

VAPOR PRESSURE OF SELECTED PURE  
MATERIALS AND MIXTURES

By

BELIED SALEH KUWAIRI

Bachelor of Science  
University of Southern California  
Los Angeles, California  
1976

Master of Science  
Oklahoma State University  
Stillwater, Oklahoma  
1980

Submitted to the Faculty of the Graduate College  
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Thesis Approved:

*G. N. Maddox*

Thesis Adviser

*J. P. ...*  
*Thurmond Bell*

*Al Hines*

*Norman N. Durbin*

Dean of the Graduate College

## PREFACE

An apparatus for measuring vapor pressure of pure compounds and mixtures was modified to improve its accuracy and consistency. Measurements of vapor pressures, over the range above about room temperature to 260°C, and 3 to 670 KPa, were made on 17 pure compounds and two mixtures.

The experimental data were correlated with the three-constant Antoine equation for vapor pressure. Experimental data, together with the values of the three constants of the Antoine equation, are reported for all compounds and mixtures.

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## CHAPTER I

### INTRODUCTION

Vapor pressure is an important thermophysical property needed in carrying out many scientific and engineering analyses. Review of the published literature reveals that most vapor pressure data reported are incomplete in the sense that they do not cover all ranges of temperatures and pressures. Also, they are generally available only for low molecular-weight compounds. Vapor pressure data for hydrocarbons containing heteroatoms are often unavailable for even lower molecular-weight compounds.

This study was undertaken to generate experimental vapor pressure measurements on pure materials and mixtures with special emphasis on those relating to gas-sweetening technology.

New modifications were made on the apparatus used in this work, and on its operation, which have resulted in noticeable improvement in its accuracy and consistency.

In addition to the usual graphical representation each set of data was fitted to the three-constant Antoine equation for vapor pressures.

## CHAPTER II

### LITERATURE SURVEY

In industrial process design, the need arises for accurate estimates of the heat and work requirements. These quantities are usually calculated from characteristic thermodynamic properties, such as internal energy and enthalpy, which are not directly measurable. For fluids in equilibrium states. These properties can be expressed as functions of measurable parameters such as temperature, volume, and pressure.

When the solid phase of a pure substance is in thermodynamic equilibrium with its vapor phase, the system is univariant and measurements of the vapor pressure of a pure solid at various-temperatures up to the melting point traverse the sublimation curve. Also, measurements of the vapor pressure of a pure liquid as a function of temperature up to the critical point traverse the vaporization curve. In this work, all measurements of vapor pressure were made along the vaporization line which separates the liquid and gas regions.

This survey covers two areas of vapor pressure research; general methods for measurement of vapor pressure; and vapor pressure-temperature relations.

## General Methods for Measurement of Vapor Pressure

Partington (45), Weissberger (61), and Weissberger et al. (62) present comprehensive summaries of the various methods for experimental determination of vapor pressures. The main methods are discussed below.

### Static Methods

Static methods for the determination of vapor pressure measure directly the pressure exerted by the vapor in equilibrium with the liquid under investigation. The pressure can be measured directly as the depression of the mercury in one of two barometric tubes, caused by the vapor of the substance placed in the Torricellian vacuum of one of the tubes. The mercury must be boiled out and the substance degassed to eliminate the effect of impurities (53).

The Smith-Menzies isoteniscope (53) was designed to avoid many of the disadvantages encountered in the static methods. The original design consists of a small bulb with a short U-tube attached. The liquid is placed in the bulb, and some liquid is placed in the U-tube. At a given temperature the external pressure is adjusted till the levels of liquid in the U-tube are at the same height, which indicates that the vapor pressure at the liquid in the bulb is equal to the external pressure. Booth et al. (8) introduced a modification to the original design of the isoteniscope by adding a small reservoir above the arm of the U-tube connected to the system. The mercury was stored in the reservoir to allow the liquid to be placed in the bulb and degassed. By tilting the isoteniscope mercury is allowed to return to the U-tube. The use of mercury, instead of the liquids under test, is one of the

most attractive features of the method, since all organic liquids have lower specific gravity. Use of the isoteniscope ensures the removal of adsorbed and dissolved gases and the more volatile impurities, but higher boiling impurities and decomposition products can not be removed.

Jones et al. (33) reported vapor pressure measurements for nitromethane placed in an insulated calorimeter under vacuum to maintain constant temperature. The apparatus was connected to a manometer to measure vapor pressures below room temperature due to lack of protection against condensation of vapors. A static method to measure vapor pressures of a number of polyethylene glycols and some of their derivatives was reported by Gallagher et al. (26). A network of mercury manometers at room temperature was connected to a differential manometer immersed in the same bath as the bulb which contained the sample. The same workers (27) outlined a method for purifying the sample consisting of vacuum distillation followed by shaking the samples in the presence of activated anhydrous alumina, and allowing the mixture to stand for two days. Finally, each product was distilled twice under reduced pressure. Thermal decomposition of most of the compounds studied was observed. Ethylene glycol had the highest rate of decomposition followed by tetraethylene, triethylene, and diethylene glycols. A bellows-type differential manometer was used by Allen et al. (3) for measurement of the vapor pressure of benzene from 0° to 80°C.

Buckler et al. (10) reported vapor pressure values for purified samples of tetraethyl-lead using a Bourdon gauge maintained at 80°C via a hot-air jacket to protect against condensation of vapors. Experimental values of vapor pressure for 15 hydrocarbons were obtained by Osborn et al. (44), in the range of 0.1 - 25 mm-Hg by means of a

method with an inclined-piston dead weight gage.

Examples of other total pressure devices which have been used in relation to the static method are radiation manometers, Knudsen "absolute manometers", mass spectrometers, vapor ionization gage, and the McLeod gage.

Carruth et al. (11) stated that static methods are not suited for low pressures and/or low temperatures, for several reasons. Because of wall adsorption at cryogenic temperatures, high-purity test samples are required. The thermal transpiration effect (40), which occurs when the measuring device and the equilibrated vapor are not at the same temperature. Correction for this effect (41) requires specific data for each vapor studied. Also, problems of cleanliness of the confining wall and the requirement of careful calibration with respect to each pressure-measuring device and the particular compound being tested.

#### Boiling-point Methods

The boiling-point methods are dynamic in nature and involve boiling and condensing the sample at a definite external pressure. The temperature of the vapor in equilibrium with the boiling liquid is measured.

Ramsay and Young's apparatus (46) was designed in such a way that the liquid was allowed to trickle on to a thermometer bulb covered with a thin layer of absorbent cotton or similar material. The thermometer was placed in a flask immersed in a heating bath. The apparatus was first evacuated and the bath brought to about 15°C above the value read on the thermometer. A little air is admitted and enough liquid is allowed to enter such that the cotton is wetted. The temperature and pressure were read as soon as they became constant. This method has

the advantage that the presence of air and traces of moisture do not affect the results.

Hoover et al. (31) devised a semimicroebulliometer which was used to measure vapor pressures of some amino acids in the range of 3 to 100 mmHg. The design was based on Cottrell (14) idea of utilizing the vapor-lift pump for determination of the boiling point of solutions. The accuracy is estimated to be  $\pm 0.5^{\circ}\text{C}$  in boiling point at a given pressure using a mercury thermometer.

Willingham and co-workers (63) designed a specific boiler with a valve for accurate control of the reflux ratio. The apparatus was connected to a mercury manometer with electrical contacts maintaining the pressure constant at 20 fixed points which were calibrated with water. Vapor pressure measurements were made on 52 purified hydrocarbons over the range 47 to 780 mmHg with an estimated error of 0.02 to 0.05 mmHg.

The boiling-point methods in general are useful in measuring relatively higher vapor pressures. The precise detection of incipient boiling and prevention of superheating are considered to be the major disadvantages of such methods.

#### The Effusion Method

The effusion methods are based on the effusion rate of the vaporized substance from a surface, or through an orifice.

Knudsen's method was thoroughly described and discussed in numerous publications (45, 60, 61), as being the first application of the effusion principle to vapor pressure measurements. The apparatus

consisted of a small box containing the sample and covered with a lid through which an orifice with known diameter was drilled. The box was placed in a wide tube connected to a cold trap and high vacuum and immersed in a thermostat. The tube was then evacuated and the loss in weight of the box was measured. The vapor pressure of the substance was related to the known and measured parameters of the system.

The major applications of this method have been the measurements of vapor pressure via electrically heated filaments of metals such as molybdenum, platinum, and tungsten by Langmuir (37) and Langmuir and Mackay (38). Similarly, the vapor pressure of some organic crystals was measured by Swan et al. (55).

Many modified versions of Knudsen's method were made by many investigators to avert some of the flaws associated with it. The breaking of the vacuum at intervals, orifice geometry, and the assumption that the mean free path must be at least an order of magnitude larger than the dimensions of the orifice, are the major problems of the effusion method.

#### Gas-Saturation Method

In this method, a stream of an inert gas is passed at a slow rate through or over the substance such that equilibrium saturation is achieved. The vapor pressure of the material at the temperature of the system can be computed by knowing the weight of material vaporized and applying Dalton's law.

Gerry et al. (28) outlined a method for the calculation of vapor pressures by this method using the Beattie-Bridgeman equation of state.



Recently, Carruth et al. (11), reported experimental measurements of the vapor pressures of the normal paraffins ethane through n-decane from the triple point to 10 mmHg using a steady-state gas-saturation technique. The virial equation truncated after the third virial coefficient was used for calculations. Baxter and co-workers (4, 5, 6, 7) reported vapor pressure measurements on hydrated salts and other chemicals using the gas-saturation method.

The accuracy of experimental data obtained by the gas-saturation method can be improved by attaining a slow flow-rate of the inert gas to achieve saturation and by developing better techniques for determining how much material has been vaporized. Also, the selection of an equation of state which can predict the vapor-liquid equilibrium properties can improve the calculation aspect of the method.

#### Vapor Pressure-Temperature Relations

Many different vapor pressure-temperature relationships have been presented by researchers in this field. The need for interpolating and extrapolating data for use in thermodynamic calculations has necessitated a constant search for simpler and more precise representations of experimental data. In this section, emphasis is placed on the most widely accepted and used relations.

When equilibrium is attained between the vapor phase of a pure fluid and its liquid phase, the equality of chemical potential, temperature, and pressure in both phases leads to the Clausius-Clapeyron equation;

$$\frac{dP}{dT} = \frac{\Delta H_v}{T\Delta V} = \frac{\Delta H_v}{T(V_g - V_l)} \quad (1)$$

where  $P$  = vapor pressure of liquid.

$t$  = temperature.

$T$  = absolute temperature.

$\Delta H_v$  = heat of vaporization.

$\Delta V$  = change in volume upon vaporization.

$V_g$  = molecular volume of vapor.

$V_l$  = molecular volume of liquid.

Assuming that the quotient " $\Delta H_v/\Delta V$ " is constant over the range of temperature considered. Equation (1) can be integrated to give the most familiar vapor-pressure relation:

$$\text{Log}P = A - B/T \quad (2)$$

where  $A$  = constant of integration.

$B$  = constant equal to  $\Delta H/\Delta V$

Constants  $A$  and  $B$  can be determined either by graphical or linear-regression techniques.

Equation (2) is simple to use, but it is accurate only over small temperature ranges. When  $\text{Log}P$  is plotted against  $1/T$ , the data are almost always curved and not a straight line as predicted by equation (2).

The Antoine equation is considered to be the most successful and simple equation for representing the vapor pressure-temperature interdependence;

$$\text{Log}P = A - \frac{B}{T+C} \quad (3)$$

where  $A$ ,  $B$ ,  $C$  = empirical constants.

An excellent review of the Antoine equation was given by Thomson (57) including methods of evaluating the empirical constants. Thomson

suggested the use of two Antoine equations, one up to a reduced temperature of 0.75, the other from that point to the critical point. This came about because of the observed inadequacy of the Antoine equation for data close to the critical region.

An extensive literature search was made for all vapor pressure data of normal aliphatic hydrocarbons by Thodos (56). He reported that the plot of  $\log P$  vs  $1/T$  was characterized by an elongated S shaped curve whose upper inflection point corresponds almost to the same point observed earlier by Thomson. Waring (60) arrived at the same observations on mathematical grounds. He also proved that the Antoine equation can not predict the inflection point.

Simmons et al. (52), derived the Antoine equation from the Van Der Waals equation of state, and the energy of Einstein oscillators. The values of the empirical constant  $C$  was found to be related to the characteristic frequency of the liquid.

Cox (15) proposed an equation in a form of a simple modification of equation (2), to represent vapor pressure over the complete range between the triple and critical points. This equation is of the form:

$$\log P = A \left( 1 - \frac{T_B}{T} \right) \quad (4)$$

where;

$$\log A = \log A_c + E \left( 1 - T_R \right) \left( F - T_R \right) \quad (5)$$

$$A_c = T_c \frac{\log P_c}{T_c - T_B}$$

$$T_R = T/T_c$$

$$T_B = \text{absolute boiling point.}$$

$$T_c = \text{absolute critical temperature.}$$

$P_C$  = critical pressure.

$T_R$  = reduced temperature.

E and F are characteristic of the compound. F was found to be 0.85 for all hydrocarbons and E was correlated by Cox with the boiling point as:

$$E = 0.0008 T_B - 0.01895 \quad (7)$$

Equation (4) can predict and follow the change in curvature of the  $\text{Log}P$  vs.  $1/T$  plot, and can extrapolate to low pressures with good accuracy (62). The need for a good experimental normal boiling point is the main drawback of the Cox equation.

Frost and Kalkwarf (25) derived a semi-empirical equation for the vapor pressure of liquids as a function of temperature. They based their derivation on the assumptions that  $\Delta H_V$  is a linear function of temperature and that the Van Der Waals  $a/V^2$  term is a first approximation to the deviation from ideal. The equation takes the form:

$$\text{Log } P = A + \frac{B}{T} + C \log T + D \frac{P}{T^2} \quad (8)$$

where  $D = a/2.303 R^2$

$a$  = Van der Waals constant

$A, B, C$  = empirical constants.

Equation 8 is capable of reproducing experimental vapor pressure data from the triple point to the critical point with a reported average deviation of 0.3% (25). The presence of  $P$  on both sides of the equation is considered to be its main disadvantage. The solution has to be carried out by successive approximation.

Since most of the experimental data obtained in this work were well below the critical region. The Antoine equation was selected to represent the data over other methods for reasons of simplicity and brevity.

## CHAPTER III

### EXPERIMENTAL APPARATUS

The original design of the experimental apparatus employed in this work was reported by Diab (17). He reported an average deviation of 4% between his measurements and published values.

In an attempt to improve the accuracy and to extend the use of the apparatus to sub-atmospheric ranges, Kuwairi (36), made modifications in the design of the sample cell and the pressure gauges.

In this work, further modifications were made in the design of the apparatus and in the experimental procedure to improve its accuracy and consistency. An overall schematic diagram of the newly modified version of the apparatus is shown in Figure 1. The major parts as follows:

#### Constant Temperature Bath

A cylindrically shaped bath (model No. 1 NB-3329) made in West Germany by Colora Company, was used. It is equipped with a built-in electric stirrer, with a thermostat and with a variable wattage immersion type electric heater. It has a capacity of 3.5 gallons. The thermal fluid is silicone oil SF-96 which has a flash point of about 570°F. This oil is a product of General Electric Company.

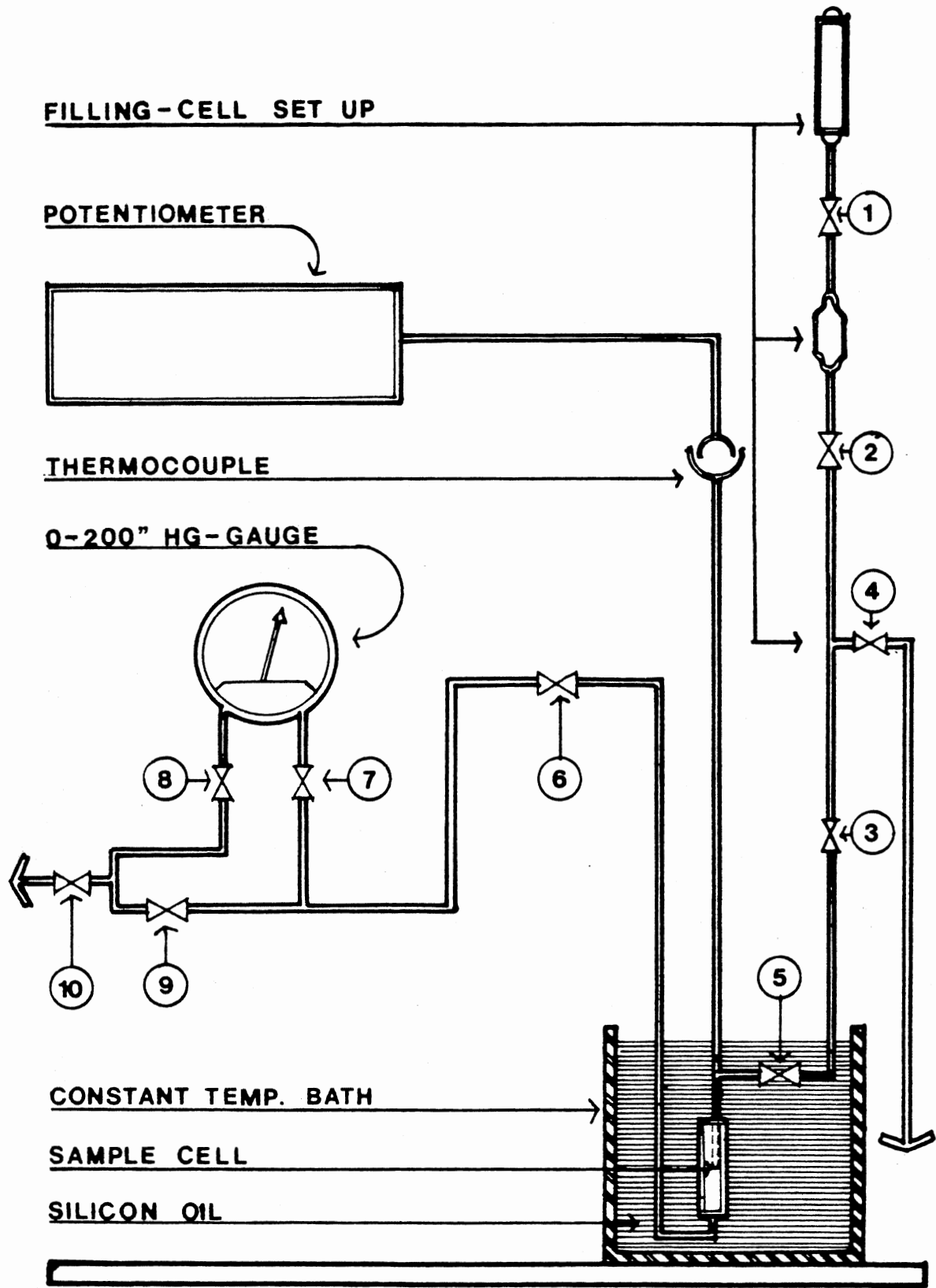


Figure 1. Overall Schematic Diagram of the Newly Modified Design

### Potentiometer

A millivolt potentiometer (model No. 8686), made by Leeds and Northrup Company was employed for temperature measurements. It has a range of -10.0 to 100.1 millivolts with the smallest division being equal to 0.005 millivolts. Its' limits of error are  $\pm 0.03\%$  of reading  $+6 \mu\text{v}$ .

### Vacuum Pump

The Duo-Seal vacuum pump (model No. 1400-W-01) was made by W. M. Welch Scientific Company of Chicago. Its' free air displacement was estimated to be 25 liter per minute. This particular model is equipped with an explosion proof motor (1/3 Hp and 1725 rpm). The guaranteed pressure by the manufacturer is 0.0001 Torr.

### Sample Cell and Thermocouple

A stainless steel sample cell (model No. 2HD30), made by Hoke Company was used. It has a capacity of 33.3 cc. A 3 way junction was installed on the top end of the cell, through which a chromel-alumel type K thermocouple and the filling-cell set up were fixed. The thermocouple was made by Omega Engineering Inc. of Connecticut.

### Filling Cell Set Up

This portion of the apparatus was designed to control the process of degassing the sample by alternate freezing and thawing under vacuum. It consisted of a stainless steel cylinder (DOT3E1800) made by Parker C. P. I., which has a capacity of 150 cc. The cylinder was closed at one end and connected at the other end to a 50 cc glass bulb.

The other end of the bulb was connected to the rest of the system as shown in Figure 1.

#### Pressure Gauge

One pressure gauge was used for all the pressure measurements made in this work. It is "Wallace and Tiernan" 0-200 in. Hg, 0°C differential gauge (series 1000, serial No. LL04510), with 0.2 in. Hg subdivision. The diameter of the dial is 8 1/2 inches with two revolutions (0-100 and 100-200 in.Hg). The gauge has a sensitivity and an accuracy of 0.03 and 0.1% of full scale respectively. The case is kept under vacuum by a valve connected to the vacuum line of the system.

The materials tested, their purities and suppliers are listed in Table I.



TABLE I  
TEST MATERIAL SPECIFICATION

Material	Supplier	Min. Purity (Mol. Percent)
N-Hexane	Phillips Petroleum Co.	99.00
2-Butanone	Aldrich Chem. Inc.	99.00
N-Propyl Acetate	Aldrich Chem. Inc.	N.S.
cyclo Hexanol	Aldrich Chem. Inc.	99.00
3-Pentanone	Aldrich Chem. Inc.	99.00
N, N-Dimethylformamide	Aldrich Chem. Inc.	99.00
Methyl Cyanacetate	Aldrich Chem. Inc.	97.00
Propylene Carbonate	Aldrich Chem. Inc.	99.00
1, 2-Butanediol	Aldrich Chem. Inc.	98.00
1, 3-Propanediol	Aldrich Chem. Inc.	98.00
1, 4-Butanediol	Aldrich Chem. Inc.	99.00
Diethylene Glycol	Alfa Products	99.00
Tripropylene Glycol	Alfa Products	N.S.
N-Methyl Pyrrolidinone	Aldrich Chem. Inc.	98.00
1, 5-Pentanediol	Aldrich Chem. Inc.	99.00
Selexol	Eastman Kodak	N.S.
Glutaronitrile	Aldrich Chem. Inc.	99.00
Methyldiethanolamine	Aldrich Chem. Inc.	97.00

N.S. - not specified.

## CHAPTER IV

### EXPERIMENTAL PROCEDURE

This chapter is subdivided into two sections; (1) Calibration of the measuring equipment; (2) Operation of the experimental apparatus.

#### Calibration of the Measuring Equipment

##### Pressure Gauge Calibration

The Wallace and Tiernan gauge calibrated against primary pneumatic piston gauge certified by the National Bureau of Standards (N.B.S.). Calibration data are tabulated in Table XXVII, Appendix C. The following quadratic equation was calculated which relates the fitted pressure in K-Pa to the indicated pressure in In.Hg:

$$P_{FIT}(\text{K-Pa}) = 0.0972 + 3.3899 * P_{IND}(\text{IN.Hg}) - 2.4895 \times 10^{-5} * P_{IND}^2(\text{IN.Hg})$$

The average absolute percent deviation (A.A.P.D.) between calculated values by this equation and the actual values is 0.06%.

##### Thermocouple Calibration

One chromel-alumel thermocouple was used for all temperature measurements. It was calibrated against a platinum. 10% rhodium

thermocouple calibrated by N.B.S. (Test No. 201293). The millivolt potentiometer described in Chapter III, was used in this calibration. Both thermocouples were referenced to the same ice junction. Calibration data are tabulated in Table XXVII, Appendix C. The following quadratic equation relates the fitted temperature in C° to the indicated temperature in °C:

$$T_{\text{FIT}} (\text{°C}) = -0.3567 + 1.00006 T_{\text{IND}} (\text{°C}) + 9.1631 \times 10^{-6} T_{\text{IND}}^2 (\text{°C})$$

The A.A.P.D. of calculated values by this equation from the actual values is 0.29%. Also, the residuals were plotted as a function of the potentiometer readings in MV., and straight lines were drawn connecting all points. This was done to estimate corrections to the calibration equation.

#### Operation of the Experimental Apparatus

As shown in Figure 1, all values have been assigned numbers to simplify the presentation of this section. The experimental operation of the apparatus consists of four distinct steps; (1) cleaning the system; (2) preparing the sample; (3) charging the sample to the system; (4) gathering the experimental data.

#### Cleaning the System

Clean apparatus is achieved by purging the system under vacuum with acetone four times, followed each time by passing dry air to drive out most of the acetone vapors in the system making sure that the air pressure does not exceed the maximum pressure of the gauge. The system

was vacuumed for at least 10 minutes after the end of each wash.

### Preparing the Sample

The cylinder in the "filling-cell set up" was washed and dried thoroughly. It was filled with about a 125 cc portion of the sample, and placed in an ice bath.

The cylinder was connected to the vacuum line through valve No. 1, for about 1 hr till the sample was frozen. This was followed by thawing the sample under vacuum by placing the cylinder in a heating bath for about 15 minutes. The same procedure was repeated two times to make sure that the sample was degassed and the moisture was also vaporized. Approximately, half of the sample in the cylinder was vaporized in the process. This was recovered by condensation in the cold traps.

Valve 1 was closed and the cylinder was reinstalled back into the apparatus under vacuum.

### Charging the Sample to the System

Valves 1 and 4 were closed, while valves 2, 3, 5, 6, 7, 8, 9 and 10 were opened. The vacuum line was connected through valve 10 to exhaust the system continuously, for about 10 hours.

Valve 10 was closed and the vacuum line was connected to vacuum the system again through valve 4 which was opened minutes later, for another 10 hours.

Valves 4, 8, and 10 were closed and the vacuum line was disconnected leaving the system idle for about 30 minutes to make sure that no

leaks exist which would be indicated by steady deflection of the gauge pointer from the zero reading.

Valves 2, 3, and 9 were closed, and valve 1 was opened to allow the sample to fill the glass bulb. Valve 1 was closed while valves 2 and 3 were opened to allow a portion of the sample in the glass-bulb to slowly charge into the sample cell, under its own weight. When about 30 cc of the sample was charged, valves 2, 3 and 5 were all tightly closed.

#### Gathering the Experimental Data

The thermostat was set to an initial setting and the electric heater and stirrer were turned on. After the bath temperature and the pressure readings were stable for about 30 minutes, the potentiometer and gauge readings were taken. Using the calibration equations, the actual temperatures and the corresponding vapor pressures were calculated.

A plot of  $\log P$  vs.  $1/T$  was found useful in detecting sudden changes in pressure measurements which may be due to leaks or possible thermal decomposition of the sample.

## CHAPTER V

### EXPERIMENTAL RESULTS

The experimental vapor pressure data for n-hexane, 2-butanone, n-propylacetate, and cyclohexanol are plotted in Figure 2, and tabulated in Tables VII, VIII, IX, and X of Appendix A. An absolute average percent deviation (A.A.P.D.) of 0.82% was obtained for n-hexane data in comparison to values calculated from data reported by the A.P.I. (50). The vapor pressures of 2-butanone were compared to calculated data reported by Reid et al. (47), some of which were extrapolated above their reported maximum temperature of 376°K. An A.A.P.D. of 1.16% was obtained. The experimental data for n-propylacetate came with an A.A.P.D. of 1.74% when compared to values calculated from data reported by Timmermans (58). The vapor pressures of cyclo-hexanol were compared to values calculated from data reported by Riddik et al. (48). An A.A.P.D. of 2.12% was obtained between them. Some of the reported data points were extrapolated above the boiling point which was the maximum temperature for the data.

The measurements of vapor pressure obtained in this work, for 3-pentanone, n, n-dimethylformamide, methylcyanoacetate, and propylenecarbonate are plotted in Figure 3, and tabulated in Tables XI, XII, XIII, and XIV of Appendix A. A comparison between the experimental data obtained for 3-pentanone and calculated values

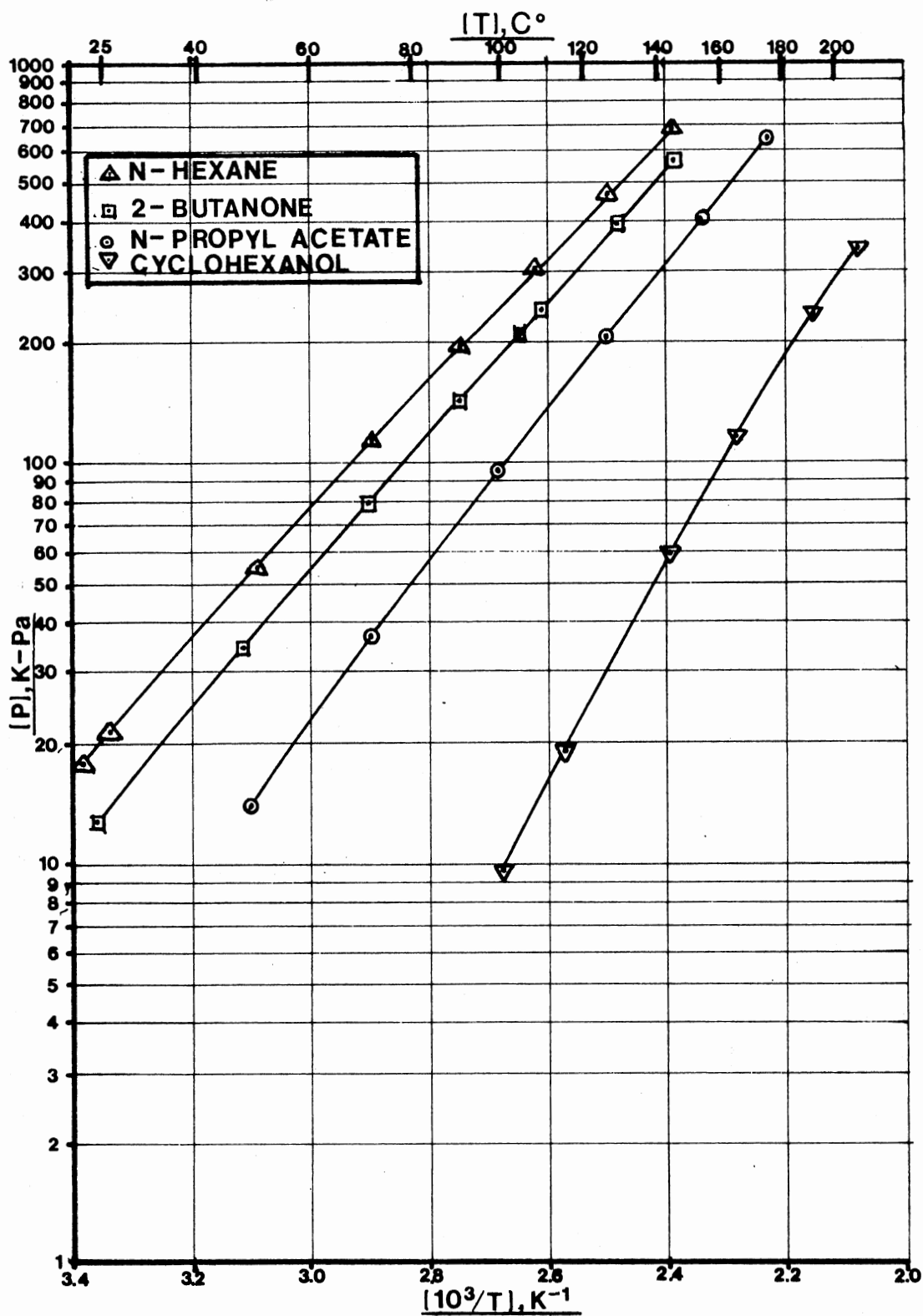


Figure 2. Vapor Pressure of N-Hexane, 2-Butanone, N-Propyl Acetate, and Cyclohexanol

from reported data by Reid et al. (47), gave an A.A.P.D. of 1.66%. Propylene carbonate showed thermal decomposition at approximately 215°C which was indicated by a steady increase of pressure, while the temperature was kept constant. Vapor pressure data for dimethylformamide were compared to data reported in a form of Antoine equation constants by Riddik et al. (48). An A.A.P.D. of 5.01% was obtained. A graphical comparison between the two is given in Figure 4. It shows that the experimental data of this work are lower than the reported values at low temperatures - and higher at high temperatures. Two runs were carried out in the low and high temperature ranges (i.e., below and above the boiling point) for new samples of N, N-dimethylformamide. The two sets of data are given in Tables II, and III and are compared to calculated values from the Antoine equation constants which were obtained by fitting data of the first run covering the whole temperature range. The comparisons show excellent reproducibility of N, N-dimethylformamide data for both ranges of temperatures. N, N-dimethylformamide is a hygroscopic liquid having high water pick-up even at low relative humidities (17). But, the methods of cleaning the system and preparing the sample for measurement employed in this work were designed to eliminate most of the impurities including water. This author was unable to determine the temperature-range and method employed in the measurement of the reported data.

The vapor pressure data gathered in this work for 1, 2-butanediol, 3-propanediol, 1, 4-butanediol, diethylene glycol (DEG) and tripropylene glycol, are plotted in Figure 5, and tabulated in Tables XV, XVI, XVII, XVIII, and XIX of Appendix A. The vapor pressure of 1,



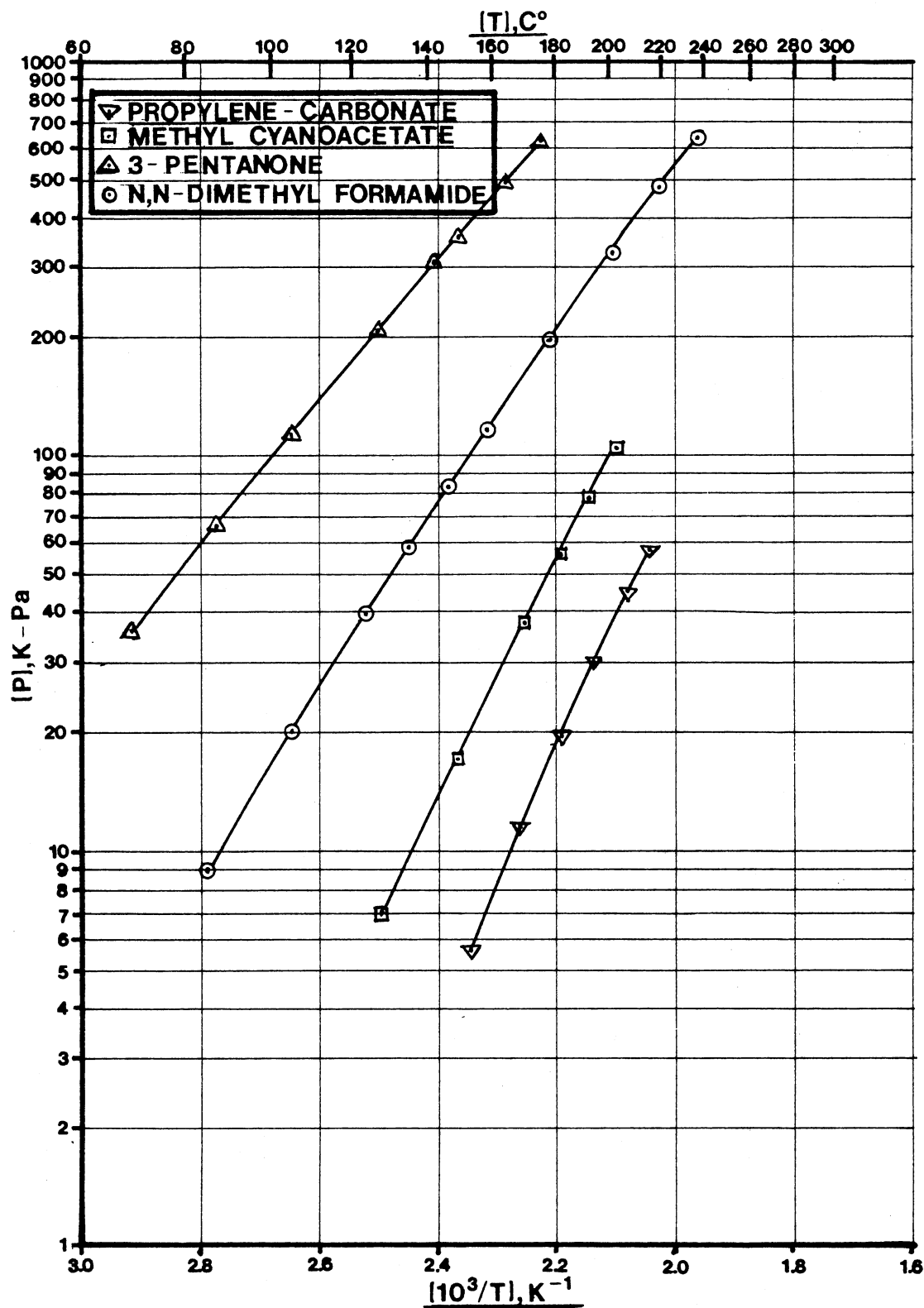


Figure 3. Vapor Pressure of 3-Pentanone, N, N-Dimethyl Formamide, Methyl Cyanoacetate, and Propylene Carbonate

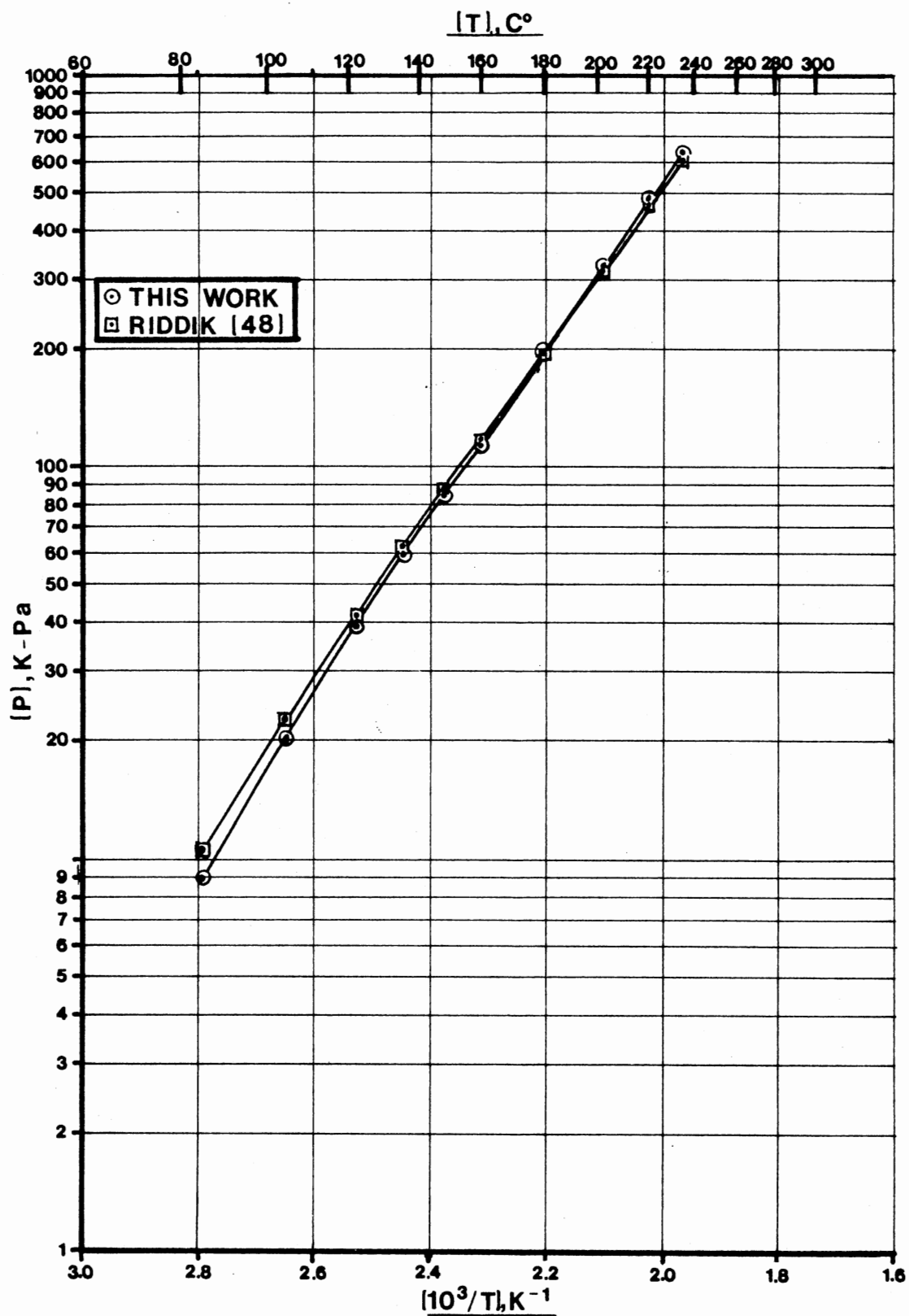


Figure 4. Graphical Comparison for N, N-Dimethyl Formamide

TABLE II  
REPRODUCED LOW-TEMPERATURE RANGE VAPOR  
PRESSURES FOR N, N-DIMETHYLFORMAMIDE

Temp. (°C)	Temp. (°K)	P <sub>fit</sub> (K-pa)	P <sub>exp</sub> New Run	ΔP (K-pa)	% Dev.
85.26	358.41	8.830	8.128	-0.703	-7.96
104.59	377.74	19.955	19.642	-0.313	-1.57
104.68	377.83	20.022	19.659	-0.363	-1.81
122.22	395.37	38.129	38.437	+0.308	+0.81
135.06	408.21	58.235	58.248	+0.013	+0.02
146.90	420.05	83.452	82.462	-0.990	-1.19
155.55	428.70	106.70	104.810	-1.890	-1.77
Overall A.A.P.D.					2.16

TABLE III  
 REPRODUCED HIGH-TEMPERATURE RANGE VAPOR  
 PRESSURES FOR N, N-DIMETHYLFORMAMIDE

Temp. (°C)	Temp. (°K)	P <sub>fit</sub> (K-pa)	P <sub>exp</sub> New Run (K-pa)	ΔP (K-pa)	% Dev.
173.35	446.50	170.16	169.61	-0.545	-0.32
189.14	462.29	247.43	247.89	+0.464	+0.19
201.59	474.74	324.90	325.96	+1.050	+0.32
220.15	493.30	472.03	474.45	+2.420	+0.51
235.52	508.67	626.45	620.75	-5.70	-0.91
Overall A.A.P.D.					0.45

3-propanediol had an A.A.P.D. of 1.93% when compared to calculated values from Antoine equation constants reported by Reid et al. (47). The experimental measurements made for tripropylene glycol were compared to calculated values from reported data by Jordan (34). An A.A.P.D. of 4.79% was obtained between them. Both sets of data, are plotted in Figure 6, which shows that the data gathered in this work are lower at low temperature and slightly higher at high temperatures. But when the data of this work were fitted to the Antoine equation, it gave an A.A.P.D. of 0.004% compared to 0.72% obtained for the data reported by Jordan. The experimental data obtained in this work for diethylene glycol were compared to values calculated from data reported by Hala et al. (9), and Gallagher et al. (26), with an A.A.P.D. of 6.21% and 16.8% respectively. The three sets of data were plotted in Figure 7. The data reported by Hala were experimentally obtained by Rinckenbach (49). He used a dynamic method which measures the boiling temperatures at reduced atmospheric pressures. The reported points were read off from a smoothed plot of data. No mention of thermal decomposition of the sample was reported. Deal et al. (16), report that in absence of air DEG degrades thermally to produce gaseous products (principally hydrogen), however, it degrades rapidly in the presence of air to produce acidic products. The data reported by Rinckenbach were obtained in the presence of air. In this work the measurements were gathered in the absence of air, and vacuum was applied over the sample shortly before the temperature and pressure were read. Decomposition, was observed when the temperature reaches approximately 200°C. Gallagher et al. (26), reported the initial decomposition temperature for DEG to be 164°C. Their data were consistently higher

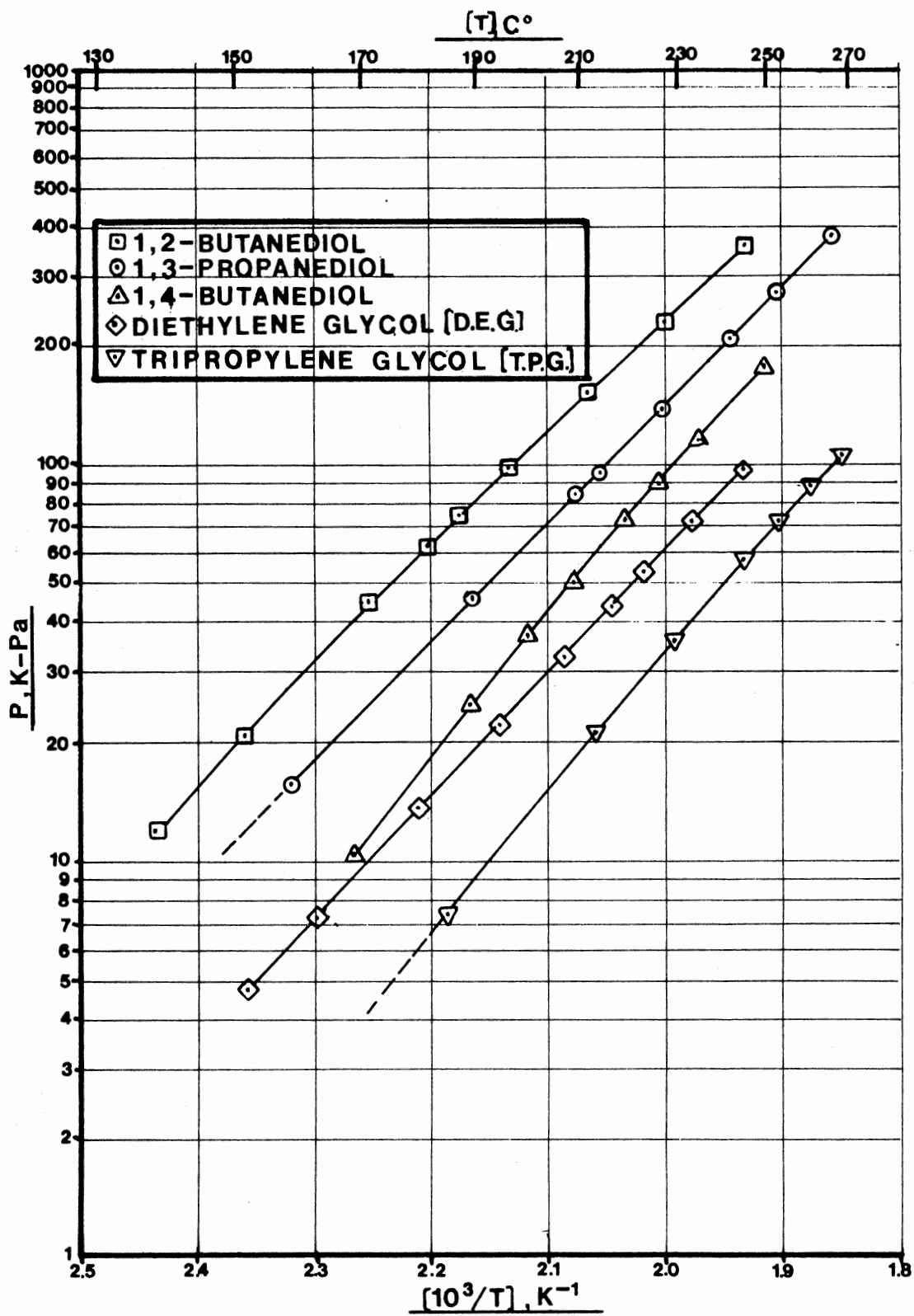


Figure 5. Vapor Pressure of 1, 2-Butanediol, 1, 3-Propanediol, 1, 4-Butanediol, D.E.G., and T.P.G.

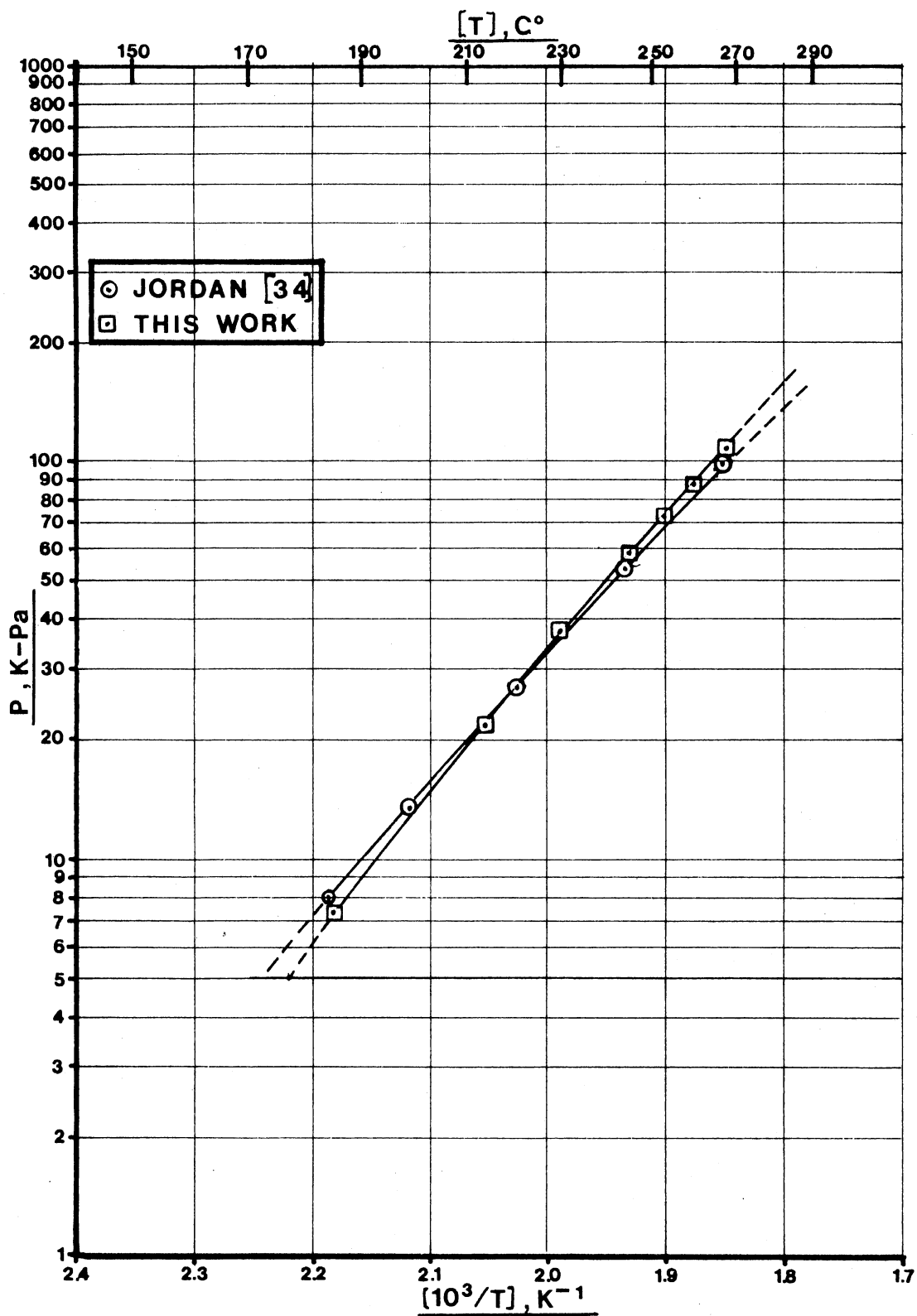


Figure 6. Graphical Comparison for Tripolyene Glycol

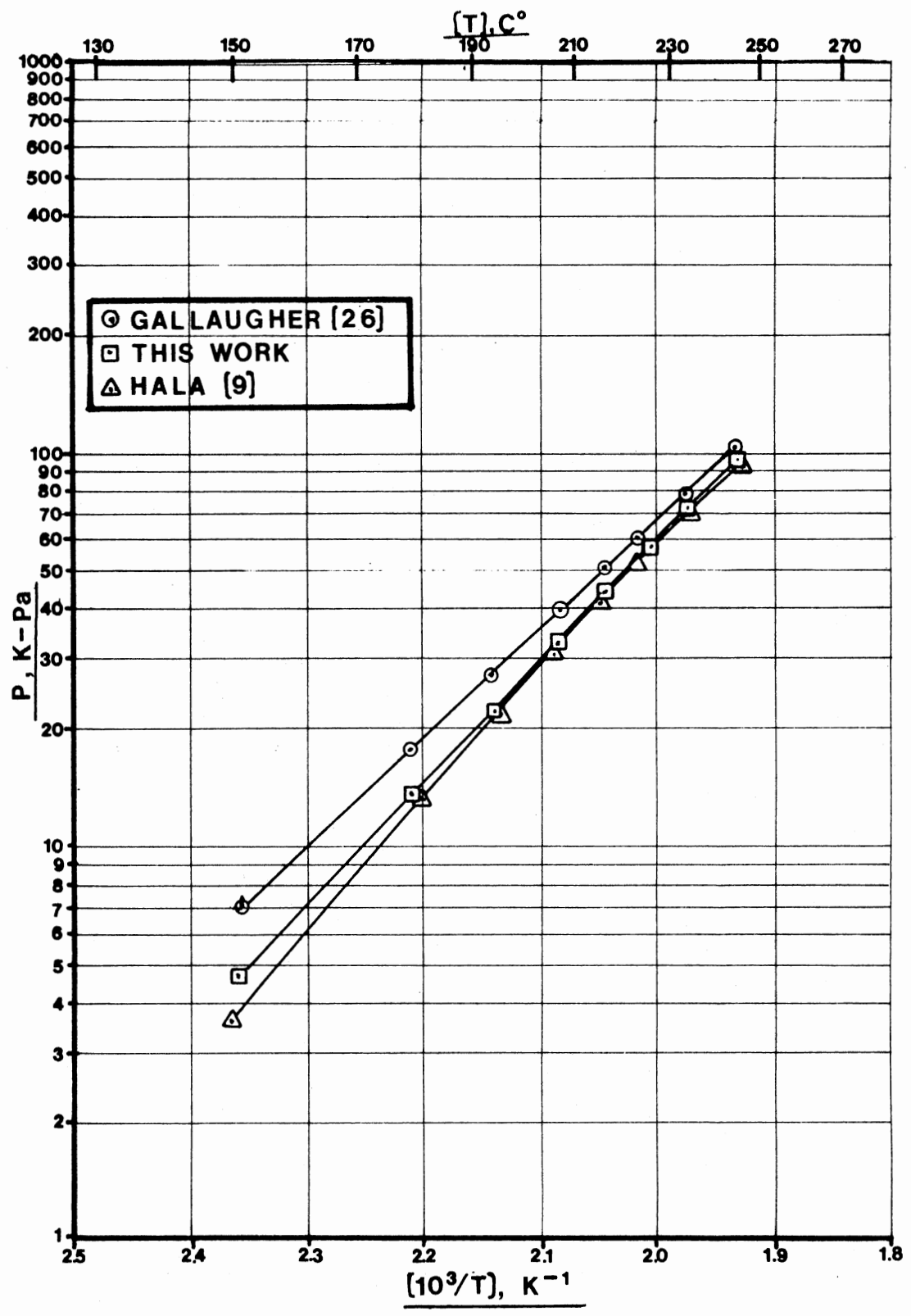


Figure 7. Graphical Comparison for Diethylene Glycol



than the data obtained in this work and the data reported by Hala.

The experimental vapor pressures measured in this work, for n-methyl-pyrrolidinone, 1, 5-pentanediol, selexol, and glutaronitrite, are plotted in Figure 8, and given in a tabular form in Tables XX, XXI, XXII, and XXIII, Appendix A, respectively.

The experimental measurements obtained in this work for two mixtures of methyldiethanolamine and water of a normality of 1 and 2 respectively, are plotted in Figure 9, and tabulated in Tables XXIV, and XXV. An A.A.P.D. of 3.85 and 4.89 was found in comparison to the calculated values based on Raoult's law for both mixtures respectively.

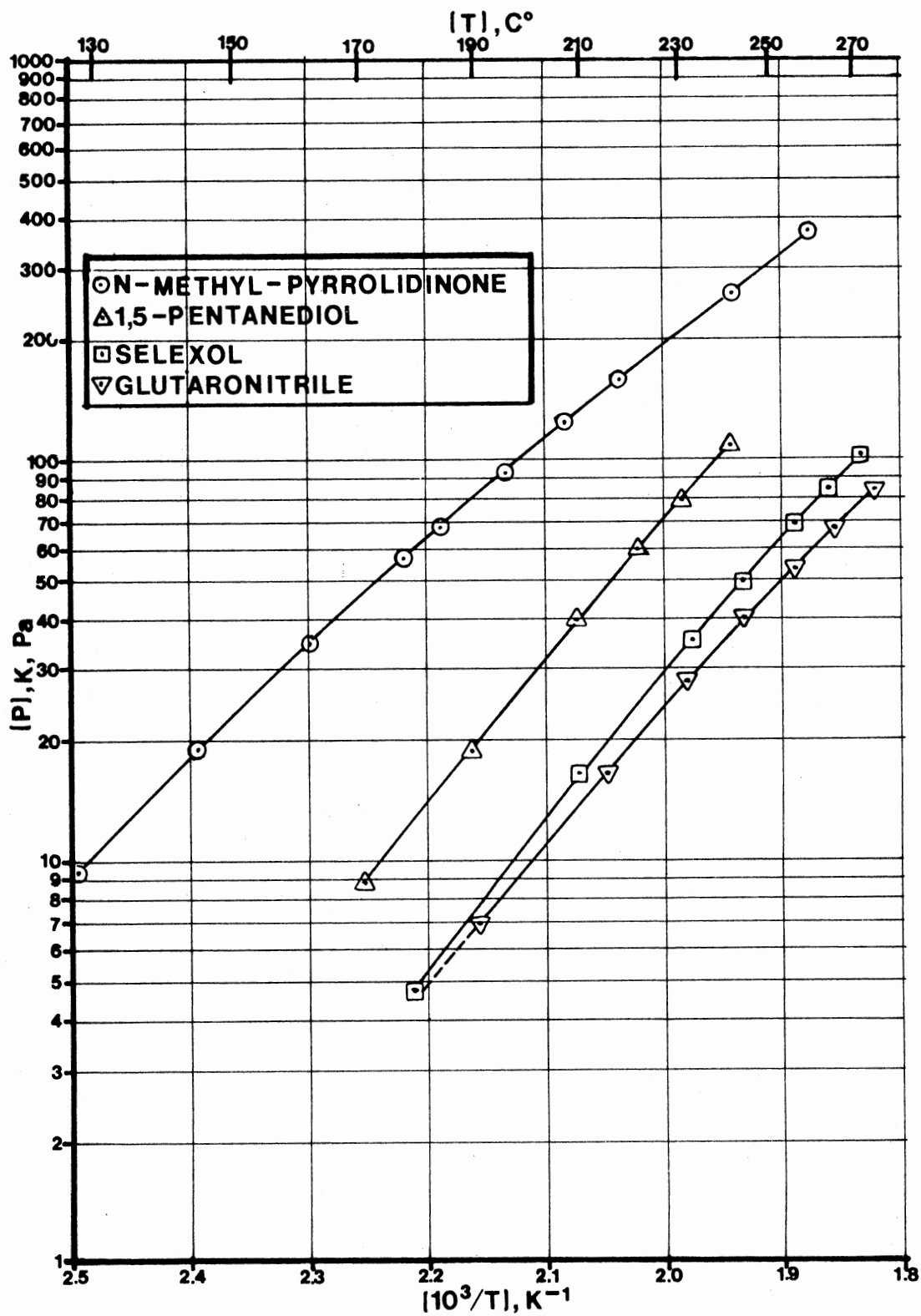


Figure 8. Vapor Pressure N-Methyl Pyrrolidinone, 1, 5-Pentanediol, Selexol, and Glutaronitrile

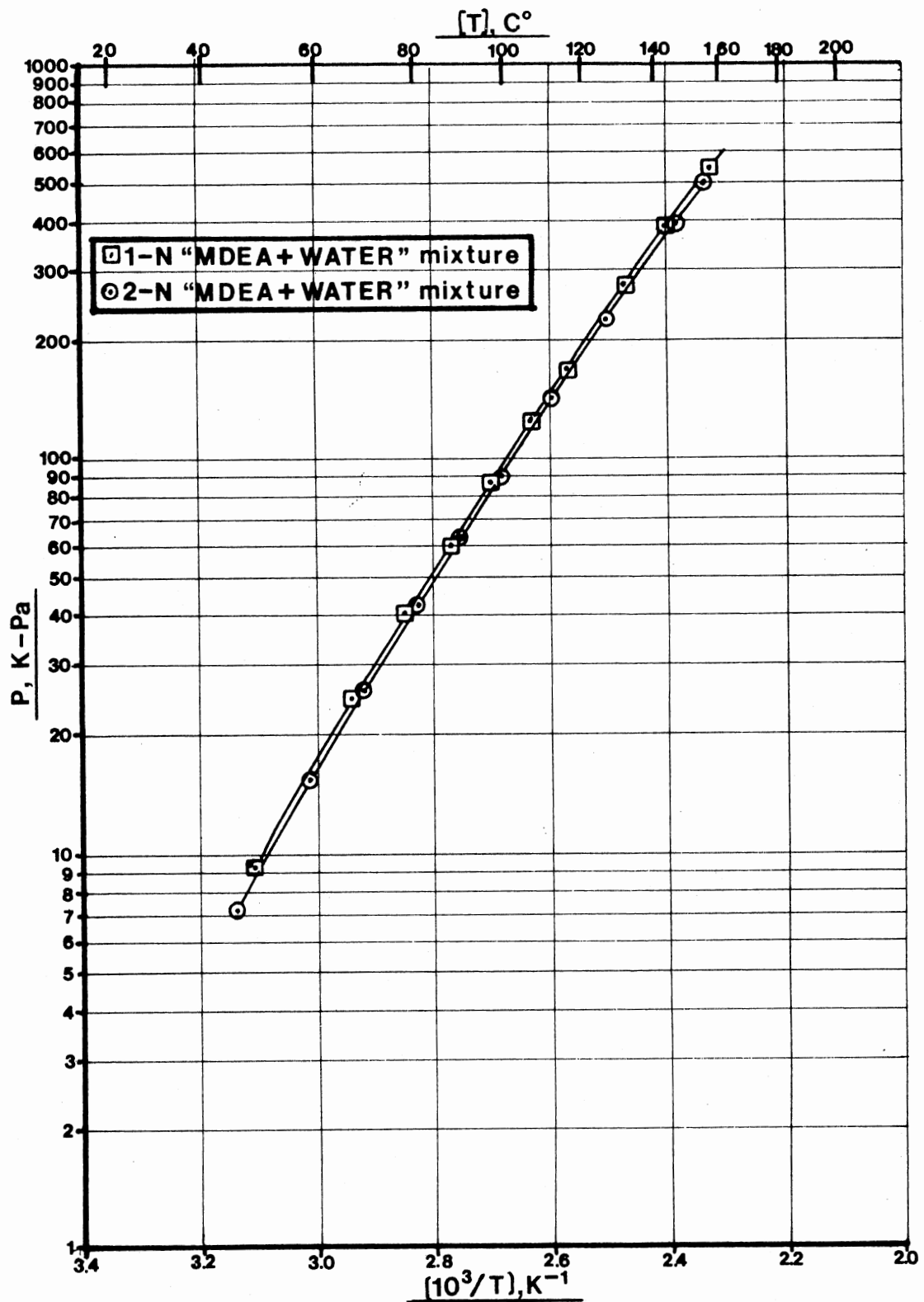


Figure 9. Vapor Pressure of 1 and 2 Normal "Methyldiethanolamine + Water" Mixtures

## CHAPTER VI

### DISCUSSION OF RESULTS

The quantitative comparisons made in this work, in terms of the A.A.P.D., between the experimental and reported data, have exhibited reasonable agreement. However, they can not be used as the only basis for determining the accuracy and consistency of the method of this work, because of three reasons. First, the lack of agreement among published data for a given compound by different workers employing different methods. This is, especially true for most heavy compounds which are seldom thermally stable even at their normal boiling point. This point is very well exemplified by the comparison made for diethylene glycol. Second, most of the experimental vapor pressures gathered in this work, were measured below atmospheric pressure. This tends to inflate the percent deviation of data points among each other, even when errors are within the systematic errors of the method. Third, some of the reported data have been extrapolated beyond the upper or lower experimental limits.

Close inspection of the plots of  $\ln P$  vs.  $1/T$  for the compounds and mixtures whose vapor pressures are measured in this work, indicate downward curvature in the shape of the lower portion of an elongated S, common to all vapor pressure data (55). This signifies that the data obtained in this work, are consistent in their conformity to the

established behavior of vapor pressure data.

The experimental vapor pressure data obtained in this work for each pure compound or mixture were correlated with the three constant Antoine equation. A nonlinear least-squares fitting subroutine, MARQ, written by Chandler (13) was used to evaluate the optimal constants. Each Table in Appendix A, gives a comparison between the experimental and fitted vapor pressure data for each compound or mixture with the constants listed at the bottom. An overall summary of all comparisons is given in Table IV. The degree of accuracy by which the experimental vapor pressure data are reproduced by the Antoine equation is indicative of the consistency of the data being gathered. For all vapor pressure data collected, the overall A.A.P.D. between the experimental and fitted data, with the Antoine equation, for all compounds and mixtures was 0.65% with maximum positive and negative percent deviation of 3.3% and 3.25% respectively. Propylene Carbonate and diethylene glycol were the only two compounds to have an overall A.A.P.D. higher than 1%, between their experimental and fitted vapor pressure data. This is probably due to the observed thermal decomposition of both compounds.

The availability of reported normal boiling temperatures for compounds which have no published experimental vapor pressure data, has provided a basis for determining the accuracy of the measured data for such compounds. Table V gives a comparison between the normal boiling temperatures, calculated via the Antoine equation, and reported values in the literature or by the supplier for each pure compound investigated in this work. The overall absolute average deviation between the two is 0.77°C, for all 17 compounds.

TABLE IV  
SUMMARY OF THE ANTOINE EQUATION CONSTANTS

Compound or Mixture Name	No. of Exptl. Pts.	Temperature Range (°K)	Pressure Range (K-pa)	Antoine Eqn. Constants			Maximum Pos. % Dev.	Maximum Neg. % Dev.	Overall A.A.P.D.
				A	B	C			
N-hexane	8	295-417	17-672	13.5378	2517.06	-59.36	0.24	0.18	0.17
2-Butanone	10	298-419	13-573	14.4578	3070.83	-40.48	0.81	3.91	0.71
N-Propyl Acetate	7	323-448	14-642	13.6738	2628.22	-84.167	1.48	1.73	1.00
Cyclohexanol	11	374-508	10-601	12.8743	2249.28	-161.29	1.30	0.48	0.37
3-Pentanone	11	343-450	36-635	14.3208	3125.50	-52.19	0.71	1.33	0.42
N, N-Dimethylformamide	10	359-509	9-633	13.5228	2833.00	-108.68	0.77	1.54	0.60
Methylcyanoacetate	6	400-476	7-106	15.7568	4230.17	-94.54	0.83	0.37	0.30
Propylene Carbonate	6	427-489	6-57	10.2070	1410.89	-260.44	3.30	3.25	1.80
1, 2-Butanediol	10	411-518	11-179	13.9670	2938.71	-154.88	0.65	0.79	0.35
1, 3-Propanediol	7	431-539	15-377	15.8304	4332.56	-101.28	0.79	2.14	0.73
1, 4-Butanediol	8	442-523	11-179	13.9913	2945.00	-188.60	0.36	1.08	0.36
Diethylene Glycol	8	424-517	5-97	17.3772	6368.23	-20.98	2.71	2.60	1.61
Tripropylene Glycol	7	458-541	7-106	13.7570	3333.91	-174.27	0.004	0.00	0.004
N-Methyl Pyrrolidinone	10	399-532	9-369	12.6774	2538.50	-157.21	1.02	0.71	0.40
1, 5-Pentanediol	6	444-514	9-109	15.4528	4022.94	-140.51	0.35	0.39	0.28
Selexol	7	452-545	5-102	11.9295	2298.80	-230.68	1.79	0.66	0.73
Glutaronitrile	8	463-557	7-100	12.3008	2802.50	-192.91	1.09	2.14	0.75
1-N Mixture, MDEA+Water	10	322-429	9-541	14.4488	2641.76	-105.34	0.70	0.91	0.47
2-N Mixture, MDEA+Water	10	318-427	7-497	14.0668	2453.61	-114.88	0.96	1.06	0.67
Overall for all com- pounds @ Mixtures	160	294-557	3-672				3.30	3.25	0.65

$$\ln P(K - pa) = A - \frac{B}{T(^{\circ}K) + C}$$

The experimental vapor pressure data obtained in this work for the two mixtures of MDEA with water, has not showed significant deviation from the calculated data via Raoult's law. In addition, the experimental vapor pressures of both mixtures did not differ significantly from each other. This is due to the negligible vapor pressure of pure MDEA relative to the vapor pressure of pure water at the measured temperatures.

TABLE V  
COMPARISON OF THE N.B.P. DETERMINED VIA THIS WORK  
WITH REPORTED VALUES IN THE LITERATURE

Compound	N.B.P. (°C) This work	N.B.P. (°C) Literature	$\Delta t$ (°C)	Ref. No.
N-Hexane	68.41	68.75	-0.34	47
2-Butanone	79.42	79.65	-0.23	47
N-Propyl Acetate	101.25	101.55	-0.30	48
Cyclo Hexanol	160.58	161.15	-0.57	47
3-Pentanone	101.18	101.95	-0.77	47
N, N-Dimethyl Formamide	153.68	152.78	+0.90	43
Methyl Cynoacetate	201.17	201.67	-0.50	43
Propylene Carbonate	239.75*	240.00	-0.25	R.S.
1, 2-Butanediol	196.40	195.32	+0.76	R.S.
1, 3-Propanediol	214.55	214.45	+0.10	47
1, 4-Butanediol	229.65	230.00	-0.36	R.S.
Diethylene Glycol	246.96*	245.85	+1.11	47
Tripropylene Glycol	265.94	267.20	-1.26	53
N-Methyl Pyrrolidinone	199.05	202.22	-3.17	43
1, 5-Pentanediol	238.67	239.00	-0.33	50
Selexol	271.95	270.00	+1.95	50
Glutaronitrile	284.55*	285-287	-0.45	R.S.

Abs. Avg.  $\Delta t$  for all Compounds = 0.77°C

\* Extrapolated

R.S.; reported by supplier.



## CHAPTER VII

### CONCLUSIONS AND RECOMMENDATIONS

#### Conclusion

The objective of this work was achieved by making modifications in the design and the experimental procedure of an existing vapor pressure apparatus to improve its accuracy and consistency. Vapor pressure data were obtained for 17 pure compounds and two mixtures. The experimental data were correlated with the Antoine equation for vapor pressure.

Quantitative comparisons were made in terms of previously published data in the literature for 9 of the 17 pure compounds investigated in this work. Table VI gives a summary of these comparisons. An analysis of the experimental errors in this work was given in Appendix C.

#### Recommendations

The following two recommendations are suggested to further improve the accuracy of any future vapor pressure measurements via the apparatus used in this work:

1. The measurement of temperature can be improved by using a digital thermometer with an internal constant reference temperature.

TABLE VI  
 SUMMARY OF COMPARISONS OF EXPERIMENTAL VAPOR  
 PRESSURE DATA FOR 9 COMPOUNDS

Compound	No. of Exp. Pts.	Temp. Range (°K)	Press. Range (K-pa)	Max. Pos. % Dev.	Max. Neg. % Dev.	Overall A.A.P.D.	Ref. No.
N-Hexane	8	295-417	17-672	1.35	1.01	0.82	50
2-Butanone	10	298-419	13-573	4.35	0.29	1.16	47
n-Propyl-Acetate	7	323-448	14-642	2.21	4.27	1.74	57
Cyclo-hexanol	11	374-508	10-601	1.50	7.61	2.12	48
3-Pentanone	11	343-450	36-635	4.46	1.41	1.66	47
N, N-Dimethyl-Formamide	10	359-509	9-633	3.66	17.9	5.01	48
1, 3-Propane-diol	7	431-539	15-377	7.12	--	1.93	47
Diethylene Glycol	8	424-517	5-97	25.8	3.64	6.21	9
					32.2	16.81	26
Tripropylene-Glycol	7	458-541	7-106	5.31	8.25	4.79	34

2. Further improvement of the measurement of pressure can be attained by using a gauge of much higher resolution. This is recommended especially for below atmospheric pressure measurements.

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APPENDIX A  
EXPERIMENTAL, REPORTED, AND  
FITTED VAPOR PRESSURE  
DATA



TABLE VII  
COMPARISON OF EXPERIMENTAL VAPOR  
PRESSURE DATA FOR n-HEXANE

Temp. (°C)	Temp. (°K)	P <sub>exp</sub> (K-pa)	P <sub>fit</sub> (K-pa)	% Dev. of P <sub>fit</sub>	P° (K-pa) A.P.I. [50]	% Dev. From P°
22.14	295.29	17.609	17.621	+0.07	17.788	-1.01
26.19	299.34	21.132	21.097	-0.17	21.230	-0.46
50.48	323.63	55.199	55.332	+0.24	54.976	+0.41
71.66	344.81	112.40	112.17	-0.21	110.96	+1.30
90.58	363.73	194.40	194.40	-0.18	191.82	+1.35
108.16	381.31	304.45	304.76	+0.10	301.68	+0.92
126.54	399.69	463.95	464.91	+0.21	461.41	+0.55
144.29	417.44	671.89	670.79	-0.16	668.08	+0.57
Overall A. A. P. D.				0.17		0.82
Antoine Eqn. Constants;						
A = 13.5378		B = 2517.06		C = -59.36		

TABLE VIII  
 COMPARISON OF EXPERIMENTAL VAPOR  
 PRESSURE DATA FOR 2-BUTANONE

Temp. (°C)	Temp. (°K)	P <sub>exp</sub> (K-pa)	P <sub>fit</sub> (K-pa)	% Dev. of P <sub>fit</sub>	P <sup>o</sup> (K-pa) Reid [47]	% Dev. From P <sup>o</sup>
24.49	297.64	12.873	12.388	-3.91	12.337	+4.35
47.99	321.14	33.970	33.667	-0.90	33.438	+1.59
71.31	344.46	78.903	77.926	-1.25	77.375	+1.98
90.17	363.32	141.22	140.58	-0.45	139.30	+1.38
104.57	377.72	209.32	211.02	+0.81	209.92	-0.29
109.44	382.59	240.61	240.27	-0.14	239.08(e)	+0.64
129.28	402.43	393.01	392.93	-0.02	391.79	+0.31
130.62	403.77	405.55	405.41	-0.04	404.31	+0.31
143.62	417.14	546.96	547.29	+0.06	546.60	+0.07
146.11	419.26	573.17	572.87	-0.05	569.06	+0.72
Overall A. A. P. D.				0.71		1.16
Antoine Eqn. Constants;						
A = 14.4578		B = 3070.83		C = -40.48		

(e); extrapolated.

TABLE IX  
 COMPARISON OF EXPERIMENTAL VAPOR  
 PRESSURE DATA FOR N-PROPYL  
 ACETATE

Temp. (°C)	Temp. (°K)	P <sub>exp</sub> (K-pa)	P <sub>fit</sub> (K-pa)	% Dev. of P <sub>fit</sub>	P° (K-pa) Timmermans [57]	% Dev. From P°
49.31	322.46	13.955	14.078	0.88	14.577	-4.27
71.32	344.47	36.404	35.776	-1.73	35.985	+1.17
98.89	372.04	94.313	94.090	-0.24	92.949	+1.47
126.89	400.04	208.270	211.360	+1.48	207.64	0.30
153.66	426.81	402.49	404.91	+0.60	398.55	0.99
175.03	448.18	642.09	635.13	-1.08	628.22	2.21
Overall A. A. P. D.				1.00		1.74
Antoine Eqn. Constants;						
A = 13.6738		B = 2628.22		C = -84.167		

TABLE X  
 COMPARISON OF EXPERIMENTAL VAPOR  
 PRESSURE DATA FOR CYCLO-HEXANOL

Temp. (°C)	Temp. (°K)	P <sub>exp</sub> (K-pa)	P <sub>fit</sub> (K-pa)	% Dev. of P <sub>fit</sub>	P° (K-pa) Riddik [48]	% Dev. From P°
100.37	373.52	9.736	9.736	0.00	10.538	-7.61
114.92	388.07	18.967	19.217	+1.30	20.218	-6.19
144.01	417.16	59.095	59.360	+0.45	59.426	-0.56
150.81	423.96	75.015	74.535	-0.64	74.986	+0.04
164.87	438.02	115.48	115.16	+0.28	114.53(e)	+0.83
168.77	441.92	129.54	128.92	-0.48	127.94	+1.25
190.71	463.86	230.79	230.51	-0.12	227.38	+1.50
199.51	472.66	283.79	284.40	+0.22	280.54	+1.16
207.66	480.81	341.70	341.79	+0.03	337.63	+1.21
235.29	508.44	601.45	598.86	-0.43	596.31	+0.86
Overall A. A. P. D.				0.37		2.12

Antoine Eqn. constants;

A = 12.8743

B = 2249.28

C = -161.29

TABLE XI  
 COMPARISON OF EXPERIMENTAL VAPOR  
 PRESSURE DATA FOR 3-PENTANONE

Temp. (°C)	Temp. (°K)	P <sub>exp</sub> (K-pa)	P <sub>fit</sub> (K-pa)	% Dev. of P <sub>fit</sub>	P° (K-pa) Reid (47)	% Dev. From P°
70.00	343.15	35.984	35.830	-0.18	34.571	+3.64
87.78	360.93	67.389	66.508	-1.33	64.514	+4.46
105.07	378.22	113.82	113.79	-0.03	111.12	+2.43
110.24	383.39	132.08	132.14	+0.05	129.36	+2.10
126.38	399.53	205.90	204.87	-0.51	202.11	+1.87
133.55	406.70	244.51	245.77	+0.51	243.34(e)	+0.48
143.09	416.24	307.50	309.68	+0.71	308.12	-0.20
149.08	422.23	354.74	355.84	+0.31	355.19	-0.13
164.52	437.67	497.15	499.08	+0.39	502.38	-1.04
170.85	444.00	571.65	568.85	-0.49	574.69	-0.53
176.40	449.55	635.32	635.96	+0.10	644.39	-1.41
Overall A. A. P. D.				0.42		1.66
Antoine Eqn. Constants;						
A = 14.3208		B = 3125.50		C = -52.19		

TABLE XII  
 COMPARISON OF EXPERIMENTAL VAPOR PRESSURE  
 DATA FOR N, N-DIMETHYL-FORMAMIDE

Temp. (°C)	Temp. (°K)	P <sub>exp</sub> (K-pa)	P <sub>fit</sub> (K-pa)	% Dev. of P <sub>fit</sub>	P° (K-pa) Riddik [48]	% Dev. From P°
85.35	358.50	8.805	8.868	+0.71	10.805	-17.9
104.65	377.80	20.082	20.001	-0.40	22.500	-10.75
122.89	396.04	39.623	39.022	-1.54	41.622	- 4.80
135.38	408.53	58.926	58.836	-0.15	61.094	- 3.55
146.90	420.05	82.801	83.447	+0.77	84.995	- 2.58
158.56	431.71	115.21	115.88	+0.58	116.26	- 0.90
179.79	452.94	198.45	199.06	+0.31	195.97	+ 1.26
201.61	474.76	323.25	325.06	+0.56	316.90	+ 2.00
221.42	494.57	482.92	483.58	+0.14	470.07	+ 2.73
235.62	508.77	632.61	627.59	-0.80	610.30	+ 3.66
Overall A. A. P. D.				0.60		5.01
Antoine Eqn. Constants;						
A = 13.5228		B = 2833.00		C = -108.683		

TABLE XIII  
COMPARISON OF EXPERIMENTAL VAPOR PRESSURE  
DATA FOR METHYL-CYANOACETATE

Temp. (°C)	Temp. (°K)	P <sub>exp</sub> (K-pa)	P <sub>fit</sub> (K-pa)	% Dev. of P <sub>fit</sub>
127.53	400.68	6.942	6.951	+ 0.13
148.82	421.97	17.099	17.074	-0.15
169.76	442.91	37.252	37.116	-0.37
182.35	455.50	56.216	56.607	+0.83
192.60	465.75	78.483	78.346	-0.18
202.77	475.92	106.34	106.17	-0.15
Overall A. A. P. D.				0.30
Antoine Eqn. Constants;				
A = 15.7568		B = 4230.17		C = -94.54

TABLE XIV  
 COMPARISON OF EXPERIMENTAL VAPOR PRESSURE  
 DATA FOR PROPYLENE CARBONATE

Temp. (°C)	Temp. (°K)	P <sub>exp</sub> (K-pa)	P <sub>fit</sub> (K-pa)	% Dev. of P <sub>fit</sub>
153.72	426.87	5.588	5.639	+ 0.91
168.28	441.43	11.514	11.152	- 3.25
182.89	456.04	19.303	19.962	+ 3.30
194.24	467.39	30.140	29.649	- 1.66
207.83	480.98	44.702	45.135	+ 0.96
216.28	488.47	57.571	57.144	+ 0.74
Overall A. A. P. D.				1.80
Antoine Eqn. Constants;				
A = 10.2070		B = 1410.89		C = -260.44



TABLE XV  
 COMPARISON OF EXPERIMENTAL VAPOR PRESSURE  
 DATA FOR 1, 2-BUTANEDIOL

Temp. (°C)	Temp. (°K)	P <sub>exp</sub> (K-pa)	P <sub>fit</sub> (K-pa)	% Dev. of P <sub>fit</sub>
137.98	411.13	12.191	12.165	-0.21
150.74	423.89	20.827	20.962	+0.65
161.02	434.17	31.326	31.342	+0.05
170.87	444.02	45.041	44.848	-0.43
180.79	453.94	63.328	62.829	-0.79
186.19	459.34	74.608	74.782	-0.23
195.65	468.80	99.905	100.04	+0.14
210.70	483.85	152.90	153.51	+0.39
227.47	500.62	236.04	236.76	+0.31
244.79	517.94	356.43	355.23	-0.34
Overall A. A. P. D.				0.35
Antoine Eqn. Constants;				
A = 13.9670		B = 2938.71		C = -154.88

TABLE XVI  
 COMPARISON OF EXPERIMENTAL VAPOR PRESSURE  
 DATA FOR 1, 3-PROPANEDIOL

Temp. (°C)	Temp. (°K)	P <sub>exp</sub> (K-pa)	P <sub>fit</sub> (K-pa)	% Dev. of P <sub>fit</sub>	P° (K-pa) Reid [47]	% Dev. From P°
158.16	431.31	15.239	14.921	-2.14	14.227	+ 7.12
188.89	462.04	46.057	45.639	-0.92	44.692	+ 3.05
208.99	482.14	85.341	86.019	+0.79	84.985	+ 0.42
224.97	498.12	135.46	136.01	-10.40	134.86	+ 0.44
240.99	514.14	207.08	207.76	-10.33	206.30	+ 0.38
252.36	525.51	275.67	275.25	-0.15	273.26	+ 0.88
265.67	538.82	376.92	375.52	-0.38	372.41(e)	+ 1.21
Overall A. A. P. D.				0.73		1.93
Antoine Eqn. Constants;						
A = 15.8304		B = 4332.56		C = -101.28		

TABLE XVII  
COMPARISON OF EXPERIMENTAL VAPOR PRESSURE  
DATA FOR 1, 4-BUTANEDIOL

Temp. (°C)	Temp. (°K)	P <sub>exp</sub> (K-pa)	P <sub>fit</sub> (K-pa)	% Dev. of P <sub>fit</sub>
168.46	441.61	10.498	10.504	+ 0.06
188.64	461.79	24.722	24.811	+ 0.36
198.92	472.07	37.083	36.682	- 1.08
208.67	481.82	51.644	51.821	+ 0.34
218.99	492.14	72.810	72.897	+ 0.12
225.46	498.61	89.07	89.270	+ 0.23
234.47	507.62	116.36	116.73	+ 0.32
249.72	522.87	178.47	177.87	- 0.34
Overall A. A. P. D.				0.36
Antoine Eqn. Constants;				
A = 13.9913		B = -2945.0		C = -188.60

TABLE XVIII

COMPARISON OF EXPERIMENTAL VAPOR PRESSURE DATA FOR DIETHYLENE-GLYCOL

Temp. (°C)	Temp. (°K)	P <sub>exp</sub> (K-pa)	P <sub>fit</sub> (K-pa)	% Dev. of P <sub>fit</sub>	P° (K-pa) Hala [10]	% Dev. From P°	P°° (K-pa) Gallaughier [27]	% Dev. From P°°
150.83	423.98	4.742	4.831	+1.85	3.769	+25.80	6.998	-32.24
179.09	452.24	13.670	13.605	-0.48	12.237	+11.71	17.659	-22.59
194.23	467.38	21.843	22.451	+2.71	21.298	+ 2.56	27.689	-21.11
206.54	479.69	32.376	32.922	+1.66	32.319	+ 0.18	39.089	-17.17
216.07	489.22	43.348	43.674	+0.75	43.813	- 1.06	50.444	-14.07
223.20	496.35	52.491	53.551	+1.98	54.475	- 3.64	60.658	-13.47
233.54	506.69	71.795	71.223	-0.81	73.677	- 2.55	78.528	- 9.30
244.21	517.36	96.857	94.400	-2.60	99.006	- 2.17	101.40	- 4.48
Overall A. A. P. D.				1.61		6.21		16.80
Antoine Eqn. Constants;								
A = 17.3772			B = 6368.33			C = -20.98		

TABLE XIX

COMPARISON OF EXPERIMENTAL VAPOR PRESSURE  
DATA FOR TRIPROPYLENE GLYCOL

Temp. (°C)	Temp. (°K)	P <sub>exp</sub> (K-pa)	P <sub>fit</sub> (K-pa)	% Dev. of P <sub>fit</sub>	P° (K-pa) Jordon [34]	% Dev. From P°
184.81	457.96	7.424	7.424	0.000	8.091	-8.25
213.13	486.28	21.575	21.575	0.000	21.158	+1.93
229.59	502.84	36.972	36.971	-0.003	35.334	+4.64
244.78	517.93	57.733	57.732	-0.002	54.823	+5.31
252.72	525.87	71.863	71.859	-0.006	68.395	+5.07
259.81	532.96	86.679	86.683	-0.005	82.876	+4.59
267.82	540.97	106.19	106.18	-0.010	102.35	+3.76
Overall A. A. P. D.				0.004		4.79
Antoine Eqn. Constants;						
A = 13.7570		B = -3333.91		C = -174.272		

TABLE XX  
 COMPARISON OF EXPERIMENTAL VAPOR PRESSURE  
 DATA FOR N-METHYL-PYRROLIDINONE

Temp. (°C)	Temp. (°K)	P <sub>exp</sub> (K-pa)	P <sub>fit</sub> (K-pa)	% Dev. of P <sub>fit</sub>
126.18	399.33	8.974	8.961	-0.14
144.47	417.62	18.626	18.712	+0.46
161.91	435.06	34.543	34.51	-0.09
177.37	450.52	56.047	55.844	-0.36
183.45	456.60	67.053	66.577	-0.71
195.47	468.62	91.438	92.372	+1.02
206.31	479.46	121.98	121.49	-0.40
217.83	490.98	159.17	159.47	+0.19
239.99	513.14	255.17	256.03	+0.34
259.07	532.22	369.13	368.06	-0.29
Overall A. A. P. D.				0.40
Antoine Eqn. Constants;				
A = 12.6774		B = 2538.50		C = -157.21

TABLE XXI  
 COMPARISON OF EXPERIMENTAL VAPOR PRESSURE  
 DATA FOR 1, 5-PENTANEDIOL

Temp. (°C)	Temp. (°K)	P <sub>exp</sub> (K-pa)	P <sub>fit</sub> (K-pa)	% Dev. of P <sub>fit</sub>
170.46	443.61	8.839	8.848	+0.10
188.65	461.80	18.795	18.757	-0.20
208.97	482.12	39.623	39.507	-0.29
221.34	494.49	59.434	59.624	+0.32
230.48	503.63	79.081	79.359	+0.35
241.07	514.22	109.05	108.62	-0.39
Overall A. A. P. D.				0.28
Antoine Eqn. Constants;				
A = 15.4528		B = 4022.94		C = -140.51

TABLE XXII  
COMPARISON OF EXPERIMENTAL VAPOR PRESSURE  
DATA FOR SELEXOL

Temp. (°C)	Temp. (°K)	P <sub>exp</sub> (K-pa)	P <sub>fit</sub> (K-pa)	% Dev. of P <sub>fit</sub>
178.95	452.19	4.742	4.720	-0.46
209.81	482.96	16.594	16.738	+0.87
232.82	505.97	35.220	35.850	+1.79
244.58	517.73	50.121	50.462	+0.68
256.12	529.27	69.085	68.781	-0.44
264.46	537.61	85.340	84.779	-0.66
272.11	545.26	101.930	101.700	-0.23
Overall A. A. P. D.				0.73
Antoine Eqn. Constants;				
A = 11.9295		B = 2298.80		C = -230.68



TABLE XXIII  
 COMPARISON OF EXPERIMENTAL VAPOR PRESSURE  
 DATA FOR GLUTARONITRILE

Temp. (°C)	Temp. (°K)	P <sub>exp</sub> (K-pa)	P <sub>fit</sub> (K-pa)	% Dev. of P <sub>fit</sub>
190.26	463.41	6.976	6.961	-0.22
214.87	488.02	16.425	16.520	+0.57
231.68	504.83	27.380	27.555	+0.63
244.18	517.33	39.792	38.959	-2.14
255.30	528.45	51.306	51.867	+1.09
265.42	538.57	66.541	66.230	-0.47
275.60	548.75	82.971	83.526	+0.67
283.93	557.08	100.240	100.010	-0.23
Overall A. A. P. D.				0.75
Antoine Eqn. Constants;				
A = 12.3008		B = -2802.5		C = -192.906

TABLE XXIV

COMPARISON OF EXPERIMENTAL VAPOR PRESSURE DATA FOR  
1 N MIXTURE OF MDEA IN PURE WATER

Temp. (°C)	Temp. (°K)	P <sub>exp</sub> (K-pa)	P <sub>fit</sub> (K-pa)	% Dev. of P <sub>fit</sub>	P° <sub>water</sub> Reid [47]	P° <sub>MDEA</sub> Maddox [43]	P°° <sub>mixture</sub> Ideal	% Dev. From P°° <sub>M</sub>
48.56	321.71	9.381	9.386	+0.06	11.469	0.0	11.241	-16.60
66.76	339.91	24.045	24.212	+0.70	27.055	0.0	26.517	- 9.32
77.57	350.72	40.130	39.767	-0.91	42.903	0.0	42.049	- 4.56
87.27	360.42	60.280	59.885	-0.66	63.159	0.0005	61.902	- 2.62
96.81	369.96	87.034	86.985	-0.06	90.318	0.0013	88.521	- 1.68
106.43	379.58	123.13	123.450	+0.25	126.880	0.0033	124.360	- 0.99
115.60	388.75	167.97	168.610	+0.38	172.370	0.0080	168.940	- 0.57
131.73	404.88	276.68	278.500	+0.66	284.400	0.0350	278.740	- 0.74
143.59	416.74	388.77	389.750	+0.25	399.820	0.0950	391.860	- 0.79
155.77	428.92	540.49	536.270	-0.79	554.720	0.2530	543.680	- 0.59
Overall A. A. P. D.				0.47				3.85
$P^{\circ\circ}_{\text{mixture}} = X_{\text{H}_2\text{O}} \cdot P^{\circ}_{\text{H}_2\text{O}} + X_{\text{MDEA}} \cdot P^{\circ}_{\text{MDEA}}, X_{\text{H}_2\text{O}} = 0.9801, X_{\text{MDEA}} = 0.0199$								
Antoine Eqn. Constants,								
A = 14.4488			B = 2641.76			C = -105.337		

TABLE XXV

COMPARISON OF EXPERIMENTAL VAPOR PRESSURE DATA FOR  
2 N MIXTURE OF MDEA IN PURE WATER

Temp. (°C)	Temp. (°K)	P <sub>exp</sub> (K-pa)	P <sub>fit</sub> (K-pa)	% Dev. of P <sub>fit</sub>	P° <sub>H<sub>2</sub>O</sub> Reid [47]	P° <sub>MDEA</sub> Maddox [43]	P°° <sub>mixture</sub> Ideal	% Dev. From P°° <sub>M</sub>
45.04	318.19	7.332	7.376	+0.60	9.589	0.0	9.160	-20.00
58.21	331.36	15.409	15.373	-0.24	18.328	0.0	17.509	-12.00
68.66	341.81	25.008	25.907	-0.39	29.410	0.0	28.095	- 7.43
78.88	352.03	41.655	41.288	-0.89	45.270	0.0	43.247	- 3.68
88.97	362.12	63.498	62.963	-0.85	67.408	0.0006	64.395	- 1.39
97.86	371.01	88.270	88.871	+0.73	93.824	0.0014	89.630	- 1.52
110.91	384.06	140.030	141.380	+0.95	147.660	0.0051	141.060	- 0.73
126.18	399.33	228.420	230.640	0.96	240.620	0.0210	229.860	- 0.63
144.86	418.01	392.330	392.490	0.04	414.090	0.1050	395.580	- 0.82
153.97	427.12	502.220	496.980	-1.06	529.200	0.2200	505.54	- 0.66
Overall A. A. P. D.				0.67				4.89
$P^{\circ\circ}_{\text{mixture}} = X_{\text{H}_2\text{O}} \cdot P^{\circ}_{\text{H}_2\text{O}} + X_{\text{MDEA}} \cdot P^{\circ}_{\text{MDEA}}, X_{\text{H}_2\text{O}} = 0.9553, X_{\text{MDEA}} = 0.0447$								
Antoine Eqn. Constants;								
A = 14.0668			B = -2453.66			C = -114.883		

APPENDIX B

ANALYSIS OF ERRORS

## Analysis of Errors

The main experimental errors in this work can come from a variety of sources such as; the vacuum pump and leaks; cleanliness of apparatus; thermal decomposition of samples and; systematic "determinate" errors.

### Vacuum Pump and Leaks

According to the vacuum pump manual (20), the condition of the oil is often the most important factor in achieving and maintaining a low pressure and maximum pumping speed with a mechanical vacuum pump such as the one used in this work. The vapors in different systems contaminate the oil at different rates. Even though the pump was equipped with vented exhaust which greatly reduces contamination, the oil was periodically checked and changed. Also, the vacuum line was connected to two cold traps cooled by crushed ice in acetone to condense some of the vapors coming out of the system before reaching the pump.

Leaks are a major source of error which can cause significant deviations in vapor pressure measurements. Large leaks are easily detectable and can be fixed. Small leaks can hardly be detected and some caution must be exercised in making sure that they have not developed while the measurements were being taken. Before the start of each run, the apparatus was left to stand for about 30 minutes. The system was confirmed to be free of leaks if no change in the zero reading of the gauge was observed.

### Cleanliness of Apparatus

The presence of impurities can cause significant deviations in the vapor pressure measurements being made. One common source of impurities is the residues left over from previous runs with absorbed and adsorbed molecules on the surface.

In this work, the method of cleaning the apparatus previously outlined, was proved to be effective in eliminating most of the impurities in the sample cell and in the lines. The removal of absorbed and adsorbed molecules requires baking the sample cell and the lines at high temperature for a long period of time. This procedure was not feasible and was not carried out in this work.

### Thermal Decomposition of Samples

Some of the substances investigated in this work showed thermal decomposition at different rates. All static methods, such as the method of this work, have the disadvantage of not permitting the removal of decomposition products. The measurements were taken at a rapid pace provided that the observed decomposition rate was small. This procedure has allowed for the collection of enough data points with small deviations due to decomposition.

### Systematic "Determinate" Errors

When errors occur due to the characteristics of the instrument or of the technique of using it that are the same for all measurements, they are termed systematic. In this section, an uncertainty term will be derived from the Antoine equation:

$$\ln P = A - \frac{B}{T + C} \quad (1)$$

An infinitesimal change  $dT$ , in the experimentally determined value of  $T$ , will produce in  $\ln P$  the infinitesimal change

$$d[\ln P] = \frac{\partial[\ln P]}{\partial T} \cdot dT \quad (2)$$

$$d[\ln P] = \frac{dP}{P} \quad (3)$$

$$\frac{\partial[\ln P]}{\partial T} = \frac{B}{(T + C)^2} \quad (4)$$

Substituting equations (3) and (4) in equation (2):

$$dP = \frac{PB}{(T + C)^2} dT \quad (5)$$

Since the changes are finite, equation (5) can be approximated as;

$$\Delta P^\circ = \frac{PB}{(T + C)^2} \cdot \Delta T \quad (6)$$

Equation (6) estimates the uncertainty in experimental vapor pressure data provided that the uncertainty in the measurement of  $T$  is known or can be estimated.

Table XXIX gives a summary of uncertainty estimates for n-hexane. The uncertainty in  $T$  was assumed to be equal to the overall absolute average deviation between experimental temperature measurements made for n-hexane and corresponding values calculated from data reported by the A. P. I. (50). As the temperature increases, the effect of  $\Delta T$  becomes significant in terms of the magnitude of the deviation, but less significant in terms of the % deviation.

TABLE XXVI  
 SUMMARY OF UNCERTAINTY ESTIMATES  
 FOR N-HEXANE DATA

Temp. Exp. (°C)	Press. Exp. (K-pa)	Temp. A.P.I. (50) (°C)	P A.P.I. (50) (K-pa)	$\Delta T$ (°C)	$\Delta P$ (K-pa)	$\Delta P^\circ$ Eqn. (6) (K-pa)	% Dev.
295.29	17.609	295.06	17.788	+0.23	-0.18	$\pm 0.23$	1.31
299.34	21.132	299.23	21.230	+0.11	-0.10	$\pm 0.27$	1.28
323.63	55.199	323.74	54.976	-0.11	+0.22	$\pm 0.58$	1.05
344.81	112.40	345.23	110.96	-0.42	+1.44	$\pm 1.01$	0.90
363.73	194.40	364.22	191.82	-0.49	+2.58	$\pm 1.53$	0.79
381.31	304.45	381.69	301.68	-0.38	+2.77	$\pm 2.14$	0.70
399.69	463.95	399.94	461.41	-0.25	+2.55	$\pm 2.92$	0.63
417.44	671.89	417.73	668.08	-0.29	+3.81	$\pm 3.81$	0.57

ABS·Average  $\Delta T = 0.29^\circ\text{C}$



APPENDIX C

CALIBRATION OF EQUIPMENT

TABLE XXVII  
 CALIBRATION OF CHROMEL-ALUMEL THERMOCOUPLE  
 AGAINST A THERMOCOUPLE CALIBRATED  
 BY THE N.B.S.

Temp. °C Actual ( $T_{act}$ )	Temp. °C Indicated ( $T_{ind}$ )	Temp. °C Fitted ( $T_{fit}$ )	Dev. (°C)	% Dev.
24.333	24.787	24.451	+ 0.118	+ 0.49
63.833	63.976	63.695	- 0.138	+ 0.22
88.506	88.658	88.427	- 0.079	- 0.09
137.19	137.250	137.150	- 0.040	- 0.03
172.63	172.850	172.870	+ 0.246	+ 0.14
212.31	212.050	212.230	- 0.080	- 0.04
264.22	263.76	264.20	- 0.027	- 0.01
A.A.P.D. = 0.29				

TABLE XXVIII

CALIBRATION OF (0-200 In.Hg, 0°C) WALLACE AND  
TIERNAN SERIES 1000 DIFFERENTIAL GAUGE

Test Pressure (PSI)	Test Pressure (K-pa)	Gauge $P_{ind}$ (In.Hg)	Gauge $P_{ind}$ (K-pa)	Pressure Fitted $P_{fit}$ (K-pa)	Dev. (K-pa)	% Dev.
0.00	0.00	0.00	0.00	0.097	0.097	--
15.00	103.46	30.45	103.12	103.300	-0.160	- 0.16
30.00	206.92	61.00	206.58	206.790	-0.130	- 0.06
40.00	275.83	81.40	275.66	275.88	+0.050	+ 0.02
50.00	344.75	101.80	344.75	344.94	+0.190	+ 0.06
60.00	413.67	122.20	413.83	413.98	+0.310	+ 0.08
70.00	482.58	142.40	482.24	482.33	-0.250	- 0.05
80.00	551.67	162.80	551.33	551.33	-0.34	- 0.06
90.00	620.58	183.35	620.92	620.81	+0.23	+ 0.04
95.00	654.96	193.45	655.12	654.96	0.00	0.00

A.A.P.D. = 0.06

2  
VITA

Belied Saleh Kuwairi

Candidate for the Degree of

Doctor of Philosophy

Thesis: VAPOR PRESSURE OF SELECTED PURE MATERIALS AND MIXTURES

Major Field: Chemical Engineering

Biographical:

Personal Data: Born in Sabri, Benghazi, Libya, August 22, 1952, the son of Mr. and Mrs. Saleh Kuwairi; married to Fawzia F. El-Muttardi, July 28, 1977. Have one daughter; Ahlam, and three sons; Ahmad, Aousama, and Abraheam.

Education: Graduated from Shouhada Yanaier Secondary School, Benghazi, Libya, in June, 1971; B.S. in Chemical Engineering from University of Southern California, Los Angeles, California in July 1976; M.S. in Chemical Engineering from Oklahoma State University, Stillwater, Oklahoma in December 1980; completed requirements for the Doctor of Philosophy Degree in Chemical Engineering at Oklahoma State University, Stillwater, Oklahoma, in December 1983.

Professional Experience: Graduate teaching assistant from 1976-1978 with the Chemical Engineering Department at the Faculty of Petroleum and Mining, University of Al-Fateh, Tripoli, Libya; Teaching Assistant at the School of Chemical Engineering, Oklahoma State University, Stillwater, Oklahoma from September 1983 to present.

Membership and Awards: Member, National Society of Professional Engineers. Received the "Excellence in Chemical Engineering Scholarship Award" from the A.I.Ch.E., Southern California Chapter in 1974; the "Student of the Year Award" from the A.S.T.M., Southern California Chapter in 1975.