in the calibration is an average value for the set.

Table 31: Calibration Data

Run No.	Thermocouple EMF at Boiling Point m.v.	Pressure mm Hg	Boiling Point °C
		Water con't.	
173E	3.6660	525.7	90.00*
174E	3.6664	526.1	
175E	3.6655	526.1	
		m-Xylene	
176E	4.5006	325.0	110.04*
177E	4.4982	324.8	
178E	4.4990	324.9	
179E	5.4031	627.2	132.13*
180E	5.4036	628.5	
181E	5.4026	628.1	
		n-Octyl Alcohol	
184E	5.7302	123.7	140.27*
185E	5.7303	124.0	
186E	5.7283	123.7	
188E	6.7496	315.5	166.09*
189E	6.7495	315.5	
190E	6.7498	315.5	
191E	7.3460	507.5	181.17*
192E	7.3480	507.7	
193E	7.3447	507.6	
194E	7.9071	760.0	195.28*
195E	7.9087	760.0	
196E	7.9042	760.0	
		Benzophenone	
202E	8.1254	47.5	200.65*
203E	8.1200	47.5	
204E	8.7054	76.0	215.50*
205E	8.7022	76.0	
206E	9.3435	123.5	231.55*
207E	9.3405	123.4	
208E	10.7620	315.6	266.90*
209E	10.7632	315.3	
210E	11.5881	506.9	287.20*
211E	11.5888	507.0	
212E	12.3570	759.0	305.90*
213E	12.3522	759.0	

Table 31: Continued

APPENDIX C

ORIGINAL EXPERIMENTAL DATA

Run No.	Thermocouple EMF at Boiling Point m.v.	Pressure mm Hg	Boiling Point °C
		1-Chloropropane	
109F	-.9688	28.8	-25.1
110F	-.7611	39.9	-19.6
111F	-.5391	55.4	-13.7
112F	-.2798	79.5	-6.9
113F	+.0395	120.5	+1.2
114F	.4782	200.2	12.1
115F	.8667	303.9	21.8
116F	1.3941	504.0	34.9
117F	1.8935	776.0	47.1
		1-Chlorobutane	
259F	-.6511	10.1	-16.7
260F	-.4169	15.2	-10.5
261F	-.2512	19.8	-6.2
262F	+.0243	29.6	+0.8
263F	.2395	40.2	6.2
264F	.4746	54.8	12.0
265F	.7814	79.8	19.7
266F	1.1460	121.6	28.8
267F	1.6461	203.1	41.1
268F	2.0641	302.0	51.3
269F	2.6502	499.1	65.5
270F	3.1878	758.8	78.5
		1-Chlorohexane	
131F	.5937	5.0	15.0
132F	1.0635	10.4	26.7
133F	1.3212	15.0	33.1
134F	1.5440	20.1	38.6
135F	1.8786	30.1	46.7
136F	2.1187	39.9	52.6
137F	2.4111	55.0	59.7
138F	2.7699	79.8	68.4
139F	3.2309	125.6	79.5
140F	3.7746	203.2	92.6
141F	4.2710	305.7	104.6
142F	4.9200	500.9	120.3
143F	5.5439	774.0	135.6
		1-Chloroheptane	
246F	1.3760	5.1	34.4
247F	1.8740	10.5	46.6

Table 32: Vapor Pressure Data for the Primary Alkyl Chlorides

Run No.	Thermocouple EMF at Boiling Point m.v.	Pressure mm Hg	Boiling Point °C
	1-Chloroheptane con't.		
248F	2.1574	15.2	53.5
249F	2.3859	20.1	59.1
250F	2.7336	30.1	67.5
251F	2.9876	39.8	73.6
252F	3.2952	55.0	81.1
253F	3.7046	81.9	90.9
254F	4.1274	121.6	101.1
255F	4.7260	203.0	115.6
256F	5.2312	302.6	127.9
257F	5.9190	502.5	145.1
258F	6.5128	753.4	160.1
	1-Chloro-octane		
144F	2.1814	5.6	54.1
145F	2.5857	9.8	63.9
146F	2.9355	15.3	72.4
147F	3.1787	20.3	78.2
148F	3.5438	30.3	87.1
149F	3.8090	40.1	93.4
150F	4.1280	55.2	101.1
151F	4.5266	80.5	110.7
152F	4.9791	121.2	121.8
153F	5.5862	201.0	136.7
154F	6.1050	301.6	149.8
155F	6.8028	501.0	167.4
156F	7.4642	773.2	184.1
	1-Chlorononane		
157F	2.7990	5.1	69.1
159F	3.2767	9.6	80.6
160F	3.6605	15.1	89.9
161F	3.8926	19.6	95.4
162F	4.2725	29.5	104.6
163F	4.5601	39.6	101.5
164F	4.8985	55.0	119.8
165F	5.2955	79.7	129.5
166F	5.7690	121.2	141.3
167F	6.3794	200.5	156.7
168F	6.9150	301.6	170.3
170F	8.2826	752.8	204.8
172F	7.6404	501.8	188.6
176F	2.8696	5.5	70.8

Table 32: Continued

Run No.	Thermocouple EMF at Boiling Point m.v.	Pressure mm Hg	Boiling Point °C
		1-Chlorodecane	
173F	3.5096	5.5	86.2
177F	4.0350	10.5	98.9
178F	4.3390	15.0	106.2
179F	4.6137	20.2	112.8
180F	5.0162	30.8	122.7
181F	5.2810	40.1	129.2
182F	5.6036	54.7	137.1
183F	6.0243	80.0	147.7
184F	6.4830	120.5	159.3
185F	7.1310	201.6	175.7
186F	7.6785	301.4	189.5
187F	8.4326	501.5	208.6
188F	9.1055	754.7	225.6
		1-Chloro-undecane	
189F	4.1404	5.5	101.4
190F	4.6714	10.4	114.3
191F	5.0000	15.1	122.3
192F	5.2521	19.8	128.4
193F	5.6572	30.1	138.5
194F	5.9386	39.8	145.6
195F	6.2927	55.6	154.5
196F	6.7087	81.0	165.1
197F	7.1724	120.5	176.8
198F	7.8456	203.0	193.7
199F	8.4345	308.0	208.7
200F	9.1836	499.1	227.6
201F	9.1848	499.8	227.6
202F	9.8980	763.0	245.4
		1-Chlorododecane	
215F	4.7447	5.5	116.0
216F	4.7483	5.6	116.1
217F	5.2372	10.0	128.1
218F	5.6027	15.1	137.1
219F	5.8709	20.1	143.9
220F	6.2600	29.9	153.7
221F	6.5614	40.0	161.3
222F	6.9084	55.3	170.1
223F	7.3355	80.3	180.9

Table 32: Continued

Run No.	Thermocouple EMF at Boiling Point m.v.	Pressure mm Hg	Boiling Point °C
	1-Chlorododecane con't.		
224F	7.8163	120.6	193.0
225F	8.5061	204.2	210.5
227F	9.0780	300.5	224.9
228F	9.9040	504.9	245.5
229F	10.6301	764.0	263.6
	1-Chlorotetradecane		
202F	5.7872	5.2	141.7
203F	6.3145	9.9	155.1
204F	6.6908	14.9	164.6
205F	6.9904	20.4	172.2
206F	7.3691	29.5	181.8
207F	7.7232	41.0	190.7
208F	8.0550	55.2	199.1
209F	8.5064	80.0	210.5
210F	9.0353	122.4	223.8
211F	9.7870	203.8	242.6
212F	10.4123	311.2	258.2
213F	11.2000	498.4	277.7
214F	11.9889	764.2	297.0
	1-Chlorohexadecane		
231F	6.7302	5.1	165.6
232F	6.7347	5.1	165.7
233F	7.3075	10.0	180.2
234F	7.7102	15.2	190.3
235F	7.7070	15.2	190.3
236F	7.9818	20.0	197.2
237F	8.4195	30.2	208.3
238F	8.7288	39.8	216.1
239F	9.1052	54.8	225.6
240F	9.5813	79.9	237.5
241F	10.1344	122.2	251.3
242F	10.8986	204.6	270.2
243F	11.5045	295.5	285.1
244F	12.3969	501.5	306.9
245F	13.2105	766.6	326.8

Table 32: Continued

Run No.	Thermocouple EMF at Boiling Point m.v.	Pressure mm Hg	Boiling Point °C
		Propanol	
5F	.7836	14.9	19.8
6F	.7649	14.7	19.3
8G	.9756	20.4	24.5
10G	1.2076	29.5	30.3
11G	1.2078	29.4	30.3
12G	1.4072	39.7	35.2
13G	1.6538	56.4	41.3
14G	1.9317	81.3	48.1
15G	2.2335	120.4	55.4
16G	2.6583	199.4	65.7
18G	3.0297	300.0	74.6
19G	3.5232	499.5	86.6
20G	3.9676	758.5	97.3
		Butanol	
8F	.8969	5.5	22.6
9F	1.2322	10.3	30.9
10F	1.4487	14.8	36.2
11F	1.6316	19.6	40.7
12F	1.9375	31.0	48.2
13F	2.1109	39.6	52.4
14F	2.3518	55.3	58.3
15F	2.6614	81.4	65.8
16F	2.9829	121.4	73.5
17F	3.4615	208.0	85.1
18F	3.8243	303.5	93.8
19F	4.3525	507.0	106.5
20F	4.8181	766.0	117.8
		Pentanol	
21F	1.3559	4.3	33.9
22F	1.8329	9.5	45.6
23F	2.1134	15.2	52.5
31F	2.2894	19.8	56.7
32F	2.5708	29.4	63.6
33F	2.8095	40.7	69.3
34F	3.0415	54.8	74.9
35F	3.3788	82.7	83.1
36F	3.6947	119.1	90.7

Table 33: Vapor Pressure Data for the Primary Alkanols

Run No.	Thermocouple EMF at Boiling Point m.v.	Pressure mm Hg	Boiling Point °C
		Pentanol con't.	
37F	4.1801	200.0	102.4
38F	4.5933	302.0	112.3
39F	5.1435	502.1	125.8
40F	5.6368	765.4	138.0
		Hexanol	
55F	2.1011	5.7	52.2
56F	2.4420	9.7	60.4
57F	2.7304	15.3	67.4
58F	2.9436	20.5	72.6
59F	3.2185	29.8	79.2
60F	3.4570	40.7	85.0
61F	3.1710	55.3	91.1
62F	4.0292	80.0	98.7
63F	4.3972	120.8	107.6
64F	4.8940	201.0	119.7
65F	5.3216	301.8	130.1
66F	5.8967	500.0	144.5
67F	6.4040	757.3	157.3
		Heptanol	
68F	2.5726	4.7	63.6
69F	3.0885	10.9	76.1
70F	3.3128	15.0	81.5
71F	3.5649	21.1	87.6
72F	3.8435	30.2	94.3
73F	4.0756	40.2	99.9
74F	4.3466	55.5	106.4
75F	4.6824	80.5	114.5
76F	5.0744	122.4	124.1
77F	5.5766	201.0	136.5
78F	6.0250	303.5	147.8
79F	6.6181	501.0	162.8
80F	7.1570	760.8	176.4
		Octanol	
96F	3.2076	5.3	78.9
97F	3.6154	10.2	88.8
98F	3.8902	15.0	95.4

Table 33: Continued

Run No.	Thermocouple EMF at Boiling Point m.v.	Pressure mm Hg	Boiling Point °C
		Octanol con't.	
99F	4.1456	21.0	101.5
100F	4.4305	30.0	108.4
101F	4.6596	39.5	114.0
102F	4.9416	54.4	120.9
103F	5.3629	85.4	131.2
		Nonanol	
273F	3.7351	5.6	91.7
278F	4.1685	10.5	102.1
279F	4.4507	15.3	108.9
280F	4.6774	20.3	114.4
281F	5.0051	30.2	122.4
282F	5.2655	40.6	128.8
283F	5.5494	55.5	135.8
284F	5.9044	80.4	144.7
285F	6.3106	120.7	155.0
286F	6.8628	201.4	169.0
287F	7.3456	302.4	181.0
288F	8.0142	502.5	198.0
289F	8.6268	763.9	213.6
		Decanol	
41F	4.2875	5.6	105.0
42F	4.6804	10.2	114.5
44F	4.9757	15.0	121.7
45F	5.2046	20.1	127.3
46F	5.5415	29.9	135.6
47F	5.8041	40.1	142.2
48F	6.1103	56.0	149.9
49F	6.4779	81.1	159.2
50F	6.8988	121.3	169.9
51F	7.4554	198.0	183.9
52F	7.9905	303.0	197.4
53F	8.6961	504.8	215.3
54F	9.3204	757.6	231.0
		Dodecanol	
81F	5.1729	5.3	126.5
82F	5.6487	9.8	138.3
83F	5.9561	14.6	146.0

Table 33: Continued

Run No.	Thermocouple EMF at Boiling Point m.v.	Pressure mm Hg	Boiling Point °C
		Dodecanol con't.	
85F	6.6082	30.1	162.5
86F	6.8830	40.9	169.5
87F	7.1861	55.6	177.1
88F	7.5826	81.2	187.1
89F	8.0416	122.3	198.7
90F	8.6635	201.3	214.5
91F	9.2163	300.2	228.4
92F	9.9941	503.7	247.8
93F	9.9920	499.0	247.7
94F	10.7026	766.0	265.4
95F	10.6980	766.0	265.3
		Tetradecanol	
332F	8.0584	48.4	199.1
333F	6.1757	5.2	151.6
334F	6.6260	10.5	163.0
335F	6.9426	15.3	171.0
336F	7.1799	19.9	177.0
337F	7.6333	32.1	188.4
338F	8.6181	80.1	213.3
339F	9.1104	120.0	225.7
340F	9.8079	202.8	243.1
341F	10.3976	302.6	257.8
342F	11.2085	501.2	277.9
343F	11.9462	755.2	295.9
		Hexadecanol	
316F	6.9875	5.9	172.1
317F	7.5085	10.3	185.3
318F	7.8306	15.1	193.4
319F	8.1310	19.8	201.0
320F	8.5270	30.1	211.0
321F	8.8311	40.4	218.6
324F	9.1709	55.3	227.3
326F	9.6290	80.3	238.7
327F	10.1456	120.3	251.6
328F	10.8610	200.5	269.3
329F	11.4995	302.1	285.0
330F	12.3555	502.4	305.9
331F	13.1424	759.2	325.1

Table 33: Continued

APPENDIX D

COMPUTER PROGRAMS

MULTIPLE LINEAR REGRESSION ANALYSIS OF THE ANTOINE EQUATION

Method

The basis for this computer program may be found on page 278 of Volk (66). Volk presents a complete set of equations which describe the solution for the regression correlation of two independent variables by the method of Gaussian multipliers. Statistical parameters useful in the analysis of the correlation are also presented. This information, in conjunction with the computer program, should adequately describe the method of correlation and data output.

Data Input

The program was written in Kingston Fortran and as such all data are in free format. The data input order is as follows:

1. listing of Student's probability factors for a probability of a deviation greater than t of .025.
2. number of compounds to be individually correlated
3. individual pressure temperature data points

NOMENCLATURE FOR THE MULTIPLE LINEAR REGRESSION OF THE ANTOINE EQUATION

TTEST = Listing of Student's probability factors

N = Number of data points

CODE = Compound identification number

PI = Vapor pressure

TI = Temperature

CN = Number of carbon atoms

A = Constant of the linearized equation, Antoine constant A

B1 = Constant of the linearized equation

B2 = Constant of the linearized equation

ALO = Lowest value of A about 95% C.I.

B1LO = Lowest value of B1 about 95% C.I.

B2LO = Lowest value of B2 about 95% C.I.

AHI = Highest value of A about 95% C.I.

B1HI = Highest value of B1 about 95% C.I.

B2HI = Highest value of B2 about 95% C.I.

SPC2 = Sum of squares of regression

R = Correlation coefficient

S2YES2 = Residual sum of squares

DFS2Y = Degrees of freedom

S2YES = Variance of estimate

B = Antoine constant, B

C = Antoine constant, C

T(J) = Temperature

P(J) = Calculated vapor pressure from determined Antoine equation

PXP = Experimental vapor pressure

PCER = Per cent error on the pressure estimate

GOOF = Error on the pressure estimate

AVERR = Total average absolute error

BIG = Maximum absolute error

AWOW = Per cent of errors under 5%

APOO = Per cent of errors over 10%

COMPUTER PROGRAM
MULTIPLE LINEAR REGRESSION ANALYSIS OF THE
ANTOINE EQUATION


```
      DIMENSION P(100),T(100),TINV(100),TERM(100),TTEST(35)
      DO 10 N=1, 34
   10 READ 2011, TTEST(N)
  300 READ 201, N, CODE
  201 FORMAT(2N)
      J=0
      DO 4 K=1, N
    3 READ 202,PI,TI,CN
  202 FORMAT (3N)
      IF(TI) 1, 3, 1
    1 J=J+1
      P(J)=PI
    4 T(J)=TI
      EN=J
      N=EN
      SY=0.0
      SX1=0.0
      SX2=0.0
      DO 5 J=1, N
      TERM(J)=LOGF(P(J))*0.43429
      SY=SY+TERM(J)
      TINV(J)=1.0/T(J)
      SX1=SX1+TINV(J)
    5 SX2=SX2+TERM(J)*TINV(J)
      YBAR=SY/EN
      X1BAR=SX1/EN
      X2BAR=SX2/EN
      SPY2=0.0
      SPYX1=0.0
      SPYX2=0.0
      SPX1X2=0.0
      S2X2=0.0
      S2X1=0.0
      N=EN
      DO 6 J=1, N
      DELY=TERM(J)-YBAR
      DELX1=TINV(J)-X1BAR
      DELX2=TERM(J)*TINV(J)-X2BAR
      DEL2X1=DELX1*DELX1
      DEL2X2=DELX2*DELX2
      DEL2Y=DELY*DELY
      SPY2=SPY2+DEL2Y
      SPYX1=SPYX1+DELY*DELX1
      SPYX2=SPYX2+DELY*DELX2
      SPX1X2=SPX1X2+DELX1*DELX2
      S2X2=S2X2+DEL2X2
      S2X1=S2X1+DEL2X1
    6 CONTINUE
      SPXX2=SPX1X2*SPX1X2
      DENOM=S2X1*S2X2-SPXX2
      B1=(SPYX1*S2X2-SPYX2*SPX1X2)/DENOM
      B2=(SPYX2*S2X1-SPYX1*SPX1X2)/DENOM
      A=YBAR-B1*X1BAR-B2*X2BAR
```

```
      SPC2=B1*SPYX1+B2*SPYX2
      R=(SPC2/SPY2)**0.5
      S2YES2=SPY2-SPC2
      DFS2Y=EN-3.0
      F=SQRTF(SPC2)/SQRTF(S2YES2)
      S2YES=S2YES2/DFS2Y
      GAUS11=S2X2/DENOM
      GAUS22=S2X1/DENOM
      GAUS12=SPX1X2/DENOM
      S2B1=S2YES*GAUS11
      S2B2=S2YES*GAUS22
      SDB1=SQRTF(S2B1)
      SDB2=SQRTF(S2B2)
      N=DFS2Y
      IF(N-30) 11, 11, 12
   11 GO TO 13
   12 IF(N-35) 14, 14, 15
   14 N=30
      GO TO 13
   15 IF(N-50) 16, 16, 17
   16 N=31
      GO TO 13
   17 IF(N-90) 18, 18, 19
   18 N=32
      GO TO 13
   19 IF(N-150) 20, 20, 21
   20 N=33
      GO TO 13
   21 N=34
   13 B1LO=B1-SDB1*TTEST(N)
      B1HI=B1+SDB1*TTEST(N)
      B2LO=B2-SDB2*TTEST(N)
      B2HI=B2+SDB2*TTEST(N)
      ALO=YBAR-B1HI*X1BAR-B2HI*X2BAR
      AHI=YBAR-B1LO*X1BAR-B2LO*X2BAR
      PUNCH 203, CODE
  203 FORMAT(33HTHE LINEAR EQUATION FOR COMPOUND , F6.0,3H IS)
      PUNCH 204, A, B1, B2
  204 FORMAT(5X,9HLOG (P)= ,E14.8,1X,1H+,E14.8,8H*(1/T) +,E14.8,
     210H*(LOGP/T) )
      PUNCH 205
  205 FORMAT(/5X,36HTHE 95 PERCENT CONFIDENCE LIMITS ARE)
      PUNCH 206, ALO, AHI
  206 FORMAT(5X,3HA= ,E14.8,4H TO ,E14.8)
      PUNCH 207, B1LO, B1HI
  207 FORMAT(5X,4HB1= ,E14.8,4H TO ,E14.8)
      PUNCH 208, B2LO, B2HI
  208 FORMAT(5X,4HB2= ,E14.8,4H TO ,E14.8)
      PUNCH 209
  209 FORMAT(/7X,43HANALYSIS OF VARIANCE OF THE LINEAR EQUATION)
      PUNCH 210, EN
  210 FORMAT(/8X,F6.0,11HDATA POINTS)
      PUNCH 211, SPC2
```

```
  211 FORMAT(8X, 30HSUM OF SQUARES OF REGRESSION= ,E14.8)
      PUNCH 212, R
  212 FORMAT(8X,27HCORRELATION COEFFICIENT R= ,F10.7)
      PUNCH 213, S2YES2, DFS2Y
  213 FORMAT(8X,25HRESIDUAL SUM OF SQUARES= ,F10.7,5H FOR ,F6.0,
     219H DEGREES OF FREEDOM)
      PUNCH 214, F
  214 FORMAT(8X,28HF TEST FOR SIGNIFICANCE, F= ,F8.2)
      PUNCH 215, DFS2Y
  215 FORMAT(8X,38HCONSULT VOLK PAGES 148'151, F2= 2,F1= ,F6.0)
      PUNCH 216
  216 FORMAT(8X,42HTO FIND PROBABILITY OF A LARGER VALUE OF F)
      PUNCH 217, S2YES
  217 FORMAT(8X,22HVARIANCE OF ESTIMATE= ,E14.8)
      PUNCH 218, S2B1, S2B2
  218 FORMAT(8X,35HVARIANCE OF REGRESSION COEFFICIENTS,/12X,
     210HS**2(B1)= ,E14.8/12X,10HS**2(B2)= ,E14.8)
      PUNCH 219
  219 FORMAT(///5X,25HTHE ANTOINE CONSTANTS ARE)
      C=-1.0*B2
      B=A*C-B1
      PUNCH 220, A, B, C
  220 FORMAT(/10X,3HA= ,E14.8,/10X,3HB= ,E14.8,/10X,3HC= ,E14.8)
      PUNCH 221
  221 FORMAT(///2X,39HERROR ANALYSIS OF THE PRESSURE ESTIMATE,/)
      BIG=0.0
      SUMPE=0.0
      M10=0
      M5=0
      PUNCH 222
  222 FORMAT(2X,71HTEMP C    P XPER    P CALC    ERROR    PC ER R      Z
     2TEMP CAL     DIFF C/)
      SUMS=0.0
      N=EN
      DO 117 J=1, N
      PXP=EXPF((A-B/(T(J)+C))*2.30259)
      TCAL=B/(A-.43429*LOGF(P(J)))-C
      GOOF=PXP-P(J)
      FOOG=T(J)-TCAL
      PCER=GOOF*100.0/P(J)
      Z=P(J)/PXP
      ABSER=ABSF(PCER)
      IF(ABSER-5.0) 60, 61, 61
   60 M5=M5+1
      GO TO 62
   61 IF(ABSER-10.0) 62, 62, 63
   63 M10=M10+1
   62 SUMPE=SUMPE+ABSER
      SUMS=SUMS+GOOF
      PUNCH 223, T(J), P(J), PXP, GOOF, PCER, Z,TCAL,FOOG
  223 FORMAT(2X,F6.1,3X,F6.1,3X,F6.1,3X,F6.1,3X,F7.1,3X,F6.3,4X,F7.2,5X,
     2F6.2)
      IF(ABSER-BIG) 117, 117, 49
```

```
   49 BIG=ABSER
  117 CONTINUE
      AVERR=SUMPE/EN
      PUNCH 227, AVERR
  227 FORMAT(/2X,24HAVERAGE ABSOLUTE ERROR= ,F8.5,8H PERCENT)
      PUNCH 228, BIG
  228 FORMAT(2X,24HMAXIMUM ABSOLUTE ERROR= ,F8.5, 8H PERCENT)
      GOOD=M5
      BAD=M10
      APOO=BAD/EN*100.0
      AWOW=GOOD/EN*100.0
      PUNCH 229, AWOW, APOO
  229 FORMAT(2X,F6.1,35H PERCENT OF ERRORS UNDER 5 PERCENT, ,
     2F5.1,24H PERCENT OVER 10 PERCENT)
      SD=SQRTF(SUMS/(EN-1.0))
      ENN=EN-1.0
      N=ENN
      RANGE=SD*TTEST(N)
      PUNCH 230
  230 FORMAT(2X,48H95 PERCENT CONFIDENCE RANGE OF VAPOR PRESSURE IS)
      PUNCH 231, RANGE
  231 FORMAT(8X,6HP+OR- ,F7.4)
      PUNCH 232
  232 FORMAT(/5X,33H''''''''''CASE COMPLETE''''''''''///)
 2011 FORMAT(1N)
      GO TO 300
      END
```

MULTIPLE LINEAR REGRESSION OF THE MODIFIED KURATA-ISIDA HEAT OF VAPORIZATION EQUATION

Method

The identical method of correlation as applied to the Antoine equation is used here. The method again is shown very clearly by Volk (66) on page 278.

Data Input

The program is written in Kingston Fortran so that the data input is in free format. The order of input is as follows:

1. listing of Student's probability factors for a probability of a deviation greater than t of .025
2. vapor pressure
3. number of compounds to be correlated
4. homologous series identification number
5. number of carbon atoms of each compound
6. the Antoine constants for each compound
7. the effective chain length power

NOMENCLATURE FOR THE MULTIPLE LINEAR REGRESSION OF THE MODIFIED KURATA-ISIDA HEAT OF VAPORIZATION CORRELATION

TTEST = Listing of Student's probability factors

PP = Vapor pressure

L = Number of compounds

SERIES = Homologous series identification number

CN = Number of carbon atoms

CODE = Compound identification number

A,B,C = Antoine constants

PW = Chain length power

AA,B1,B2 = Linearized equation constants

ALO = Lowest value of AA about 95% C.I.

B1LO = Lowest value of B1 about 95% C.I.

B2LO = Lowest value of B2 about 95% C.I.

AHI = Highest value of AA about 95% C.I.

B1HI = Highest value of B1 about 95% C.I.

B2HI = Highest value of B2 about 95% C.I.

SPC2 = Sum of squares of regression

R = Correlation coefficient

S2YES2 = Residual sum of squares

DFS2Y = Degrees of freedom

A,B,C = Modified Kurata-Isida equation constants

X1LV = Experimental heat of vaporization

CX1LV = Calculated heat of vaporization

GOOF = Error on heat of vaporization estimate

PCER = Per cent error on heat of vaporization estimate

COMPUTER PROGRAM
MULTIPLE LINEAR REGRESSION OF THE MODIFIED KURATA-ISIDA HEAT OF VAPORIZATION EQUATION


```
      DIMENSION P(9,20),PP(9),C(20),CN(20),TC(9,20),CODE(20),A(20),B(20)
     2,XILV(9,20),X(20),TTEST(34)
      DO 600 N=1,34
  600 READ 601, TTEST(N)
  601 FORMAT(1N)
      DO 200 J=1,9
  200 READ 201, PP(J)
  201 FORMAT(1N)
      READ 203, L
  203 FORMAT(1N)
      READ 301, SERIES
  301 FORMAT(1N)
      DO 204 K=1,L
      READ 206, CN(K)
  206 FORMAT(1N)
      READ 405, CODE(K), A(K), B(K), C(K)
  405 FORMAT(4N)
      DO 204 J=1,9
      P(J,K)=PP(J)
      ZTERM=LOGF(P(J,K))*0.43429
  204 TC(J,K)=(B(K)/(A(K)-ZTERM))-(C(K))
      DO 4 K=1,L
      DO 4 J=1,9
      TA=TC(J,K)+273.16
      TB=TC(9,K)+273.16
      TN=TC(J,K)
      TR=TA/TB
      IF(TR-.99)6,5,5
    5 DZ=.95
      GO TO 10
    6 IF(TR-.96)8,7,7
    7 DZ=.96
      GO TO 10
    8 IF(TR-.92)11,9,9
    9 DZ=.97
      GO TO 10
   11 IF(TR-.87)13,12,12
   12 DZ=.98
      GO TO 10
   13 IF(TR-.79)15,14,14
   14 DZ=.99
      GO TO 10
   15 IF(TR-.74)16,16,16
   16 DZ=1.00
      GO TO 10
   10 R=1.987
      XLV=((2.303)*(R)*(TA**2.0)*(B(K))*(DZ))/((TN+C(K))**2.0)
    4 XILV(J,K)=XLV-DZ*R*TA
      EN=9*L
  111 READ 205, PW
  205 FORMAT(1N)
      SY=0.0
      SX1=0.0
```

```
      SX2=0.0
      DO 300 K=1,L
      X(K)=CN(K)**PW
      DO 300 J=1,9
      SY=SY+XILV(J,K)
      SX1=SX1+X(K)*LOGF(P(J,K))
  300 SX2=SX2+X(K)
      YBAR=SY/EN
      X1BAR=SX1/EN
      X2BAR=SX2/EN
      SPY2=0.0
      SPYX1=0.0
      SPYX2=0.0
      SPX1X2=0.0
      S2X2=0.0
      S2X1=0.0
      DO 701 K=1,L
      DO 701 J=1,9
      DELY=XILV(J,K)-YBAR
      DELX1=X(K)*LOGF(P(J,K))-X1BAR
      DELX2=X(K)-X2BAR
      DEL2X1=DELX1*DELX1
      DEL2X2=DELX2*DELX2
      DEL2Y=DELY*DELY
      SPY2=SPY2+DEL2Y
      SPYX1=SPYX1+DELY*DELX1
      SPYX2=SPYX2+DELY*DELX2
      SPX1X2=SPX1X2+DELX1*DELX2
      S2X2=S2X2+DEL2X2
  701 S2X1=S2X1+DEL2X1
      SPXX2=SPX1X2*SPX1X2
      DENOM=S2X1*S2X2-SPXX2
      B1=(SPYX1*S2X2-SPYX2*SPX1X2)/DENOM
      B2=(SPYX2*S2X1-SPYX1*SPX1X2)/DENOM
      AA=YBAR-B1*X1BAR-B2*X2BAR
      SPC2=B1*SPYX1+B2*SPYX2
      R=(SPC2/SPY2)**0.5
      S2YES2=SPY2-SPC2
      DFS2Y=EN-3.0
      F=SQRTF(SPC2)/SQRTF(S2YES2)
      S2YES=S2YES2/DFS2Y
      GAUS11=S2X2/DENOM
      GAUS22=S2X1/DENOM
      GAUS12=SPX1X2/DENOM
      S2B1=S2YES*GAUS11
      S2B2=S2YES*GAUS22
      SDB1=SQRTF(S2B1)
      SDB2=SQRTF(S2B2)
      N=DFS2Y
      IF(N-30)31,31,32
   31 GO TO 33
   32 IF(N-35)34,34,35
   34 N=30
```

```
      GO TO 33
   35 IF(N-50)36,36,37
   36 N=31
      GO TO 33
   37 IF(N-90)38,38,39
   38 N=32
      GO TO 33
   39 IF(N-150)30,30,41
   30 N=33
      GO TO 33
   41 N=34
   33 B1LO=B1-SDB1*TTEST(N)
      B1H1=B1+SDB1*TTEST(N)
      B2LO=B2-SDB2*TTEST(N)
      B2H1=B2+SDB2*TTEST(N)
      ALO=YBAR-B1H1*X1BAR-B2H1*X2BAR
      AHI=YBAR-B1LO*X1BAR-B2LO*X2BAR
      PUNCH 303, SERIES,PW
  303 FORMAT(31HTHE LINEAR EQUATION FOR SERIES ,F7.2,3H IS,/
     2,5X,7HX=CN**,F7.4,/)
      PUNCH 304, AA, B1, B2
  304 FORMAT(    6HINHV= ,E12.6,3H + ,E12.6,4HXLNP,3H + ,E12.6,1HX,//)
      PUNCH 402
  402 FORMAT(75X,36HTHE 95 PERCENT CONFIDENCE LIMITS ARE)
      PUNCH 406,ALO,AHI
  406 FORMAT(5X,3HA= ,E14.8,4H TO ,E14.8)
      PUNCH 407,B1LO,B1H1
  407 FORMAT(5X,4HB1= ,E14.8,4H TO ,E14.8)
      PUNCH 408, B2LO,B2H1
  408 FORMAT(5X,4HB2= ,E14.8,4H TO ,E14.8,/)
      PUNCH 20
   20 FORMAT(17X,43HANALYSIS OF VARIANCE OF THE LINEAR EQUATION)
      PUNCH 21
   21 FORMAT(17X,43H-------------------------------------------,/)
      PUNCH 22, EN
   22 FORMAT(18X,F6.0,11HDATA POINTS/)
      PUNCH 211,SPC2
  211 FORMAT(8X, 30HSUM OF SQUARES OF REGRESSION= ,E14.8)
      PUNCH 212, R
  212 FORMAT(8X,27HCORRELATION COEFFICIENT R= ,F10.7)
      PUNCH 213, S2YES2, DFS2Y
  213 FORMAT(8X,25HRESIDUAL SUM OF SQUARES= ,E14.8,5H FOR ,F6.0,
     219H DEGREES OF FREEDOM)
      PUNCH 214, F
  214 FORMAT(8X,28HF TEST FOR SIGNIFICANCE, F= ,F8.2)
      PUNCH 215, DFS2Y
  215 FORMAT(8X,38HCONSULT VOLK PAGES 148-151, F2= 2,F1= ,F6.0)
      PUNCH 216
  216 FORMAT(8X,42HTO FIND PROBABILITY OF A LARGER VALUE OF F)
      PUNCH 217, S2YES
  217 FORMAT(8X,22HVARIANCE OF ESTIMATE= ,E14.8)
      PUNCH 218, S2B1, S2B2
  218 FORMAT(8X,35HVARIANCE OF REGRESSION COEFFICIENTS,/12X,
```

```
   210HS**2(B1)= ,E14.8/12X,10HS**2(B2)= ,E14.8,//)
    PUNCH 501
501 FORMAT(///5X,29HTHE KEMME-KREPS CONSTANTS ARE)
    PUNCH 502, AA, B1, B2
502 FORMAT(/10X3HA= ,E14.8,/10X,3HB= ,E14.8,/10X,3HC= ,E14.8,)
    PUNCH 503
503 FORMAT(///,2X,48HERROR ANALYSIS OF THE INT. HEAT OF VAP. ESTIMATE)
    BIG=0.0
    SUMPE=0.0
    M10=0.0
    M5=0.0
    PUNCH 504
504 FORMAT(2X,69HTEMP C    INHV XP    INHV CAL    ERROR      PC ERR    Z
   2  PRESSURE MM HG,/)
    SUMS=0.0
    DO 506 K=1,L
    PUNCH 507, CODE(K)
507 FORMAT(23X, 9HCOMPOUND ,F7.2,)
    DO 506 J=1,9
    CXILV=AA+B1*X(K)*LOGF(P(J,K))+B2*X(K)
    GOOF=CXILV-XILV(J,K)
    PCER=GOOF*100.0/XILV(J,K)
    Z=XILV(J,K)/CXILV
    ABSER=ABSF(PCER)
    IF(ABSER-5.0)60,61,61
 60 M5=M5+1
    GO TO 62
 61 IF(ABSER-10.0)62,62,63
 63 M10=M10+1
 62 SUMPE=SUMPE+ABSER
    SUMS=SUMS+GOOF
    PUNCH 508,TC(J,K),XILV(J,K),CXILV,GOOF,PCER,Z,P(J,K)
508 FORMAT(2X,F6.1,2X,F10.3,1X,F10.3,1X,F9.3,1X,F7.2,1X,F7.4,1X,F8.2)
    IF(ABSER-BIG)506,506,56
 56 BIG=ABSER
506 CONTINUE
    AVERR=SUMPE/EN
    PUNCH 57,AVERR
 57 FORMAT(/12X,24HAVERAGE ABSOLUTE ERROR= ,F10.5,8H PERCENT)
    PUNCH 58, BIG
 58 FORMAT(12X,24HMAXIMUM ABSOLUTE ERROR= ,F10.5,8H PERCENT)
    GOOD=M5
    BAD=M10
    APOO=BAD/EN*100.0
    AWOW=GOOD/EN*100.0
    PUNCH59,AWOW,APOO
 59 FORMAT(2X,F6.1,35H PERCENT OF ERRORS UNDER 5 PERCENT, ,
   2F5.1,24H PERCENT OVER 10 PERCENT/)
    SD=SQRTF(SUMS/(EN-1.0))
    ENN=EN-1.0
    N=ENN
    IF(N-30)40,40,91
 40 GO TO 42
```

```
91 IF(N-35)43,43,44
43 N=30
   GO TO 42
44 IF(N-50)45,45,46
45 N=31
   GO TO 42
46 IF(N-60)47,47,48
47 N=32
   GO TO 42
48 IF(N-150)49,49,50
49 N=33
   GO TO 42
50 N=34
42 CONTINUE
   RANGE=SD+TTEST(N)
   PUNCH 51
51 FORMAT(2X,51H95 PERCENT CONFIDENCE RANGE OF HEAT OF VAPORIZATION)
   PUNCH 52, RANGE
52 FORMAT(8X,7HD +OR- ,F7.4)
   PUNCH 53
53 FORMAT(25X,33H----------CASE COMPLETE----------///)
   GO TO 111
   END
```

MULTIPLE LINEAR REGRESSION OF THE KEMME-KREPS DENSITY EQUATION

Method

The regression correlation is solved using the equations shown by Volk (66) pages 262 and 287. The program was written in Fortran II-D incorporating fourteen significant figures in the floating point variables. Because the program required more core storage than was available, it was divided into sections and stored in disc storage. Thus each section was called from the disc into core storage, the statements carried out, and placed back into the disc. The different sections may be identified in the computer program as REPEAT, MAIN, ADDD, BDDD and CDDD.

Data Input

The following order was used for the data input. Data format as shown in the program must be used.

1. listing of Student's probability factors for a probability of a deviation greater than t of .025
2. point by point error analysis, yes or no indicated by 2 or 1 respectively
3. homologous series identification
4. number of compounds
5. Antoine constants for each compound

6. number of carbon atoms, molecular weight and number of data points per compound

7. density-temperature data

8. effective chain length power

NOMENCLATURE FOR THE MULTIPLE LINEAR REGRESSION OF THE KEMME-KREPS DENSITY EQUATION

TTEST = Listing of Student's probability factors

CHOICE = Variable to indicate whether a point by point error analysis is to be carried out

SERIES = Homologous series identification number

K = Number of compounds

CODE = Compound identification number

AA,BB,CC = Antoine constants

CN = Number of carbon atoms

W = Molecular weight

EN = Number of data points per compound

TC = Temperature

TERM = Density

PW = Chain length power

A = Constants for the Kemme-Kreps equation

B1 = Constants for the Kemme-Kreps equation

B2 = Constants for the Kemme-Kreps equation

B3 = Constants for the Kemme-Kreps equation

SEN = Total number of data points

SPC2 = Sum of squares of regression

R = Correlation coefficient

S2YES2 = Residual sum of squares

DFS2Y = Degrees of freedom

GOOF = Error on density estimate

PCER = Per cent error on density estimate

AVERR = Average absolute error

BIG = Maximum absolute error

COMPUTER PROGRAM

MULTIPLE LINEAR REGRESSION OF THE KEMME-KREPS DENSITY EQUATION

```
C
C
C
C
C
      CALL LINK (REPEAT)

*LDISKREPEAT
      DIMENSION AA(20),BB(20),CC(20),CN(20),W(20),EN(20),TC(20,12),
     2          TA(20,12),DM(20,12),P(20,12),X(20    ),TERM(20,12),
     3TTEST(34)
      COMMON AA,BB,CC,CN,W,EN,TC,TA,DM,P,X,TERM,TTEST,SERIES,K,SEN,
     2N,SY,SX1,SX2,SX3,X1,X2,YBAR,X1BAR,X2BAR,X3BAR,SPY2,SPYX2,SPYX3,
     3SPYX1,SPX1X2,SPX2X3,SPX1X3,SP2X1,SP2X2,SP2X3,DELY,DELX1,DELX2,
     4DELX3,DEL2Y,E,Y,Z,S,R,T,U,Q,F,B1,B2,B3,A,SPC2,S2YES2,DFS2Y
      COMMON     D,BIG,SUMPE,M10,M5,SUMS,PXP,GOOF,PCER,ABSER,AVERR,
     1GOOD,BAD,APOO,AWOW,SD,ENN,RANGE,S2YES,B,C,DXP,PW,CHOICE,PASS
      PASS=0.0
      CALL LINK (MAIN)


   JOB
   FOR  3
*FANDK1404
*LDISKMAIN
      DIMENSION AA(20),BB(20),CC(20),CN(20),W(20),EN(20),TC(20,12),
     2          TA(20,12),DM(20,12),P(20,12),X(20    ),TERM(20,12),
     3TTEST(34)
      COMMON AA,BB,CC,CN,W,EN,TC,TA,DM,P,X,TERM,TTEST,SERIES,K,SEN,
     2N,SY,SX1,SX2,SX3,X1,X2,YBAR,X1BAR,X2BAR,X3BAR,SPY2,SPYX2,SPYX3,
     3SPYX1,SPX1X2,SPX2X3,SPX1X3,SP2X1,SP2X2,SP2X3,DELY,DELX1,DELX2,
     4DELX3,DEL2Y,E,Y,Z,S,R,T,U,Q,F,B1,B2,B3,A,SPC2,S2YES2,DFS2Y
      COMMON     D,BIG,SUMPE,M10,M5,SUMS,PXP,GOOF,PCER,ABSER,AVERR,
     1GOOD,BAD,APOO,AWOW,SD,ENN,RANGE,S2YES,B,C,DXP,PW,CHOICE,PASS
      IF(PASS-1.0)7000,7000,3000
 7000 DO 10 N=1,34
   10 READ 2011, TTEST(N)
 2011 FORMAT(F7.4)
  300 READ 301, SERIES
  301 FORMAT(F5.1)
      READ 302, K
  302 FORMAT(F5.1)
      SEN=0
      DO 2 L=1, K
      READ 303, CODE,AA(L),BB(L),CC(L)
  303 FORMAT(F7.1,F10.5,F10.5,F 10.5)
      READ 304, CN(L), W(L), EN(L)
  304 FORMAT(F4.1,F10.5,F10.5 )
      N=EN(L)
      DO 3 J=1,N
      READ 305, TC(L,J), TERM(L,J)
```

```
  305 FORMAT(F7.1,F7.6)
      TA(L,J)=TC(L,J) + 273.16
      DM(L,J)=TERM(L,J)/W(L)
    3 P(L,J)=EXPF((AA(L)-BB(L)/(TC(L,J)+CC(L)))*2.30259)
    2 SEN=SEN+EN(L)
 3000 READ 556, PW
  556 FORMAT(F10.7)
      READ 555, CHOICE
  555 FORMAT(F10.7)
      TERM(L,J)=0.0
      SY=0.0
      SX1=0.0
      SX2=0.0
      SX3=0.0
      DO 4 L=1,K
      N=EN(L)
      X(L)=CN(L)**PW
      DO 5 J=1, N
      TERM(L,J)=LOGF(TA(L,J)*DM(L,J))
      SY=SY+TERM(L,J)
      X1=LOGF(P(L,J))
      SX1=SX1+X1
      X2=X(L   )*LOGF(P(L,J))
      SX2=SX2+X2
    5 SX3=SX3+X(L   )
    4 CONTINUE
      YBAR=SY/SEN
      X1BAR=SX1/SEN
      X2BAR=SX2/SEN
      X3BAR=SX3/SEN
      SPY2=0.0
      SPYX1=0.0
      SPYX2=0.0
      SPYX3=0.0
      SPX1X2=0.0
      SPX2X3=0.0
      SPX1X3=0.0
      SP2X1=0.0
      SP2X2=0.0
      SP2X3=0.0
      CALL LINK (ADDD)
C
C
*LDISKADDD
      DIMENSION AA(20),BB(20),CC(20),CN(20),W(20),EN(20),TC(20,12),
     2          TA(20,12),DM(20,12),P(20,12),X(20    ),TERM(20,12),
     3TTEST(34)
      COMMON AA,BB,CC,CN,W,EN,TC,TA,DM,P,X,TERM,TTEST,SERIES,K,SEN,
     2N,SY,SX1,SX2,SX3,X1,X2,YBAR,X1BAR,X2BAR,X3BAR,SPY2,SPYX2,SPYX3,
     3SPYX1,SPX1X2,SPX2X3,SPX1X3,SP2X1,SP2X2,SP2X3,DELY,DELX1,DELX2,
     4DELX3,DEL2Y,E,Y,Z,S,R,T,U,Q,F,B1,B2,B3,A,SPC2,S2YES2,DFS2Y
      COMMON    D,BIG,SUMPE,M10,M5,SUMS,PXP,GOOF,PCER,ABSER,AVERR,
     1GOOD,BAD,APOO,AWOW,SD,ENN,RANGE,S2YES,B,C,DXP,PW,CHOICE,PASS
```

```
      DO 6 L=1,K
      N=EN(L)
      DO 7 J=1, N
      DELY=TERM(L,J)-YBAR
      DELX1=LOGF(P(L,J))-X1BAR
      DELX2=(X(L)*LOGF(P(L,J)))-X2BAR
      DELX3=X(L   )-X3BAR
      DEL2Y=DELY*DELY
      SPY2=SPY2+DEL2Y
      SPYX1=SPYX1+DELY*DELX1
      SPYX2=SPYX2+DELY*DELX2
      SPYX3=SPYX3+DELY*DELX3
      SPX1X2=SPX1X2+DELX1*DELX2
      SPX2X3=SPX2X3+DELX2*DELX3
      SPX1X3=SPX1X3+DELX1*DELX3
      SP2X1=SP2X1+DELX1*DELX1
      SP2X2=SP2X2+DELX2*DELX2
    7 SP2X3=SP2X3+DELX3*DELX3
    6 CONTINUE
      E=SP2X1
      Y=SPX1X2
      Z=SPX1X3
      S=SPX2X3
      R=SP2X2
      T=SP2X3
      U=SPYX1
      Q=SPYX2
      F=SPYX3
      B1=((((Q*S)-(F*R))*((Z*R)-(S*Y)))-(((U*R)-(Q*Y))*((S*S)-(R*T))))/
     2((((Y*S)-(Z*R))*((Z*R)-(S*Y)))-(((E*R)-(Y*Y))*((S*S)-(R*T))))
      B2=((((U*Y)-(Q*E))*((S*Z)-(T*Y)))-(((Q*Z)-(F*Y))*((Z*Y)-(S*E))))/
     2((((Y*Y)-(R*E))*((S*Z)-(T*Y)))-(((R*Z)-(S*Y))*((Z*Y)-(S*E))))
      B3=((((U*Y)-(Q*E))*((R*Z)-(S*Y)))-(((Q*Z)-(F*Y))*((Y*Y)-(R*E))))/
     2((((Z*Y)-(S*E))*((R*Z)-(S*Y)))-(((Y*Y)-(R*E))*((S*Z)-(T*Y))))
      A=(YBAR)-(B1*X1BAR)-(B2*X2BAR)-(B3*X3BAR)
      SPC2=(B1*U)+(B2*Q)+(B3*F)
      S2YES2=SPY2-SPC2
      DFS2Y=SEN-3.0
      R=(SPC2/SPY2)**0.5
      F=SQRTF(SPC2)/SQRTF(S2YES2)
      S2YES=S2YES2/DFS2Y
      CALL LINK (BDDD)
C
C
*LDISKBDDD
      DIMENSION AA(20),BB(20),CC(20),CN(20),W(20),EN(20),TC(20,12),
     2          TA(20,12),DM(20,12),P(20,12),X(20    ),TERM(20,12),
     3TTEST(34)
      COMMON AA,BB,CC,CN,W,EN,TC,TA,DM,P,X,TERM,TTEST,SERIES,K,SEN,
     2N,SY,SX1,SX2,SX3,X1,X2,YBAR,X1BAR,X2BAR,X3BAR,SPY2,SPYX2,SPYX3,
     3SPYX1,SPX1X2,SPX2X3,SPX1X3,SP2X1,SP2X2,SP2X3,DELY,DELX1,DELX2,
     4DELX3,DEL2Y,E,Y,Z,S,R,T,U,Q,F,B1,B2,B3,A,SPC2,S2YES2,DFS2Y
      COMMON     D,BIG,SUMPE,M10,M5,SUMS,PXP,GOOF,PCER,ABSER,AVERR,
```

```
     1GOOD,BAD,APOO,AWOW,SD,ENN,RANGE,S2YES,B,C,DXP,PW,CHOICE,PASS
      PUNCH 203, SERIES
  203 FORMAT(41HTHE LINEAR EQUATION FOR THE HOMO. SERIES ,F6.1,3H IS)
      PUNCH 204, A, B1, B2, B3
  204 FORMAT (//2X,11HLN(TA*DM)= ,E14.8,1H+,E14.8,8HLN(P) + ,/E14.8,
     29HXLN(P) + ,E14.8,1HX//)
      PUNCH 209
  209 FORMAT(17X,43HANALYSIS OF VARIANCE OF THE LINEAR EQUATION)
      PUNCH 2099
 2099 FORMAT(17X,43H-------------------------------------------/)
      PUNCH 210, SEN, PW
  210 FORMAT(18X,F6.0,11HDATA POINTS/,6HX=CN**,F10.7,/)
      PUNCH 211, SPC2
  211 FORMAT(8X, 30HSUM OF SQUARES OF REGRESSION= ,E14.8)
      PUNCH 212, R
  212 FORMAT(8X,27HCORRELATION COEFFICIENT R= ,F10.7)
      PUNCH 213, S2YES2, DFS2Y
  213 FORMAT(8X, 25HRESIDUAL SUM OF SQUARES= ,F10.7,5H FOR ,F6.0,
     218HDEGREES OF FREEDOM)
      PUNCH 214, F
  214 FORMAT(8X,28HF TEST FOR SIGNIFICANCE, F= ,F8.2)
      PUNCH 215, DFS2Y
  215 FORMAT(8X, 38HCONSULT VOLK PAGES 148-151, F2= 2,F1= ,F6.0)
      PUNCH 216
  216 FORMAT(8X,42HTO FIND PROBABILITY OF A LARGER VALUE OF F)
      PUNCH 217, S2YES
  217 FORMAT(8X,22HVARIANCE OF ESTIMATE= ,E14.8)
      PUNCH 219
  219 FORMAT(///5X,23HTHE KEMME CONSTANTS ARE)
      B=B1
      C=B2
      D=B3
      PUNCH 220, A, B, C, D
  220 FORMAT(/10X3HA= ,E14.8,/10X,3HB= ,E14.8,/10X,3HC= ,E14.8,/10X,3HD=
     2 ,E14.8)
      IF(CHOICE-1.0)5000,5000,4000
 4000 PUNCH 221
  221 FORMAT(///2X,38HERROR ANALYSIS OF THE DENSITY ESTIMATE,/)
      BIG=0.0
      SUMPE=0.0
      M10=0
      M5=0
      PUNCH 222
  222 FORMAT(2X,70HTEMP C    DEN XP   DEN CAL    ERROR    PC ERR      Z
     2   PRESSURE MM HG,/)
      SUMS=0.0
 5000 CONTINUE
      CALL LINK (CDDD)
C
C
*LDISKCDDD
      DIMENSION AA(20),BB(20),CC(20),CN(20),W(20),EN(20),TC(20,12),
     2          TA(20,12),DM(20,12),P(20,12),X(20    ),TERM(20,12),
```

```
     3TTEST(34)
      COMMON AA,BB,CC,CN,W,EN,TC,TA,DM,P,X,TERM,TTEST,SERIES,K,SEN,
     2N,SY,SX1,SX2,SX3,X1,X2,YBAR,X1BAR,X2BAR,X3BAR,SPY2,SPYX2,SPYX3,
     3SPYX1,SPX1X2,SPX2X3,SPX1X3,SP2X1,SP2X2,SP2X3,DELY,DELX1,DELX2,
     4DELX3,DEL2Y,E,Y,Z,S,R,T,U,Q,F,B1,B2,B3,A,SPC2,S2YES2,DFS2Y
      COMMON     D,BIG,SUMPE,M10,M5,SUMS,PXP,GOOF,PCER,ABSER,AVERR,
     1GOOD,BAD,APOO,AWOW,SD,ENN,RANGE,S2YES,B,C,DXP,PW,CHOICE,PASS
      IF(CHOICE-1.0)5000,5000,4000
 4000 DO 117 L=1, K
      N=EN(L)
      DO 118 J=1, N
      D=B3
      DXP=((EXPF(A+B*LOGF(P(L,J))+C*X(L)*LOGF(P(L,J))+D*X(L)))/
     2(TA(L,J)))*(W(L))
      D=DM(L,J)*W(L)
      GOOF=DXP-D
      PCER=GOOF*100.0/D
      Z=D/DXP
      ABSER=ABSF(PCER)
      IF(ABSER-5.0) 60, 61, 61
   60 M5=M5+1
      GO TO 62
   61 IF(ABSER-10.0) 62, 62, 63
   63 M10=M10+1
   62 SUMPE=SUMPE+ABSER
      SUMS=SUMS+GOOF
      PUNCH 223,TC(L,J), D      ,DXP,GOOF,PCER,Z,P(L,J)
  223 FORMAT(2X,F6.1,2X,F8.5,1X,F8.5,1X,F8.5,1X,F7.2,2X,F6.3,5X,F8.2)
      IF(ABSER-BIG) 118, 118, 49
   49 BIG=ABSER
  118 CONTINUE
  117 CONTINUE
      AVERR=SUMPE/SEN
      PUNCH 227, AVERR
  227 FORMAT(/12X,24HAVERAGE ABSOLUTE ERROR= ,F10.5,8H PERCENT)
      PUNCH 228, BIG
  228 FORMAT(12X,24HMAXIMUM ABSOLUTE ERROR= ,F10.5,8H PERCENT)
      GOOD=M5
      BAD=M10
      APOO=BAD/SEN*100.0
      AWOW=GOOD/SEN*100.0
      PUNCH 229, AWOW, APOO
  229 FORMAT(2XF6.1,35H PERCENT OF ERRORS UNDER 5 PERCENT, ,
     2F5.1,24H PERCENT OVER 10 PERCENT/)
      SD=SQRTF(SUMS/(SEN-1.0))
      ENN=SEN-1.0
      N=ENN
      IF(N-30) 11, 11, 12
   11 GO TO 13
   12 IF(N-35) 14, 14, 15
   14 N=30
      GO TO 13
   15 IF(N-50) 16, 16, 17
```

```
   16 N=31
      GO TO 13
   17 IF(N-60) 18, 18, 19
   18 N=32
      GO TO 13
   19 IF(N-150) 20, 20, 21
   20 N=33
      GO TO 13
   21 N=34
   13 CONTINUE
      RANGE=SD+TTEST(N)
      PUNCH 230
  230 FORMAT(2X,48H95 PERCENT CONFIDENCE RANGE OF VAPOR PRESSURE IS)
      PUNCH 231, RANGE
  231 FORMAT(8X,7HD +OR- ,F7.4)
 5000 PUNCH 232
  232 FORMAT(15X,33H----------CASE COMPLETE----------///)
      PASS=2.0
      CALL LINK (MAIN)
      END
```

NOMENCLATURE FOR DENSITY PREDICTION EQUATION

A,B,C,D = Kemme-Kreps density equation constants

CODE = Compound identification number

AA = Antoine constant, A

BB = Antoine constant, B

CC = Antoine constant, C

CN = Number of carbon atoms

W = Molecular weight

TC = Temperature

DXPW = Molal density

DXP = Density

P = Vapor pressure

COMPUTER PROGRAM
DENSITY PREDICTION EQUATION


```
111 READ 10, A,B,C,D
 10 FORMAT(4N)
    PUNCH 6,A,B,C,D
  6 FORMAT(/10X3HA= ,E14.8,/10X,3HB= ,E14.8,/10X,3HC= ,E14.8,/10X,3HD=
   2 ,E14.8,///)
  1 READ 2, CODE, AA, BB, CC
  2 FORMAT(4N)
    READ 3, CN, W, DATA
  3 FORMAT(3N)
    PLO=5.0
    PHI=760.0
    TCLO=(BB)/(AA-.43429*LOGF(PLO))-CC
    TCHI=(BB)/(AA-.43429*LOGF(PHI))-CC
    MTCLO=TCLO/10.0
    MTCHI=TCHI/10.0
    J=MTCLO*10
    K=MTCHI*10
    PUNCH 7
  7 FORMAT(5X, 6HTEMP C,5X,13HDENSITY GM/ML,5X,17HDENSITY GM MOL/ML,5X
   2,14HPRESSURE MM HG,)
    PUNCH 5, CODE
  5 FORMAT(/  ,23X9HCOMPOUND ,F7.1,/)
    DO 4 L=J, K, 10
    TC=L
    TA=TC+273.16
    X=CN**.55
    P=EXPF((AA-BB/(TC+CC))*2.30259)
    DXP=((EXPF(A+B*LOGF(P)+C*X*LOGF(P)+D*X))/(TA))
    DXPW=DXP*W
  4 PUNCH 9,TC,DXPW,DXP,P
  9 FORMAT(5X,F6.1,5X,F8.5,10X,F10.7,12X,F8.2)
    GO TO 1
    END
```

APPENDIX E

LITERATURE DATA

Compound	Antoine Constants A	B	C
Ethane	6.80266	656.40	256.00
Propane	6.82973	813.20	248.00
Butane	6.83029	945.90	240.00
Pentane	6.85221	1064.63	232.00
Hexane	6.87776	1171.530	224.366
Heptane	6.90240	1268.115	216.900
Octane	6.92377	1355.126	209.517
Nonane	6.93513	1428.811	201.619
Decane	6.95367	1501.268	194.480
Undecane	6.97674	1572.477	188.022
Dodecane	6.98059	1625.928	180.311
Tridecane	6.9887	1677.43	172.90
Tetradecane	6.9957	1725.46	165.75
Pentadecane	7.0017	1768.82	158.60
Hexadecane	7.03044	1831.317	154.528
Heptadecane	7.0115	1847.82	145.52
Octadecane	7.0156	1883.73	139.46

Table 34: The Antoine Constants for the n-Alkanes (57)

Compound	Antoine Constants A	B	C
Ethene	6.7476	585.00	255.00
Propene	6.8196	785.00	247.00
Butene	6.8429	926.10	240.00
Pentene	6.8465	1044.895	233.516
Hexene	6.86572	1152.971	225.849
Heptene	6.9007	1257.505	219.179
Octene	6.93263	1353.486	212.764
Nonene	6.95387	1345.359	205.535
Decene	6.96034	1501.872	197.578
Undecene	6.96662	1562.469	189.743
Dodecene	6.97522	1619.862	182.271
Tridecene	6.9692	1662.68	173.90
Tetradecene	6.9615	1699.76	165.53
Pentadecene	6.9503	1730.30	157.02
Hexadecene	6.936	1755.2	148.4
Heptadecene	6.920	1774.6	139.7
Octadecene	6.901	1789.4	130.9

Table 35: The Antoine Constants for the n-Alkenes (57)

Compound	Antoine Constants A	B	C
Ethanol	8.21337	1652.05	231.48
Undecanol	6.655	1372.	118.
Tridecanol	6.503	1362.	100.
Pentadecanol	6.372	1351.	82.
Heptadecanol	6.264	1338.	63.
Octadecanol	6.214	1330.	54.

Table 36: Antoine Constants for the n-Alcohols (57)

Compound	Antoine Constants A	B	C
1-Chloro-ethane	6.94914	1012.771	236.67
1-Chloropentane	6.96617	1332.890	218.50
1-Chlorotridecane	7.391	2087.9	186
1-Chloropentadecane	7.474	2240.5	180
1-Chloroheptadecane	7.543	2378.8	175
1-Chloro-octadecane	7.573	2443.5	173

Table 37: Antoine Constants for the n-Alkyl Chlorides (42)

Temperature °C	Density gm/ml
Methane	
-180.0	.4497
-170.0	.4362
-160.0	.4218
Ethane	
-140.0	.6086
-130.0	.5972
-120.0	.5856
-110.0	.5737
-100.0	.5613
-90.0	.5482
Propane	
-110.0	.656
-100.0	.646
-90.0	.635
-80.0	.6241
-70.0	.6130
-60.0	.6017
-50.0	.5900
-40.0	.5784
Butane	
-80.0	.6801
-70.0	.6703
-60.0	.6605
-50.0	.6511
-40.0	.6416
-30.0	.6318
-20.0	.6218
-10.0	.6115
0.0	.6011
Pentane	
-50.0	.6908
-40.0	.6820
-30.0	.6731
-20.0	.6640
-10.0	.6546
0.0	.6452
Pentane con't.	
10.0	.6357
20.0	.6262
30.0	.6159
40.0	.6053
Hexane	
-30.0	.7032
-20.0	.6946
-10.0	.6858
0.0	.6769
10.0	.6679
20.0	.6594
30.0	.6502
40.0	.6411
50.0	.6316
60.0	.6214
70.0	.6102
Heptane	
0.0	.7006
10.0	.6920
20.0	.6838
30.0	.6753
40.0	.6669
50.0	.6583
60.0	.6493
70.0	.6398
80.0	.6303
90.0	.6207
100.0	.6110
Octane	
20.0	.7025
30.0	.6945
40.0	.6866
50.0	.6784
60.0	.6701
70.0	.6614
80.0	.6528
90.0	.6442

Table 38: Literature Density Data for the n-Alkanes (57)

Temperature °C	Density gm/ml
Octane con't.	
100.0	.6352
110.0	.6261
120.0	.6166
Nonane	
30.0	.7099
40.0	.7022
50.0	.6944
60.0	.6864
70.0	.6781
80.0	.6701
90.0	.6620
100.0	.6536
110.0	.6451
120.0	.6363
130.0	.6270
140.0	.6180
150.0	.6090
Decane	
50.0	.7073
60.0	.6996
70.0	.6917
80.0	.6840
90.0	.6761
100.0	.6681
110.0	.6600
120.0	.6517
130.0	.6432
140.0	.6348
150.0	.6260
160.0	.6169
170.0	.6074
Undecane	
70.0	.7029
80.0	.6954
90.0	.6878
100.0	.6800
110.0	.6722

Temperature °C	Density gm/ml
Undecane con't.	
120.0	.6641
130.0	.6560
140.0	.6479
150.0	.6396
160.0	.6311
170.0	.6223
180.0	.6133
190.0	.6040
Dodecane	
90.0	.6976
100.0	.6900
110.0	.6824
120.0	.6745
130.0	.6667
140.0	.6589
150.0	.6509
160.0	.6427
170.0	.6344
180.0	.6260
190.0	.6173
200.0	.6082
210.0	.5985
220.0	.5878
Tridecane	
120.0	.6834
130.0	.6757
140.0	.6681
150.0	.6604
160.0	.6525
170.0	.6446
180.0	.6365
190.0	.6283
200.0	.6200
210.0	.6107
220.0	.6010
230.0	.5910
240.0	.5807

Table 38: Continued

Temperature °C	Density gm/ml
Tetradecane	
120.0	.6911
130.0	.6836
140.0	.6761
150.0	.6685
160.0	.6609
170.0	.6532
180.0	.6454
190.0	.6375
200.0	.6295
210.0	.6209
220.0	.6119
230.0	.6026
240.0	.5933
250.0	.5839
Pentadecane	
140.0	.6830
150.0	.6756
160.0	.6682
170.0	.6606
180.0	.6531
190.0	.6454
200.0	.6378
210.0	.6296
220.0	.6211
230.0	.6124
240.0	.6036
250.0	.5949
260.0	.5858
Hexadecane	
150.0	.6819
160.0	.6745
170.0	.6672
180.0	.6598
190.0	.6523
200.0	.6447

Temperature °C	Density gm/ml
Hexadecane con't.	
210.0	.6370
220.0	.6289
230.0	.6206
240.0	.6124
250.0	.6041
260.0	.5955
Heptadecane	
160.0	.6802
170.0	.6730
180.0	.6657
190.0	.6584
200.0	.6510
210.0	.6435
220.0	.6357
230.0	.6278
240.0	.6199
250.0	.6119
260.0	.6037
Octadecane	
170.0	.6781
180.0	.6710
190.0	.6638
200.0	.6566
210.0	.6492
220.0	.6416
230.0	.6340
240.0	.6264
250.0	.6187
260.0	.6108

Table 38: Continued

Temperature °C	Density gm/ml	Temperature °C	Density gm/ml
Ethene		**Hexene**	
-150.0	.6318	-30.0	.720
-140.0	.6182	-20.0	.711
-130.0	.6046	-10.0	.702
-120.0	.5910	0.0	.6920
-110.0	.5774	10.0	.6826
-100.0	.5638	20.0	.6732
		30.0	.6637
Propene		40.0	.6543
-110.0	.682	50.0	.6449
-100.0	.671	60.0	.6354
-90.0	.659		
-80.0	.647	**Heptene**	
-70.0	.6358	0.0	.7146
-60.0	.6237	10.0	.7058
-50.0	.6116	20.0	.6970
-40.0	.5995	30.0	.6882
		40.0	.6793
Butene		50.0	.6705
-80.0	.707	60.0	.6617
-70.0	.6962	70.0	.6528
-60.0	.6854	80.0	.6440
-50.0	.6746	90.0	.6352
-40.0	.6638		
-30.0	.6529	**Octene**	
-20.0	.6419	0.0	.7316
-10.0	.6306	10.0	.7233
0.0	.6190	20.0	.7149
		30.0	.7066
Pentene		40.0	.6982
-60.0	.723	50.0	.6899
-50.0	.713	60.0	.6816
-40.0	.702	70.0	.6732
-30.0	.692	80.0	.6649
-20.0	.688	90.0	.6565
-10.0	.672	100.0	.6482
0.0	.6612	110.0	.640
10.0	.6508	120.0	.632
20.0	.6405		

Table 39: Literature Density Data for the n-Alkenes (57)

Temperature °C	Density gm/ml
Nonene	
20.0	.7292
30.0	.7213
40.0	.7135
50.0	.7056
60.0	.6977
70.0	.6898
80.0	.6819
90.0	.6741
100.0	.6662
110.0	.658
120.0	.650
Decene	
40.0	.7253
50.0	.7175
60.0	.7097
70.0	.7020
80.0	.6942
90.0	.6864
100.0	.6786
110.0	.671
120.0	.663
Undecene	
50.0	.7276
60.0	.7201
70.0	.7125
80.0	.7050
90.0	.6974
100.0	.6898
110.0	.682
120.0	.675
Dodecene	
70.0	.7217
80.0	.7144
90.0	.7070

Temperature °C	Density gm/ml
Dodecene con't.	
100.0	.6997
110.0	.692
120.0	.685
Tridecene	
90.0	.7146
100.0	.7073
110.0	.700
120.0	.693
Tetradecene	
100.0	.7140
110.0	.707
120.0	.700
Pentadecene	
110.0	.713
120.0	.706

Table 39: Continued

Temp. °C	Density gm/ml	Lit. Source
	Ethanol	
20.0	.78931	(57)
25.0	.78504	(57)
	Propanol	
20.0	.80342	(57)
25.0	.79948	(57)
	Butanol	
20.0	.8096	(57)
20.53	.8078	(17)
25.0	.8058	(57)
40.27	.7929	(17)
60.31	.7775	(17)
78.09	.7631	(17)
	Pentanol	
39.91	.7987	(17)
40.0	.7981	(63)
59.01	.7848	(17)
60.0	.7834	(63)
78.00	.7711	(17)
80.0	.7680	(63)
100.0	.7515	(63)
120.0	.7356	(63)
	Hexanol	
59.01	.7915	(17)
60.0	.7924	(63)
78.00	.7772	(17)
80.0	.7766	(63)
100.0	.7599	(63)
120.0	.7432	(63)
140.0	.7247	(63)
	Heptanol	
60.31	.7928	(17)
78.09	.7804	(17)
	Decanol	
120.0	.7550	(63)
140.0	.7387	(63)
160.0	.7224	(63)
180.0	.7053	(63)
200.0	.6883	(63)
220.0	.6708	(63)

Temp. °C	Density gm/ml	Lit. Source
	Dodecanol	
140.0	.7468	(63)
160.0	.7307	(63)
180.0	.7144	(63)
200.0	.6982	(63)
220.0	.6810	(63)
240.0	.6635	(63)
260.0	.6457	(63)
	Tetradecanol	
160.0	.7340	(63)
180.0	.7188	(63)
200.0	.7032	(63)
220.0	.6865	(63)
240.0	.6700	(63)
260.0	.6534	(63)
280.0	.6362	(63)
	Hexadecanol	
180.0	.7233	(63)
200.0	.7082	(63)
220.0	.6928	(63)
240.0	.6770	(63)
260.0	.6607	(63)
280.0	.6454	(63)
300.0	.6288	(63)
	Octadecanol	
200.0	.7103	(63)
220.0	.6956	(63)
240.0	.6808	(63)
260.0	.6661	(63)
280.0	.6498	(63)
300.0	.6316	(63)

Table 40: Literature Density Data for the n-Alcohols

Temperature °C	Density gm/ml	Literature Source
	1-Chloropropane	
20.0	.8909	(57)
25.0	.8850	(57)
	1-Chlorobutane	
20.0	.8862	(57)
20.0	.8866	(63)
25.0	.8809	(57)
25.0	.8811	(63)
	1-Chloropentane	
0.0	.90137	(63)
15.0	.88657	(63)
20.0	.8840	(63)
20.0	.8818	(57)
25.0	.8769	(57)
25.0	.8795	(63)
30.0	.87163	(63)
	1-Chlorohexane	
20.0	.8785	(57)
20.0	.8790	(63)
25.0	.8739	(57)
25.0	.8745	(63)

Table 41: Literature Density Data for the n-Alkyl Chlorides

APPENDIX F

PREDICTED DENSITY DATA

Temperature °C	Density gm/ml
Ethane	
-140.0	.60986
-130.0	.60068
-120.0	.58955
-110.0	.57723
-100.0	.56425
-90.0	.55096
-80.0	.53761
Propane	
-110.0	.65415
-100.0	.64639
-90.0	.63702
-80.0	.62656
-70.0	.61538
-60.0	.60379
-50.0	.59198
-40.0	.58011
Butane	
-80.0	.67657
-70.0	.66894
-60.0	.66013
-50.0	.65048
-40.0	.64027
-30.0	.62970
-20.0	.61892
-10.0	.60806
.0	.59721
Pentane	
-50.0	.68792
-40.0	.68010
-30.0	.67144
-20.0	.66220
-10.0	.65254
.0	.64263
10.0	.63256
20.0	.62243
30.0	.61231

Temperature °C	Density gm/ml
Hexane	
-30.0	.69977
-20.0	.69238
-10.0	.68425
.0	.67556
10.0	.66648
20.0	.65714
30.0	.64763
40.0	.63804
50.0	.62843
60.0	.61885
Heptane	
-10.0	.70685
.0	.69957
10.0	.69165
20.0	.68326
30.0	.67453
40.0	.66556
50.0	.65644
60.0	.64727
70.0	.63802
80.0	.62882
90.0	.61967
Octane	
.0	.71702
10.0	.71037
20.0	.70302
30.0	.69515
40.0	.68689
50.0	.67835
60.0	.66961
70.0	.66075
80.0	.65184
90.0	.64291
100.0	.63400
110.0	.62515
120.0	.61638

y = .57
C = 1.1382
D = .068721

E = -.19568
F = -.0090056

Table 42: Density Predictions for the n-Alkanes

Temperature °C	Density gm/ml
Nonane	
20.0	.71848
30.0	.71152
40.0	.70401
50.0	.69609
60.0	.68785
70.0	.67939
80.0	.67079
90.0	.66210
100.0	.65338
110.0	.64466
120.0	.63597
130.0	.62735
140.0	.61881
150.0	.61036
Decane	
40.0	.71676
50.0	.70951
60.0	.70183
70.0	.69383
80.0	.68560
90.0	.67721
100.0	.66872
110.0	.66018
120.0	.65163
130.0	.64311
140.0	.63463
150.0	.62622
160.0	.61790
170.0	.60968
Undecane	
60.0	.71367
70.0	.70609
80.0	.69819
90.0	.69008
100.0	.68180
110.0	.67343
120.0	.66500
130.0	.65656
140.0	.64814
150.0	.63976
160.0	.63145

Temperature °C	Density gm/ml
Undecane con't.	
170.0	.62322
180.0	.61508
190.0	.60706
Dodecane	
70.0	.71631
80.0	.70878
90.0	.70095
100.0	.69290
110.0	.68469
120.0	.67639
130.0	.66804
140.0	.65968
150.0	.65133
160.0	.64303
170.0	.63478
180.0	.62662
190.0	.61855
200.0	.61059
210.0	.60273
Tridecane	
90.0	.71017
100.0	.70234
110.0	.69430
120.0	.68613
130.0	.67787
140.0	.66956
150.0	.66124
160.0	.65295
170.0	.64470
180.0	.63651
190.0	.62840
200.0	.62038
210.0	.61247
220.0	.60467
230.0	.59699
Tetradecane	
100.0	.71054
110.0	.70265
120.0	.69458
130.0	.68639

Table 42: Continued

Temperature °C	Density gm/ml
Tetradecane con't.	
140.0	.67812
150.0	.66982
160.0	.66152
170.0	.65325
180.0	.64503
190.0	.63687
200.0	.62880
210.0	.62082
220.0	.61295
230.0	.60520
240.0	.59755
250.0	.59004
Pentadecane	
120.0	.70212
130.0	.69398
140.0	.68573
150.0	.67744
160.0	.66912
170.0	.66081
180.0	.65255
190.0	.64433
200.0	.63620
210.0	.62815
220.0	.62020
230.0	.61236
240.0	.60464
250.0	.59704
260.0	.58955
270.0	.58220
Hexadecane	
130.0	.70125
140.0	.69294
150.0	.68455
160.0	.67615
170.0	.66775
180.0	.65938
190.0	.65106
200.0	.64283
210.0	.63467
220.0	.62662
230.0	.61868

Temperature °C	Density gm/ml
Hexadecane con't.	
240.0	.61085
250.0	.60314
260.0	.59556
270.0	.58810
280.0	.58078
Heptadecane	
140.0	.69925
150.0	.69085
160.0	.68240
170.0	.67394
180.0	.66550
190.0	.65710
200.0	.64877
210.0	.64053
220.0	.63237
230.0	.62433
240.0	.61639
250.0	.60858
260.0	.60089
270.0	.59333
280.0	.58590
290.0	.57860
300.0	.57144
Octadecane	
150.0	.69696
160.0	.68839
170.0	.67980
180.0	.67123
190.0	.66270
200.0	.65424
210.0	.64586
220.0	.63758
230.0	.62940
240.0	.62134
250.0	.61340
260.0	.60559
270.0	.59791
280.0	.59037
290.0	.58296
300.0	.57568
310.0	.56854

Table 42: Continued

Temperature °C	Density gm/ml	Temperature °C	Density gm/ml
Ethene		**Hexene**	
-150.0	.6435	-30.0	.7217
-140.0	.6334	-20.0	.7138
-130.0	.6209	-10.0	.7051
-120.0	.6068	.0	.6959
-110.0	.5919	10.0	.6863
-100.0	.5767	20.0	.6765
		30.0	.6666
Propene		40.0	.6566
-110.0	.6650	50.0	.6466
-100.0	.6568	60.0	.6366
-90.0	.6471		
-80.0	.6362	**Heptene**	
-70.0	.6247	-10.0	.7275
-60.0	.6127	.0	.7197
-50.0	.6006	10.0	.7112
-40.0	.5884	20.0	.7024
		30.0	.6932
Butene		40.0	.6838
-80.0	.6940	50.0	.6743
-70.0	.6860	60.0	.6647
-60.0	.6768	70.0	.6551
-50.0	.6668	80.0	.6456
-40.0	.6562	90.0	.6361
-30.0	.6453		
-20.0	.6342	**Octene**	
-10.0	.6230	.0	.7362
.0	.6118	10.0	.7290
		20.0	.7211
Pentene		30.0	.7128
-60.0	.7177	40.0	.7040
-50.0	.7102	50.0	.6951
-40.0	.7017	60.0	.6859
-30.0	.6924	70.0	.6767
-20.0	.6826	80.0	.6674
-10.0	.6724	90.0	.6582
.0	.6619	100.0	.6489
10.0	.6513	110.0	.6398
20.0	.6407	120.0	.6307

C = 1.1146
D = .066227
E = -.14185

F = -.0064619
y = .68

Table 43: Density Predictions for the n-Alkenes

Temperature °C	Density gm/ml
Nonene	
20.0	.7339
30.0	.7264
40.0	.7185
50.0	.7101
60.0	.7015
70.0	.6926
80.0	.6837
90.0	.6747
100.0	.6657
110.0	.6567
120.0	.6477
130.0	.6388
140.0	.6301
Decene	
40.0	.7293
50.0	.7216
60.0	.7134
70.0	.7050
80.0	.6964
90.0	.6877
100.0	.6789
110.0	.6700
120.0	.6612
130.0	.6524
140.0	.6437
150.0	.6350
160.0	.6265
170.0	.6181
Undecene	
50.0	.7300
60.0	.7224
70.0	.7144
80.0	.7061
90.0	.6976
100.0	.6890
110.0	.6803
120.0	.6716
130.0	.6629
140.0	.6543
150.0	.6457
160.0	.6371

Temperature °C	Density gm/ml
Undecene con't.	
170.0	.6287
180.0	.6204
190.0	.6122
Dodecene	
70.0	.7214
80.0	.7135
90.0	.7052
100.0	.6968
110.0	.6883
120.0	.6796
130.0	.6710
140.0	.6624
150.0	.6538
160.0	.6453
170.0	.6368
180.0	.6286
190.0	.6203
200.0	.6121
210.0	.6041
Tridecene	
90.0	.7112
100.0	.7030
110.0	.6945
120.0	.6860
130.0	.6775
140.0	.6689
150.0	.6603
160.0	.6518
170.0	.6433
180.0	.6349
190.0	.6266
200.0	.6185
210.0	.6104
220.0	.6025
230.0	.5947
Tetradecene	
100.0	.7077
110.0	.6994
120.0	.6910
130.0	.6824

Table 43: Continued

Temperature °C	Density gm/ml
Tetradecene con't.	
140.0	.6739
150.0	.6653
160.0	.6568
170.0	.6482
180.0	.6398
190.0	.6315
200.0	.6232
210.0	.6151
220.0	.6071
230.0	.5992
240.0	.5915
250.0	.5839
Pentadecene	
110.0	.7035
120.0	.6951
130.0	.6866
140.0	.6780
150.0	.6694
160.0	.6608
170.0	.6522
180.0	.6437
190.0	.6353
200.0	.6270
210.0	.6188
220.0	.6107
230.0	.6027
240.0	.5949
250.0	.5872
260.0	.5797
Hexadecene	
130.0	.6898
140.0	.6811
150.0	.6725
160.0	.6638
170.0	.6552
180.0	.6466
190.0	.6381
200.0	.6297
210.0	.6214
220.0	.6132
230.0	.6052

Temperature °C	Density gm/ml
Hexadecene con't.	
240.0	.5973
250.0	.5895
260.0	.5818
270.0	.5743
280.0	.5670
Heptadecene	
140.0	.6839
150.0	.6751
160.0	.6663
170.0	.6576
180.0	.6489
190.0	.6403
200.0	.6318
210.0	.6234
220.0	.6151
230.0	.6069
240.0	.5989
250.0	.5910
260.0	.5833
270.0	.5757
280.0	.5682
290.0	.5609
Octadecene	
150.0	.6772
160.0	.6683
170.0	.6595
180.0	.6506
190.0	.6419
200.0	.6333
210.0	.6247
220.0	.6163
230.0	.6080
240.0	.5999
250.0	.5919
260.0	.5840
270.0	.5763
280.0	.5687
290.0	.5613
300.0	.5540
310.0	.5469

Table 43: Continued

Temperature °C	Density gm/ml	Temperature °C	Density gm/ml
Ethanol		**Pentanol con't.**	
-10.0	.8043	100.0	.7520
.0	.7980	110.0	.7427
10.0	.7909	120.0	.7334
20.0	.7831	130.0	.7241
30.0	.7749	**Hexanol**	
40.0	.7663	50.0	.8007
50.0	.7574	60.0	.7938
60.0	.7483	70.0	.7862
70.0	.7391	80.0	.7781
Propanol		90.0	.7695
.0	.8107	100.0	.7607
10.0	.8045	110.0	.7516
20.0	.7974	120.0	.7425
30.0	.7897	130.0	.7332
40.0	.7815	140.0	.7239
50.0	.7729	150.0	.7146
60.0	.7641	**Heptanol**	
70.0	.7550	60.0	.7971
80.0	.7458	70.0	.7908
90.0	.7366	80.0	.7836
Butanol		90.0	.7757
20.0	.8062	100.0	.7674
30.0	.8002	110.0	.7587
40.0	.7933	120.0	.7498
50.0	.7856	130.0	.7407
60.0	.7774	140.0	.7315
70.0	.7687	150.0	.7222
80.0	.7596	160.0	.7129
90.0	.7503	170.0	.7036
100.0	.7409	**Octanol**	
110.0	.7314	70.0	.7926
Pentanol		80.0	.7865
30.0	.8079	90.0	.7795
40.0	.8016	100.0	.7718
50.0	.7946	110.0	.7637
60.0	.7868	120.0	.7551
70.0	.7786	130.0	.7463
80.0	.7700	140.0	.7373
90.0	.7611	150.0	.7282

C = 3.8072
D = .069556
E = -2.0470

F = -.026009
y = .20

Table 44: Density Predictions for the n-Alcohols

Temperature °C	Density gm/ml
Octanol con't.	
160.0	.7190
170.0	.7098
180.0	.7006
190.0	.6915
Nonanol	
80.0	.7893
90.0	.7825
100.0	.7751
110.0	.7671
120.0	.7588
130.0	.7503
140.0	.7415
150.0	.7326
160.0	.7237
170.0	.7147
180.0	.7057
190.0	.6968
200.0	.6879
210.0	.6791
Decanol	
100.0	.7754
110.0	.7686
120.0	.7611
130.0	.7532
140.0	.7450
150.0	.7364
160.0	.7277
170.0	.7188
180.0	.7099
190.0	.7010
200.0	.6921
210.0	.6833
220.0	.6745
230.0	.6658
Undecanol	
110.0	.7724
120.0	.7649
130.0	.7571
140.0	.7488
150.0	.7404
160.0	.7318
170.0	.7231
180.0	.7144

Temperature °C	Density gm/ml
Undecanol con't.	
190.0	.7056
200.0	.6968
210.0	.6881
220.0	.6795
230.0	.6709
240.0	.6625
Dodecanol	
120.0	.7634
130.0	.7560
140.0	.7482
150.0	.7401
160.0	.7318
170.0	.7234
180.0	.7149
190.0	.7064
200.0	.6979
210.0	.6894
220.0	.6809
230.0	.6725
240.0	.6642
250.0	.6560
260.0	.6479
Tridecanol	
130.0	.7588
140.0	.7515
150.0	.7438
160.0	.7359
170.0	.7277
180.0	.7194
190.0	.7110
200.0	.7025
210.0	.6941
220.0	.6856
230.0	.6772
240.0	.6689
250.0	.6607
260.0	.6525
270.0	.6444
Tetradecanol	
140.0	.7513
150.0	.7441
160.0	.7365
170.0	.7287

Table 44: Continued

Temperature °C	Density gm/ml
Tetradecanol con't.	
180.0	.7207
190.0	.7125
200.0	.7043
210.0	.6960
220.0	.6877
230.0	.6794
240.0	.6712
250.0	.6630
260.0	.6549
270.0	.6469
280.0	.6390
290.0	.6312
Pentadecanol	
150.0	.7436
160.0	.7365
170.0	.7291
180.0	.7214
190.0	.7135
200.0	.7055
210.0	.6974
220.0	.6893
230.0	.6812
240.0	.6730
250.0	.6650
260.0	.6570
270.0	.6490
280.0	.6412
290.0	.6334
300.0	.6257
Hexadecanol	
160.0	.7350
170.0	.7281
180.0	.7209
190.0	.7134
200.0	.7057
210.0	.6979
220.0	.6901
230.0	.6821
240.0	.6742
250.0	.6663
260.0	.6584
270.0	.6506
280.0	.6428

Temperature °C	Density gm/ml
Hexadecanol con't.	
290.0	.6351
300.0	.6275
310.0	.6200
Heptadecanol	
170.0	.7271
180.0	.7203
190.0	.7132
200.0	.7058
210.0	.6983
220.0	.6906
230.0	.6829
240.0	.6751
250.0	.6673
260.0	.6595
270.0	.6518
280.0	.6441
290.0	.6365
300.0	.6290
310.0	.6216
320.0	.6142
330.0	.6070
Octadecanol	
180.0	.7194
190.0	.7126
200.0	.7056
210.0	.6984
220.0	.6910
230.0	.6834
240.0	.6758
250.0	.6682
260.0	.6606
270.0	.6530
280.0	.6454
290.0	.6378
300.0	.6304
310.0	.6230
320.0	.6157
330.0	.6085
340.0	.6014

Table 44: Continued

Temperature °C	Density gm/ml
1-Chloropropane	
-40.0	.9448
-30.0	.9387
-20.0	.9310
-10.0	.9221
.0	.9123
10.0	.9018
20.0	.8908
30.0	.8795
40.0	.8678
1-Chlorobutane	
-20.0	.9215
-10.0	.9142
.0	.9057
10.0	.8963
20.0	.8863
30.0	.8757
40.0	.8647
50.0	.8535
60.0	.8420
70.0	.8306
1-Chloropentane	
.0	.9013
10.0	.8924
20.0	.8827
30.0	.8725
40.0	.8619
50.0	.8510
60.0	.8399
70.0	.8287
80.0	.8175
90.0	.8063
100.0	.7951
1-Chlorohexane	
10.0	.8874
20.0	.8788
30.0	.8693
40.0	.8593
50.0	.8488
60.0	.8380

Temperature °C	Density gm/ml
1-Chlorohexane con't.	
70.0	.8271
80.0	.8160
90.0	.8048
100.0	.7937
110.0	.7826
120.0	.7716
130.0	.7607
1-Chloroheptane	
30.0	.8669
40.0	.8572
50.0	.8469
60.0	.8363
70.0	.8255
80.0	.8145
90.0	.8035
100.0	.7924
110.0	.7814
120.0	.7704
130.0	.7596
140.0	.7489
150.0	.7383
160.0	.7278
1-Chloro-octane	
50.0	.8460
60.0	.8355
70.0	.8247
80.0	.8137
90.0	.8026
100.0	.7915
110.0	.7804
120.0	.7694
130.0	.7585
140.0	.7477
150.0	.7370
160.0	.7265
170.0	.7161
180.0	.7060

C = 1.3960
D = .080328
E = -.26550

F = -.015683
y = .55

Table 45: Density Predictions for the n-Alkyl Chlorides

Temperature °C	Density gm/ml
1-Chlorononane	
60.0	.8360
70.0	.8250
80.0	.8137
90.0	.8024
100.0	.7910
110.0	.7797
120.0	.7685
130.0	.7574
140.0	.7464
150.0	.7365
160.0	.7249
170.0	.7145
180.0	.7042
190.0	.6941
200.0	.6842
1-Chlorodecane	
80.0	.8150
90.0	.8032
100.0	.7915
110.0	.7798
120.0	.7682
130.0	.7568
140.0	.7455
150.0	.7344
160.0	.7235
170.0	.7128
180.0	.7023
190.0	.6920
200.0	.6819
210.0	.6721
220.0	.6625
1-Chloroundecane	
90.0	.8049
100.0	.7926
110.0	.7805
120.0	.7685
130.0	.7567
140.0	.7451
150.0	.7336
160.0	.7224
170.0	.7114
180.0	.7006
190.0	.6901

Temperature °C	Density gm/ml
1-Chloroundecane con't.	
200.0	.6798
210.0	.6697
220.0	.6599
230.0	.6502
240.0	.6408
1-Chlorododecane	
110.0	.7823
120.0	.7698
130.0	.7575
140.0	.7454
150.0	.7335
160.0	.7219
170.0	.7106
180.0	.6994
190.0	.6886
200.0	.6780
210.0	.6676
220.0	.6575
230.0	.6477
240.0	.6381
250.0	.6287
260.0	.6196
1-Chlorotridecane	
120.0	.7732
130.0	.7601
140.0	.7473
150.0	.7348
160.0	.7226
170.0	.7107
180.0	.6992
190.0	.6879
200.0	.6770
210.0	.6663
220.0	.6559
230.0	.6458
240.0	.6360
250.0	.6265
260.0	.6172
270.0	.6081
1-Chlorotetradecane	
140.0	.7483
150.0	.7353
160.0	.7227

Table 45: Continued

Temperature °C	Density gm/ml
1-Chlorotetradecane cont.	
170.0	.7104
180.0	.6984
190.0	.6868
200.0	.6754
210.0	.6644
220.0	.6536
230.0	.6432
240.0	.6330
250.0	.6232
260.0	.6135
270.0	.6042
280.0	.5951
290.0	.5863
1-Chloropentadecane	
150.0	.7375
160.0	.7240
170.0	.7110
180.0	.6984
190.0	.6862
200.0	.6743
210.0	.6628
220.0	.6517
230.0	.6409
240.0	.6305
250.0	.6203
260.0	.6105
270.0	.6009
280.0	.5917
290.0	.5827
300.0	.5739
310.0	.5654
1-Chlorohexadecane	
160.0	.7265
170.0	.7129
180.0	.6998
190.0	.6870
200.0	.6747
210.0	.6628
220.0	.6512
230.0	.6400
240.0	.6292
250.0	.6187
260.0	.6085

Temperature °C	Density gm/ml
1-Chlorohexadecane cont.	
270.0	.5986
280.0	.5891
290.0	.5798
300.0	.5708
310.0	.5620
320.0	.5535
1-Chloroheptadecane	
170.0	.7161
180.0	.7021
190.0	.6887
200.0	.6757
210.0	.6632
220.0	.6511
230.0	.6394
240.0	.6282
250.0	.6173
260.0	.6067
270.0	.5965
280.0	.5867
290.0	.5771
300.0	.5679
310.0	.5589
320.0	.5502
330.0	.5418
1-Chloro-octadecane	
180.0	.7045
190.0	.6903
200.0	.6767
210.0	.6636
220.0	.6510
230.0	.6388
240.0	.6271
250.0	.6158
260.0	.6049
270.0	.5944
280.0	.5842
290.0	.5743
300.0	.5648
310.0	.5556
320.0	.5467
330.0	.5380
340.0	.5297

Table 45: Continued

REFERENCES

1. Antoine, C., Comptes Rendus, vol. 107, 1888, pp. 681 and 836.

2. Barrall, E., S. Porter and J. Johnson, Analytical Chemistry, vol. 37, July 1965, pp. 1053-54.

3. Biddiscombe, D. P., R. R. Collerson, R. Handley, G. Harrington, J. F. Martin and C. Sprake, J. Chem. Soc., 1963, p. 1954.

4. Brunel, R. F., J. L. Crenshaw and E. Tobin, J. Am. Chem. Soc., vol. 43, 1921, p. 561.

5. Butler, J., C. N. Ramchandani and D. Thompson, J. Chem. Soc., vol. 138, 1935, p. 280.

6. Calingaert, G., H. A. Beatty, R. C. Kuder and G. W. Thompson, Ind. Eng. Chem., vol. 33, 1941, p. 103.

7. Calingaert, G. and J. W. Hladky, J. Am. Chem. Soc., vol. 58, 1936, p. 153.

8. Carley, J. F. and L. W. Bertelsen, Ind. Eng. Chem., vol. 41, 1949, p. 2806.

9. Chipman, J., J. Phys. Chem., vol. 33, 1929, p. 1131.

10. Chiu, J., Analytical Chemistry, vol. 27, 1955, p. 1102.

11. Chu, J. C., M. Dmytryszyn, J. Moder and R. Overbeck, Ind. Eng. Chem., vol. 41, 1949, pp. 131-5.

12. Debye, P., Ann. d. Physik, vol. IV - 39, 1912, p. 789.

13. Dreisbach, R. R., Ind. Eng. Chem., vol. 41, 1949.

14. Dreisbach, R. R. and R. A. Martin, Ind. Eng. Chem., vol. 41, 1949, p. 2879.

15. Dreisbach, R. R. and S. A. Shrader, Ind. Eng. Chem., vol. 41, 1949.

16. Egloff, G. and R. C. Kuder, J. Phys. Chem., vol. 45, 1941, pp. 836-45.

17. Feurstein, Erwin, Masters Thesis, Newark College of Engineering, 1964.

18. Fishtine, S. H., Ind. Eng. Chem., vol. 55, 1963.

19. Flory, Paul J., J. Chem. Phys., vol. 10, 1942, pp. 51-61.

20. Francis, A. W., Ind. Eng. Chem., vol. 33, 1941, p. 554.

21. Francis, A. W., Ind. Eng. Chem., vol. 49, 1957.

22. Francis, A. W., Ind. Eng. Chem., vol. 49, 1957, pp. 1787-8.

23. Frenkel, J., Kinetic Theory of Gases and Liquids. New York: Dover Publications, Inc., 1946.

24. Frost and Kalkwarf, J. Chem. Phys., vol. 21, 1953, pp. 264-67.

25. Glasstone, Samuel, Textbook of Physical Chemistry. New York: D. Van Nostrand Co., Inc., 1946, p. 496.

26. Gorden, D. H., Ind. Eng. Chem., vol. 35, 1943, pp. 851-3.

27. Greenshields, J. B. and F. D. Rossini, J. Phys. Chem., vol. 62, 1958, p. 271.

28. Gutmann, F. and L. Simmons, J. Chem. Phys., vol. 18, 1950.

29. Haggenmacher, J. E., Ind. Eng. Chem., vol. 40, 1948, pp. 436-7.

30. Handbook of Chemistry and Physics. Cleveland, Ohio: Chemical Rubber Publishing Co., Fortieth Ed.

31. Hirschfelder, J. O., C. F. Curtiss and R. B. Bird, Molecular Theory of Gases and Liquids. New York: John Wiley & Sons, Inc., 1954.

32. Hovorka, F., H. P. Lankelma and S. C. Stanford, J. Am. Chem. Soc., vol. 60, 1938, p. 820.

33. Kemme, H. R., The Determination of Boiling Points by Differential Thermal Analysis, Masters Thesis, Newark College of Engineering, 1963.

34. Kistiakowsky, W., Z. Physik. Chem., vol. 65, 1923, p. 107.

35. Krawetz, A. A. and T. Tovrog, Rev. Sci. Inst., vol. 33, 1962, p. 1465.

36. Kreglewski, B. and B. J. Zwolinski, J. Phys. Chem., vol. 65, 1961, pp. 1050-2.

37. Kurata, M. and S. Isida, J. Chem. Phys., vol. 23, 1955, pp. 1126-31.

38. Kurtz, S. S. and A. Sankin, Ind. Eng. Chem., vol. 46, 1954, p. 2186.

39. Lee, J., F. Sears and D. Turcotte, Statistical Thermodynamics. Reading, Mass.: Addison-Wesley Pub. Co. Inc., 1963, pp. 73-75.

40. Lenth, C. W., J. Am. Chem. Soc., vol. 55, 1933, p.3283.

41. Lewis, G. N. and M. Randall, Revised by K. S. Pitzer and L. Brewer, Thermodynamics. New York: McGraw-Hill Book Co., 1961.

42. Li, C. M. J. and F. Rossini, J. Chem. Eng. Data, vol. 6, 1961, pp. 268-270.

43. Li, K., R. Arnett, M. Epstein, R. Ries, L. Bitler, J. Lynch and F. Rossini, J. Phys. Chem., vol. 60, 1956, pp. 1400-6.

44. Marcus, J., J. Chem. Phys., vol. 26, 1957, pp. 1765-6.

45. McCurdy, C. and K. Laidler, Can. J. Chem., vol. 41, 1963, pp. 1867-71.

46. Meisner, H. P. and O. H. Paddison, Ind. Eng. Chem., vol. 33, 1941, pp. 1189-91.

47. Miller, A. A., J. Phys. Chem., vol. 68, 1964, pp. 3900-02.

48. Nakanishi, K., M. Kurata and M. Tamora, J. Chem. Eng. Data, vol. 5, 1960, pp. 210-19.

49. Osborne, N. S. and C. H. Meyers, J. Rsch. Natl. Bur. Stds., vol. 13, 1934, pp. 1-20.

50. Othmer, F. D. and H. Huang, Ind. Eng. Chem., vol. 57, 1965, pp. 42-48.

51. Parkell, personal communication. E. I. DuPont de Nemours and Co., Del.

52. Partington, J., An Advanced Treatise on Physical Chemistry, vol. 1. London: Longmans, Green and Co., Ltd., 1949.

53. Pratap, R. and G. Narsimhan, Brit. Chem. Eng., vol. 7, 1962, pp. 757-9.

54. Reid, R. C. and T. K. Sherwood, The Properties of Gases and Liquids. New York: McGraw-Hill Book Co., Inc., 1958.

55. Rose, A., B. T. Papakronis and E. Williams, Chem. Eng. Data, vol. 3, 1958, p. 216.

56. Rose, A. and W. R. Supina, J. Chem. Eng. Data, vol. 6, 1961, p. 173.

57. Rossini, Frederick D., Selected Values of Physical Properties and Related Compounds. Pittsburgh, Pa.: Carnegie Press, 1953.

58. Smyth, C. P. and E. W. Engel, J. Am. Chem. Soc., vol. 51, 1929, p. 2646.

59. Steward, G. W., Phys. Rev., vol. 35, 1930, pp. 296 and 726.

60. Temporary Operating Manual for DuPont 900 Differential Thermal Analyzer. E. I. DuPont de Nemours and Co., Wilmington, Del., 1962.

61. Tetrode, H., Physik. Zeits., vol. 14, 1913, p. 212.

62. Thompson, G. W., Chem. Rev., vol. 38, 1946, pp. 1-39.

63. Timmerman, J., Physico Chemical Constants of Pure Organic Compounds.

64. Vassallo, D. A. and J. C. Harden, Analytical Chem., vol. 34, 1962, pp. 132-35.

65. Verkada, P. E. and J. Coops Jr., Rec. Trav. Chim., vol. 46, 1927, p. 903.

66. Volk, William, Applied Statistics for Engineers. New York: McGraw-Hill Book Co., 1958.

67. Wall, F. T., J. Chem. Phys., vol. 16, 1948, p. 508.

68. Waring, C. E. and P. Becker, J. Chem. Phys., vol. 16, 1947, p. 488.

69. Weissberger, A., Technique of Organic Chemistry, vol. I, Part I. New York: Interscience Publishers Inc., 1959, pp. 434-51.

70. Willingham, C. B., W. J. Taylor, J. M. Pignocco and F. D. Rossini, J. Rsch. Natl. Bur. Stds., vol. 35, 1945, p. 219.

71. Winslow, D. H., A Correlation of Vapor Pressure, Temperature and Carbon Numbers of Homologous Series. Masters Thesis, Newark College of Engineering, 1965.

VITA

Herbert R. Kemme was awarded the degree of Bachelor of Science in Chemical Engineering from Newark College of Engineering in 1962. That year he received a three year grant through the National Defense and Education Act for Doctoral studies at the same institution. In 1963 he was granted the degree of Master of Science in Chemical Engineering.

His experience includes summers spent as a chemical engineer at Colgate-Palmolive Co. in Jersey City, N. J. and Marbon Chemical Co. in Parkersburg, West Virginia. Presently he is employed by the American Cyanamid Company in Bound Brook, N. J. as a Chemical Research Engineer in Process Development.