VAPOR PRESSURE MEASUREMENTS OF SOME PURE MATERIALS

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PREFACE

An apparatus for measuring vapor pressure was previously designed and constructed. Using the apparatus this work presents experimental vapor pressure data on five pure materials, i.e., n-Heptane, n-Octane, Methyl-tert-butyl ether, Tri-propylene Glycol, and 1-2-propanediol. Comparisons were made between experimental data obtained via this work and corresponding data in the published literature.

I wish to thank Professor R. N. Maddox who provided invaluable advice and assistance while serving as my adviser throughout the course of this project. Dr. John Erbar and Dr. G. Mains for serving as members of my advisory committee; R. Fox and J. Watkins of F.P.R.I. Also, I would like to thank Mr. S. Diab, Graduate student at the Chemical Engineering Department of Oklahoma State University, who aided me in the operation of the apparatus at the start of this project. Finally, I would like to express my personal gratitude and appreciation for my parents and my wife, Fawzia, who were constant source of support and encouragement.

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CHAPTER I

INTRODUCTION

Vapor pressure is an important thermophysical property in many scientific and engineering applications, such as vapor-liquid separation processes in the chemical industry. A thorough survey 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. And, also, in the sense that no data are reported for many chemical compounds.

This study was undertaken to experimentally measure the vapor pressure of some light and heavy hydrocarbons.

A previously designed and constructed apparatus was used to obtain experimental measurements of the vapor pressure of those compounds, covering wider ranges of temperatures and pressures. Modifications were made to the apparatus and its operation.

In addition to the usual graphical representation, an attempt was made to represent each set of data by a straight line equation for each range of temperature and pressure considered.

CHAPTER II

LITERATURE REVIEW

Previous Experimental Measurements

In 1900, Taylor (19) reported one of the first investigations of vapor pressure relations in mixtures of two liquids. He used a boiling-point apparatus with a mercury pump to measure the vapor-pressure of water, acetone and nine of their binary mixtures (10, 20, 30, 40, 50, 60, 70, 80, and 90 percent by weight acetone). His pressure range was from 100 to 800 mm Hg at temperatures from 25 to 95°C. In the same year, Taylor published another paper (20) which contained a theoretical analysis of the data he previously obtained. He claimed that vapor compositions given off by any given acetone solution can be predicted within one or two percent by the Vanit Hoff-Raoult equation. On the other hand, pressure relations did not agree well for they depend on the molecular concentration which is very sensitive to the fact that the molecular weights of water and acetone are so very different.

Experimental vapor pressure data for liquid tertiary butyl alcohol were published in 1956 by Krone and Johnson (8). The data were obtained with equipment modeled after that of Kay. An accuracy of 0.14 percent in the high range and 4 percent in the low range was claimed. Their pressure range was from 14.7 psia to 613.8 psia. Also, they reported that their data in the range above one atm were found to be lower than those reported by Stull (19) and by Jordan (7). In 1966, Timmermans (23)

reported additional vapor pressure data on the same compound obtained by other workers.

Ambrose et al. (1) reported in 1973 measurements of the vapor pressure of acetone in the range from 0.6 to 682 psia. Measurements in the range from 33 to 102 psia were made ebulliometrically in an apparatus designed for use at these pressures. Measurements in the range of 255 psia to 682 psia were made by a static method.

In 1975, as apart of the same project, Ambrose et al. (2) reported extensive vapor pressure data on methyl t-butyl ether a long with similar data on another eight aliphatic ethers. Their pressure range was from 0.7 to 30 psia and temperatures from 60 to 530°F. The measured values were fitted by Antoine and Chebyshev equations and a single equation was developed in which an effective carbon number is a parameter.

In 1952, White et al. (25) reported vapor pressure measurements on fifteen alkane sulfides, eight alkane disulfides, nine cyclic sulfides, and three thiophenes. Two ebulliometers were used, working under a range of constant pressure varying from 100 to 1000 mm Hg. In addition, several correlations were given, relating the boiling points at 760 mm Hg and the constants of the Antoine equation to the structure of both the alkane sulfides and disulfides.

In 1947, Stull (18) reported one of the first assemblies of vapor pressure data on over 1200 organic compounds gathered from the literature and private sources. This collection was presented in tabular form for both below and above atmoshperic pressures. Jordan (7) reported in 1954 a similar vapor pressure data network in both tabular and graphical forms.

In 1970, the American Petroleum Institue (21) presented vapor pressure-temperature relation plots of a number of the more common hydrocarbons.

Generalized methods were given for estimating the vapor pressures of pure hydrocarbons for the case when only the critical properties along with the acentric factors are known and, also for the case when only the normal boiling points of those pure hydrocarbons are known.

Finally, vapor pressure data on most of the light normal hydrocarbons covering the low and high pressure ranges were reported extensively and adequately by many sources in the published literature. Therefore, those sources will be cited as they are used in this study.

A.P.I. Generalized Method (21)

The following equation is valid only for nonpolar substances and is restricted to reduced temperatures greater than 0.38:

$$\text{Log } P_r^* = (\text{Lob } P_r^*)^{(0)} + w(\text{Log } P_r^*)^{(1)} \quad \text{at constant } T_r \quad (2.1)$$

where:

$$(\text{Log } P_r^*)^{(0)} = C - 1.192 \text{ B} \qquad (2.2)$$

$$(\text{Log } P_r^*)^{(1)} = 4.93 \text{ B}$$

$$A = \frac{36}{T_r} - 35 - T_r^6 + 96.73 \text{ Log } (T_r)$$

$$B = \text{Log } (T_r) - 0.03644$$

$$C = 7 \text{ Log } (T_r) - 0.118 \text{ A}$$

CHAPTER III

"EXPERIMENTAL APPARATUS"

The apparatus employed was the same as constructed by Diab (4), ex-
cept for a slight modification in the sample cell and in the pressure
gauges set up. The over all schematic diagram of the original design of
the apparatus (1) is shown in Figure 1. Figure 2 shows the modified ver-
sion of the same design and its major parts are as follows:

Constant Temperature Bath

A model "No. 1 NB-3329" Cylindrically shaped bath made by Colora
Company in West Germany, was used. It is equipped with a built-in elec-
tric stirrer, with a thermostate and with a variable wattage immersion
type electric heater. The heating medium used is silicone oil SF-96
which has a flash point of $\approx 570^{\circ}F$. This oil is a product of General
Electric Company.

Potentiometer

A Volt Potentiometer model No. 8687, made by Leeds D Northup Com-
pany was used. It has two ranges of "x1.0v Range" and "x0.1v Range".
The former which was used for all temperature measurements, has a range
of 0.0 to 0.1601 volts with the smallest division $5\mu V$ adjustable to 0.1
volts. Its' limits of error are 0.04 percent of +3 reading.

Venting Valve

Pressure Gauge

Filling Cell

Potentiometer

Thermocouple

Silicon Oil

To Vacuum Pump

Constant Temp. Bath

Sample Cell
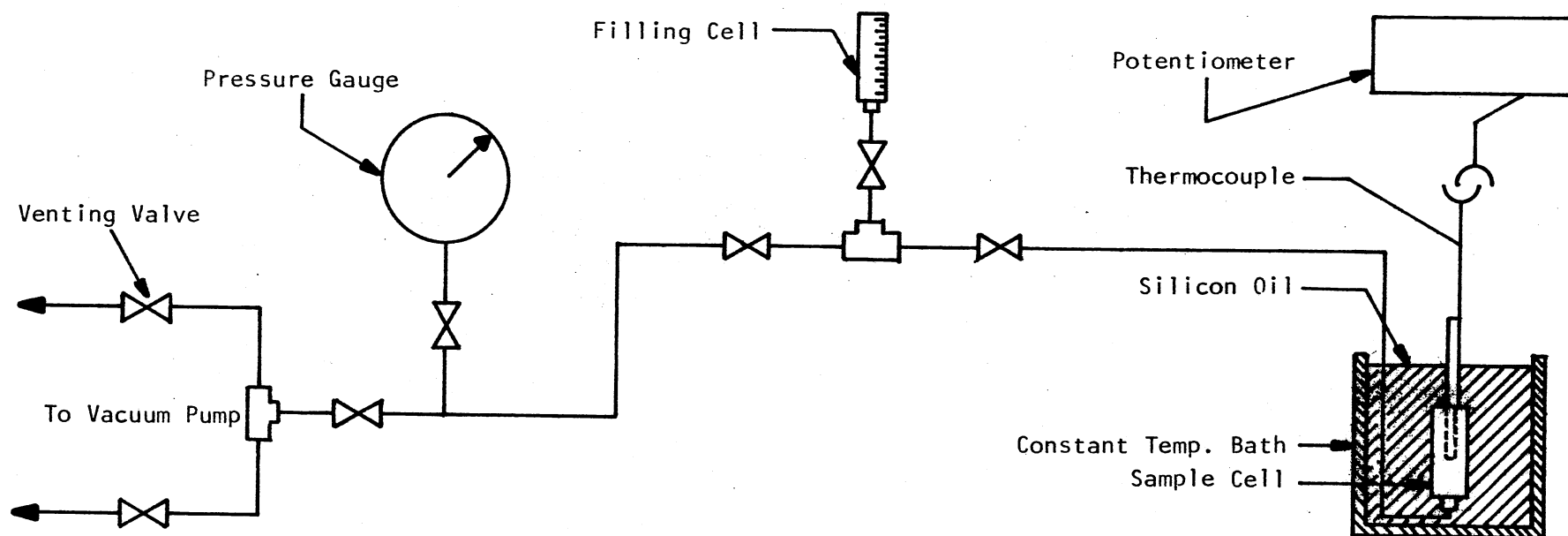
Figure 1. Overall Schematic Diagram of Original Design
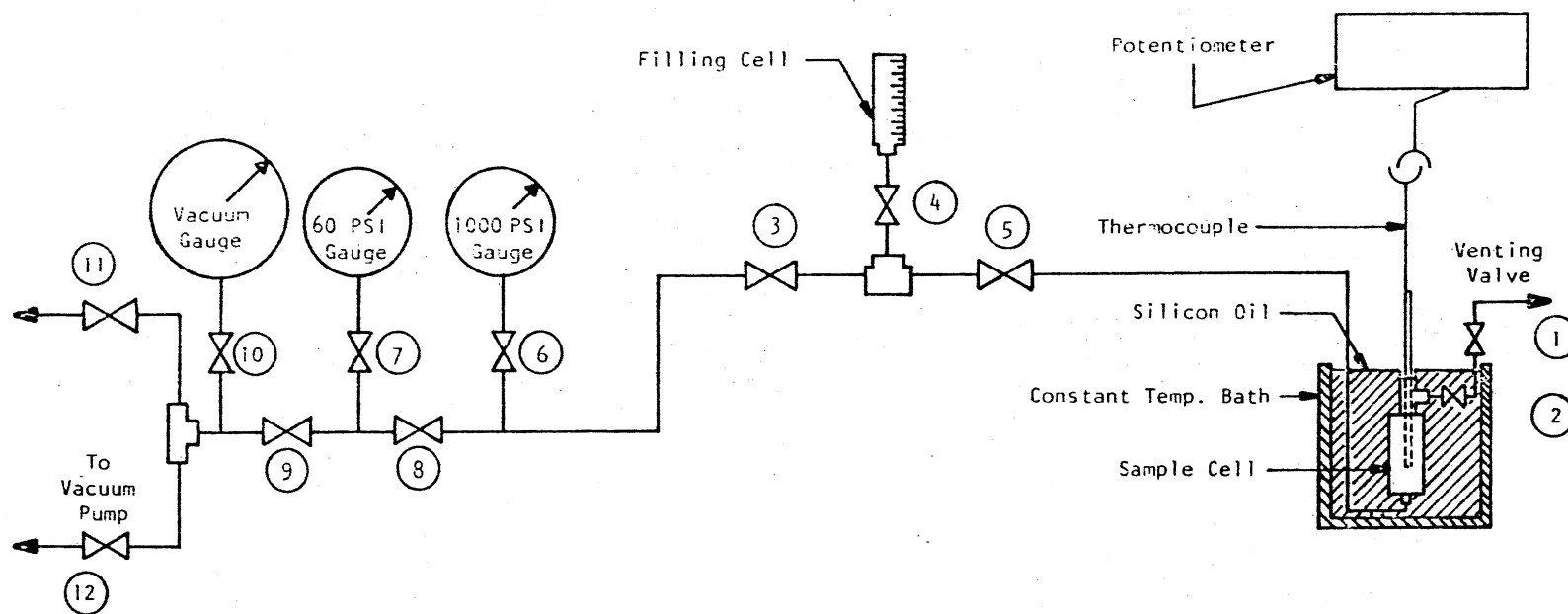
Figure 2. Overall Schematic Diagram of Modified Design

"Vacuum Pump"

A model No. 60482-0 Duo-Seal Vacuum Pump was used. It was made by
W. M. Welch Scientific Company. This particular model is equipped with
an electric motor which has a power of 1/3 H.P.

Sample Cell and Thermocouple

A model No. 2HD30 Stainless Steel Cell, made by Hoke Company, and
with a capacity of 33.3 ml., was used. On the top end of the cell a 3
way junction was installed, through which a chromel-alumel-type K thermo-
couple, and a venting valve are fixed. The thermocouple was made by
Omega Engineering Inc. of Connecticut.

Pressure Gauges

Three different pressure gauges were connected in series. The first
one is "Roylyn" 1000 psi Direct Drive gauge with 2 psi subdivisions and
0.1 percent accuracy.

The second is "Roylyn" 60 psi Direct Drive compound gauge, with 0.25
percent accuracy. It has a vacuum scale with 1" of Hg subdivisions and
above atmoshperic pressure scale of 0.2 psi subdivisions.

The third is "Matheson" vacuum gauge with 5 mm Hg absolute sub-
divisions.

The following table shows a list of the chemicals used in this work
which were made available by "Fluid Properties Research Inc."

TABLE 1

CHEMICALS USED IN THIS WORK

Name of Chemical as it Appeared on Bottle	Manufacturer	Purity
Normal Heptane	Phillips Pet. Comp.	99.69%
Normal Octane	Phillips Pet. Comp.	99.0 %
Methyl tert-Butyl Ether	Dow Chem. Comp.	None
Tripropylene Glycol	Alfa Products, Thikol Ventron Division	None
1, 2-Propanediol	Alfa Products, Thikol Ventron Division	None

CHAPTER IV

EXPERIMENTAL PROCEDURE

This chapter as a matter of organization could be subdivided into
two parts; (1) Calibration of the measuring equipment and (2) Operation
of the experimental apparatus.

Calibration of the Measuring Equipment

Pressure Gauges Calibration

The Matheson vacuum gauge was calibrated against a Mercury manometer.
An abs average deviation of 0.2503 psi was found. Calibration results
are tabulated on Table IX, Appendix A. The following straight line equa-
tion was calculated which relates the actual pressure in psia to the in-
dicated pressure in mm Hg:

$$P_{act} \text{ (psia)} = (0.019392) \ P_{IND} \text{(mm Hg)} - 0.2722$$

The Roylyn "60 psig" compound gauge was calibrated against the dead
weight load tester, 2400 HL Ruska Pressure System (15). The calibration
results obtained are tabulated in Table X, Appendix A. An absolute aver-
age deviation of 0.043 psi was found. And the following straight line
equation was calculated for this particular gauge:

$$P_{act} \text{ (psi)} = (1.001172) \ P_{IND} \text{(psi)} - 0.07033$$

The vacuum range of the 60 psig "Roylyn" gauge, was calibrated against a mercury manometer. An average deviation of -0.2076 psi was found. Calibration results were tabulated in Table XI, Appendix A. The following straight line equation was calculated for the vacuum scale:

$$P_{act} \text{ (psi)} = (0.4999) [P_{atm}(\text{"Hg"}) - P_{IND}(\text{"Hg"})] + 0.0737$$

The Roylyn "1000 psig" gauge was calibrated on April 4, 1980, just one before it was actually used in this work. This calibration results are tabulated in Table XII, Appendix A. An abs average deviation of 1.223 psi was reported. The following straight line equation was calculated for this particular gauge also:

$$P_{act} \text{(psi)} = 1.00124 \; (P_{IND}\text{(psi)}) + 0.60425$$

Thermocouple Calibration

Only one chromel-alumel thermocouple was used during the entire period of this work. It was calibrated against the N.B.S. calibrated platinum resistance thermometer, Serial No. 1761202 made by Leeds D. Northrup. The same volt potentiometer described in the previous chapter as apart of the apparatus, was also used in this calibration. The temperature range covered was from 124 to 440°F.

Two quadratic fitting equations were evaluated. The coefficients were obtained by a computer program courtesy of Fluid Properties Research Inc. Each equation gives a relation between the actual and the indicated temperature in terms of both C^o and F^o scales. Calibration results a long with the computer output are tabulated in Table XIII and Table XIV, Appendix A respectively. The C^o scale quadratic equation is as follows:

$$T_{act}(C^O) = 0.92006 + (0.97393) \; T_{IND}{}^1 + 9.4327x/o^{-5} \; T_{IND}{}^2$$

Avg abs percent deviation is 0.18.

The F^O scale quadratic equation is as follows:

$$T_{act}(F^O) = 2.5416 + (0.97060) \; T_{IND} + (5.2364 \; x/o^{-5}) \; T_{IND}{}^2$$

Avg abs percent deviation is 0.15.

Operation of Experiment Apparatus

As shown on Figure 2 in the last chapter, all values have been as-signed numbers to simplify the presentation of this section. The experi-mental operation of the apparatus consists of three distinct steps; (1) Cleaning of the system; (2) Charging the sample in the system; and (3) Gathering the experimental data.

Cleaning of the System

This could be achieved by purging the system with acetone at least two times, followed each time by passing nitrogen gas to drive out most of acetone vapors in the system, making sure that Matheson Gouge's valve no. 10 was closed and that the gas pressure does not exceed the upper limits of either one of the other two gauges.

Charging the Sample in the System

First the filling cell was filled by about 100 m/. of a degasified portion of the sample. Then valves no. 1, 2, 4, and 11 were closed and the vacuum pump line was connected to valve no. 12 for about 15 minutes making sure that we are achieving the best vacuum we possibly could get from the pump. If that was not so, then the pump oil had to be replaced.

Second, the vacuum line was connected to valve no. 1 after valves 12 and 5 were closed. Then valve 21, 2, and 1 were opened simultaneously allowing the sample to charge in the sample cell until the liquid sample was seen in a continuous stream in the transparent vacuum line. When that happened valves 4, 2, and 1 were tightly closed and valve 5 was opened.

Gathering the Experimental Data

The themostrat was set to an initial setting. Then the electric heater and stirrer were turned on. After the bath temperature, and the pressure readings were stable for a sufficient period of time, the potentiometer and gauge readings were taken. Whenever the vapor pressure approaches the upper limit of any of the gauges, the corresponding valve of that particular gauge was closed.

CHAPTER V

EXPERIMENTAL RESULTS

Methyl-Tert-Butyl-Ether (M.T.B.E.)

Table II gives the experimental data obtained in this work in comparison to those interpolated data obtained by Ambrose et. al., (1). An abs average percent deviation of about 2.0 percent was found. The data are plotted in Figure 3.

N-Heptane

Table III gives the experimental and calculated data for n-heptane. A comparison was made between the experiment data and the corresponding values interpolated and calculated from Jordan (7) and A.P.I. method respectively. An abs average percent deviation of about 6.4 and 4.7 percent was found between the experimental data obtained in this work, and those obtained via Jordan and the A.P.I. method respectively. The data are plotted in Figure 4.

N-Octane

Table IV gives the experimental and calculated data for n-octane which were plotted in Figure 5.

An abs average percent deviation of 4.6 and 6.4 was found in comparison to the calculated A.P.I. values and to Jordan's (7) interpolated data.

TABLE II

COMPARISON OF VAPOR PRESSURE DATA FOR
METHYL-BUTYL-ETHER

Temp. (of)	Exp. P* "psia"	P* Ambrose (1) psia	Percent Dev.
216.570	58.31	55.82	4.46
269.430	109.8	107.2	2.43
311.160	170.3	168.0	1.37
339.610	224.3	220.0	1.96
375.000	304.3	300.6	1.23
448.320	534.3	527.5	1.29
470.000	620.3	611.6	1.42

*abs avg percent deviation ≈ <u>2.023</u> percent
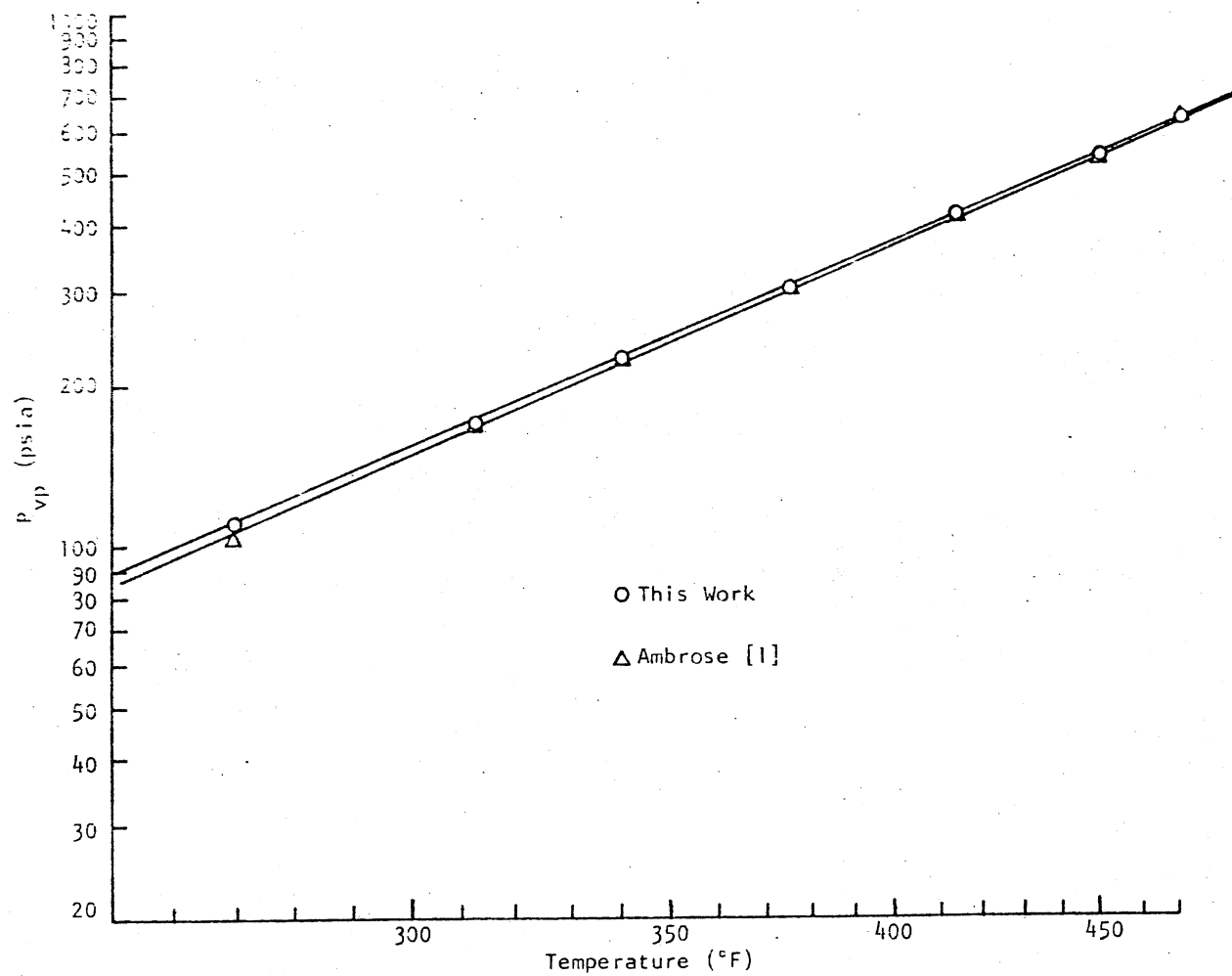
Figure 3. Methyl-Tert-Buty-Ether

TABLE III

COMPARISON OF EXPERIMENTAL VAPOR PRESSURE DATA
FOR N-HEPTANE

Temp. (of)	Exp. P^* "psia"	P^* A.P.I. "psia"	P^{**} Jordan (1) "psia"	Percent Dev. From A.P.I.	Percent Dev. From Jordan
207.870	16.10	14.43	14.41	11.6	11.7
230.478	22.20	20.53	20.32	8.13	9.25
264.609	35.02	32.98	32.79	6.19	6.80
290.304	47.80	47.01	45.67	1.68	4.66
308.652	59.10	58.81	57.11	0.493	3.49
236.870	72.40	72.61	70.51	-0.289	2.68

*abs average percent deviation from A.P.I. = 4.7

**abs average percent deviation from Jordan = 6.4
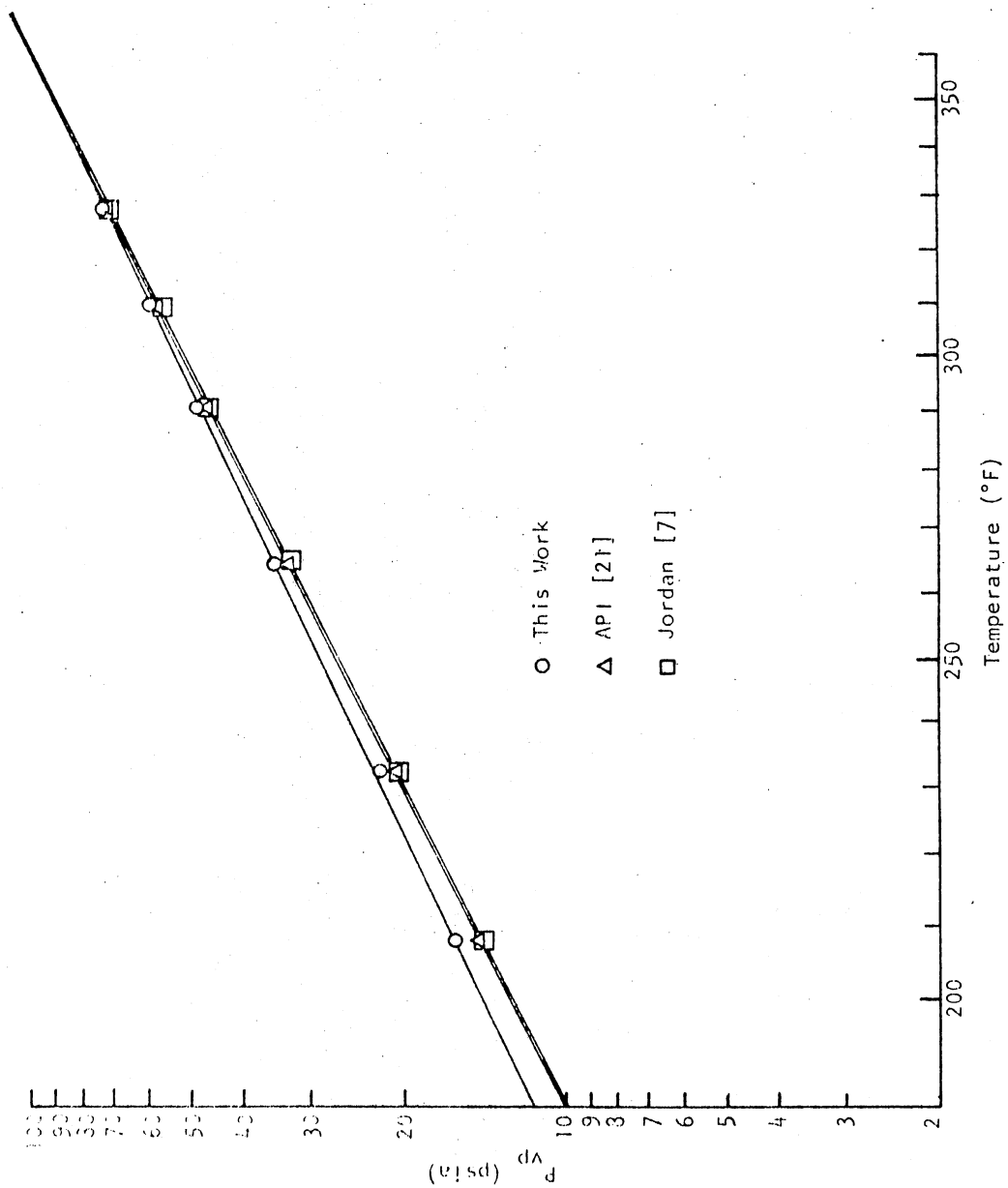
Figure 4. N-Heptane

TABLE IV

COMPARISON OF EXPERIMENTAL VAPOR PRESSURE
FOR N-OCTANE

Temp. (of)	Exp. P "psia"	P* A.P.I. "psia"	P** Jordan (7) "psia"	Percent Dev. From A.P.I.	Percent Dev. From Jordan
276.700	22.57	19.57	19.34	15.3	16.7
312.000	34.37	31.81	31.08	8.05	10.6
347.000	50.97	49.02	47.74	3.98	6.77
376.000	68.87	67.96	66.30	1.34	3.88
421.550	109.9	108.2	106.4	1.60	3.29
460.230	156.4	154.7	153.1	1.10	2.16
521.200	259.4	258.0	256.6	0.543	1.09

*abs average percent deviation from A.P.I. = 4.6

**abs average percent deviation from Jordan = 6.4
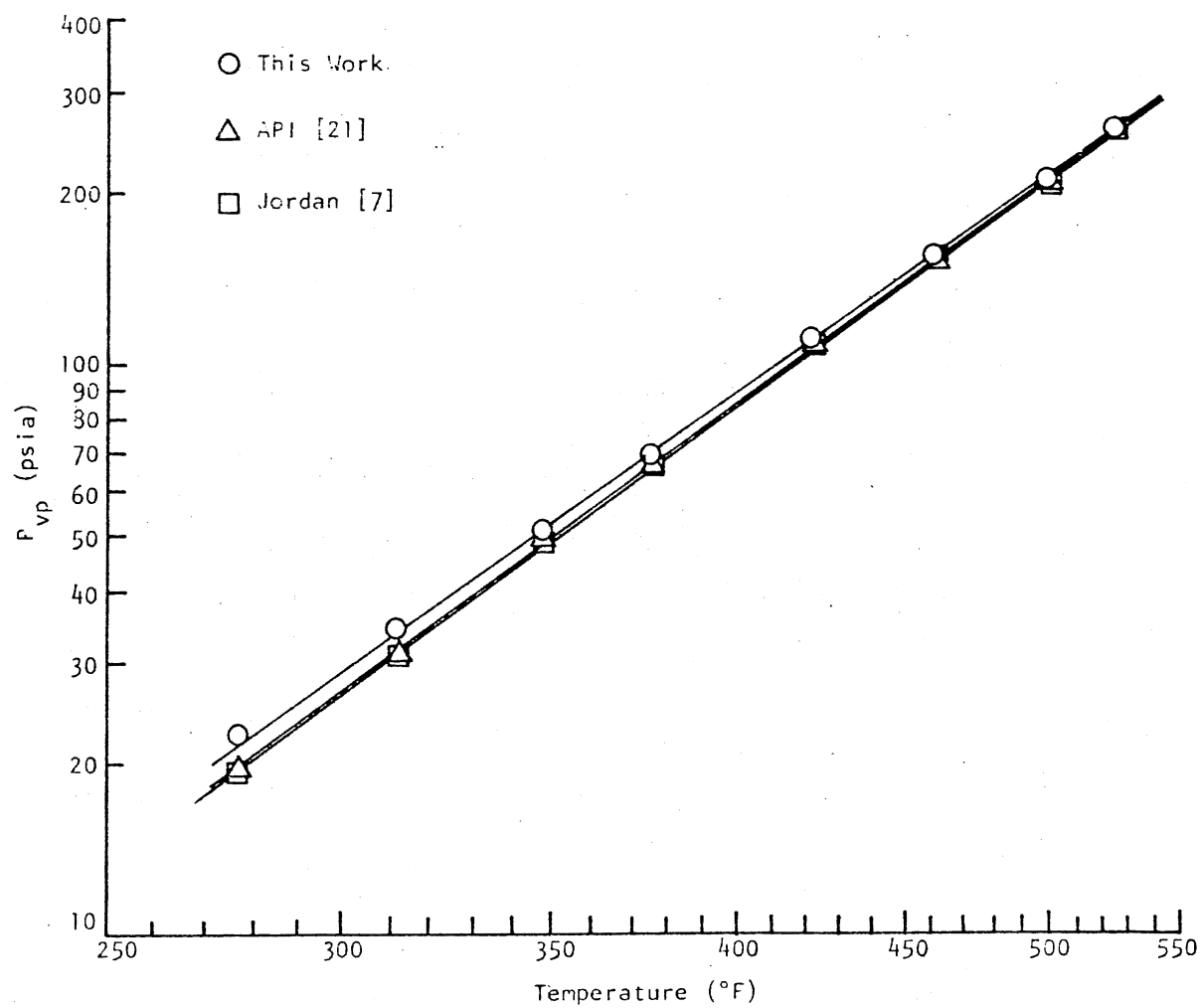
Figure 5. N-Octane

1, 2-Propanediol

Table V gives the experimental and interpolated data reported by Jordan (7) and Reid (14) respectively covering below atmospheric pressures. Experimental data were obtained after pump was changed. An abs average percent deviation of about 1.2 percent was found between experimental data and what have been reported by Jordan and Reid. The data are plotted in Figure 6.

Tri-Propylene Glycol (T.P.G.)

Tables VI and VII give experimental data for T.P.G. obtained in this work, before and after the pump was changed respectively. A comparison between the experimental data and corresponding interpolated values reported by Jordan (7). All data are plotted in Figure 7.

TABLE V

COMPARISON OF EXPERIMENTAL VAPOR PRESSURE
DATA FOR 1, 2-PROPANEDIOL
(AFTER PUMP WAS CHANGED)

Temp. (of)	Exp. P^* "psia"	P^* Jordan (7) "psia"	P^{**} Reid (14) "psia"	Percent Dev. From Jordan	Percent Dev. From Reid
208.087	0.4065	0.4123	0.4105	-1.407	-0.974
275.864	2.224	2.226	2.256	-0.090	-1.418
311.773	4.721	4.824	4.897	-2.135	-3.594
342.609	8.910	8.868	8.986	+0.474	-0.846
356.261	11.576	11.442	11.577	+7.171	-0.009
366.273	13.932	13.720	13.863	+1.545	-0.498

* abs average percent deviation from Jordan = 1.137

** abs average percent deviation from Reid = 1.223
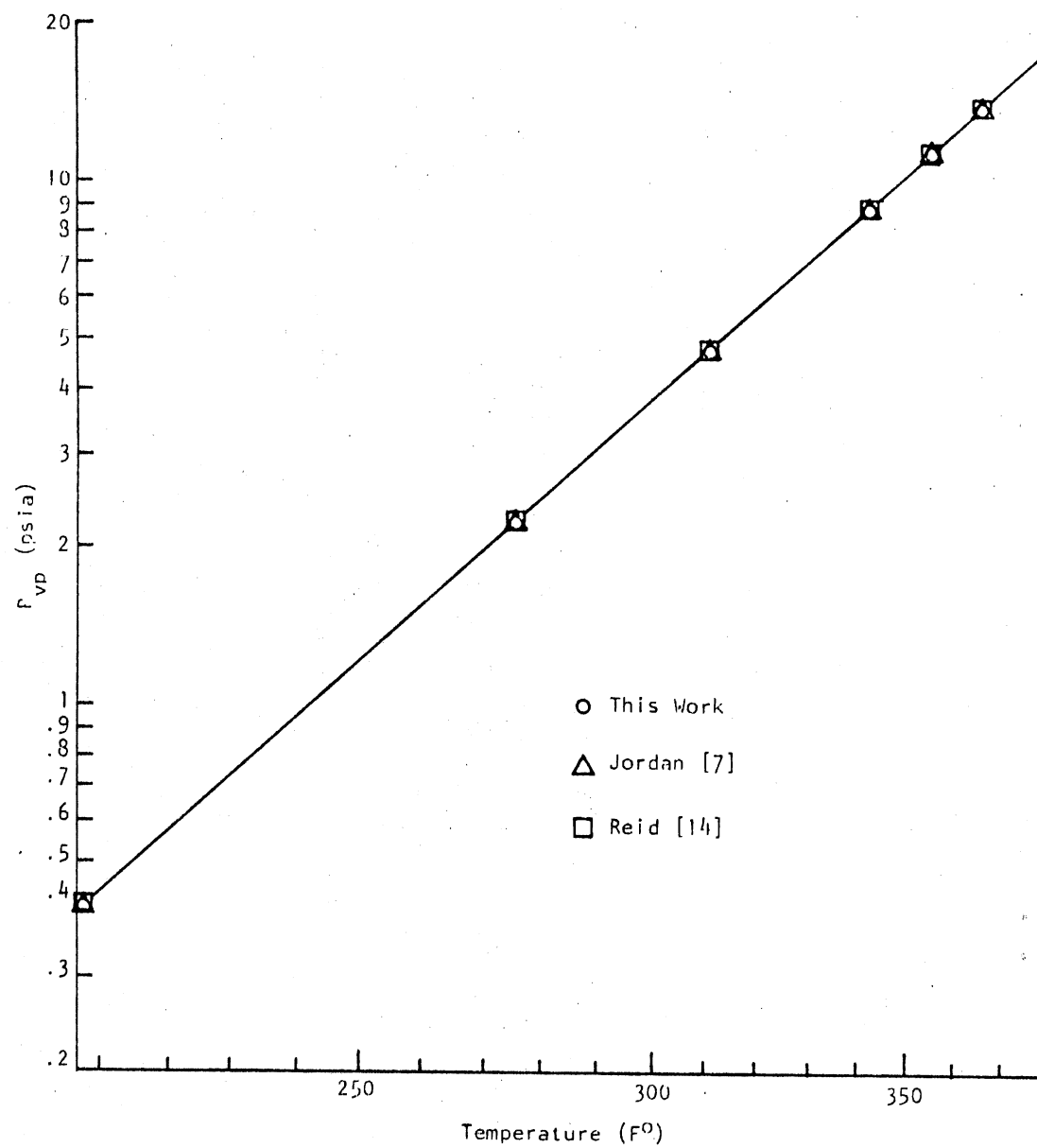
Figure 6.   1-2-Propanediol

TABLE VI

COMPARISON OF EXPERIMENTAL VAPOR PRESSURE
DATA FOR TRIPROPYLENE GLYCOL
(BEFORE PUMP WAS CHANGED)

Temp. (of)	Exp. P^* "psia"	P^* Jordan (7) "psia"	Percent Dev. From Jordan
356.304	3.634	0.9910	266
408.000	6.876	2.679	157
431.682	8.939	4.065	120
448.680	10.90	5.412	101
479.000	15.46	8.790	76
494.091	18.26	11.05	65

* abs average percent deviation = 131

TABLE VII

COMPARISON OF EXPERIMENTAL VAPOR PRESSURE
DATA FOR TRIPROPYLENE GLYCOL
(AFTER PUMP WAS CHANGED)

Temp. (°F)	Exp. P^* "psia"	P^* Jordan (7) "psia"	Percent Div. From Jordan
327.174	1.512	1.534	− 1.434
365.318	2.947	1.189	+147.9
439.273	8.047	4.626	+ 73.9
458.410	10.355	6.345	+ 63.2
474.296	12.740	8.167	+ 56.0

* abs average percent deviation from Jordan = 69
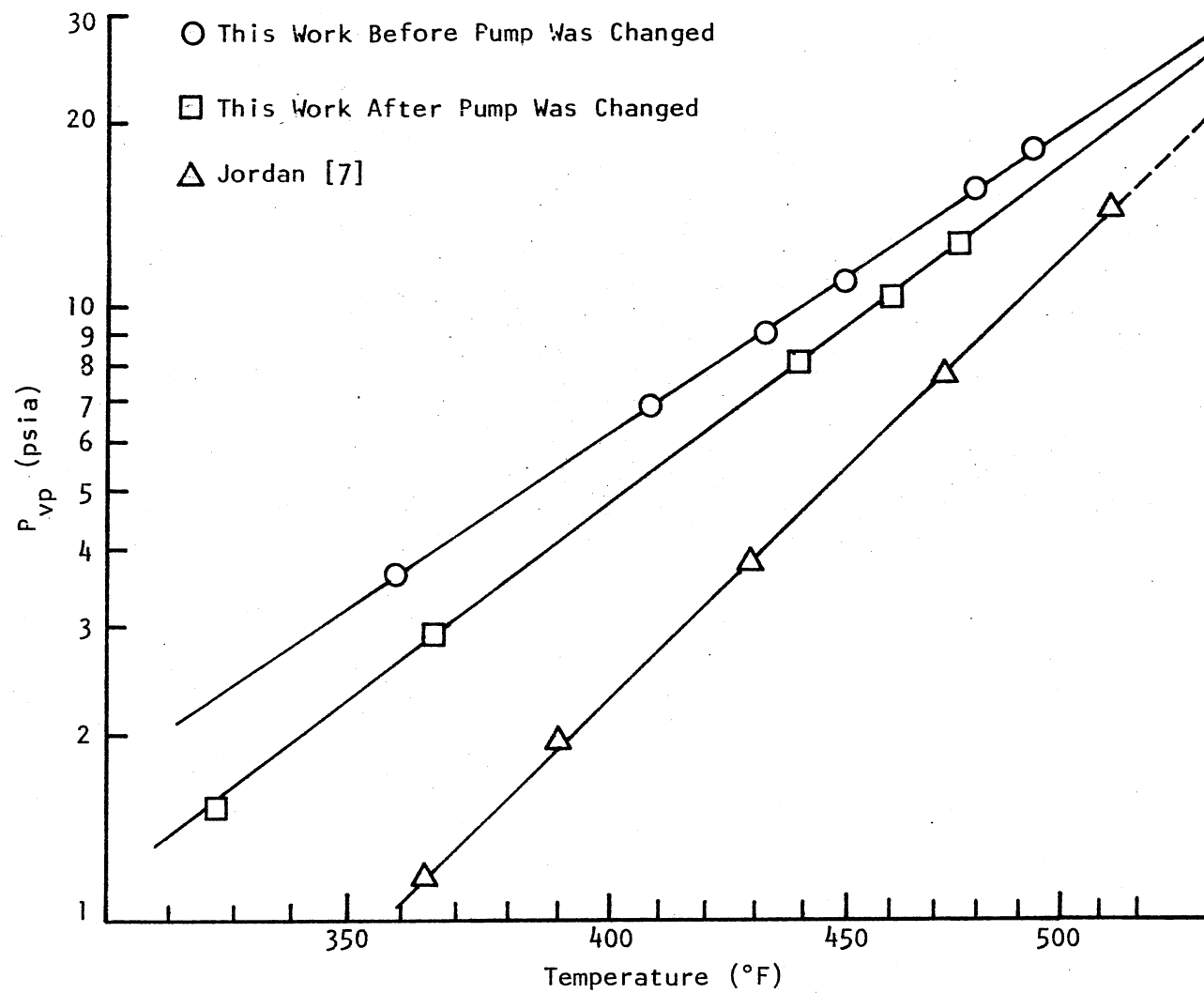
Figure 7. Tripropylene Glycol

CHAPTER VI

DISCUSSION OF RESULTS

Vapor pressure measurements for M.T.B.E., n-heptane, and n-octane were within an abs average deviation of 2 to 4 percent from what had been calculated or reported in the literature. This is a very significant deviation since those measurements were made well above atmoshperic pressure. As a result, an investigation was carried out to explain the cause of such a large deviation. It was believed then, that the inability of the pump to evacuate the system below an absolute pressure of about 25 mm Hg, was largely responsible for the observed large deviation.

Consequently, the pump was exchanged with another Duo seal pump model no. 12102, which has a free air displacement of 160 liters/mm.

After the pump was changed, vapor pressure measurements were obtained for 1, 2-propanediol. The experimental results came within 1 percent of what have been reported by Jordan (7), in spite of the fact that all measurements were made below atmospheric pressure.

Finally, experimental vapor pressure measurements were obtained for tri-propylene glycol before and after the pump was changed. Eventhough the results were improved as a result of the pump change, the deviation from those reported by Jordan was still considerably large. This casts some doubt on the quality of the material used since a separate normal boiling point determination under atmospheric conditions came out to be about $25^{\circ}F$ below that reported by Jordan (7).

CHAPTER VII

CONCLUSION AND RECOMMENDATIONS

Conclusion

The purpose of this work was achieved by obtaining vapor pressure measurements of 5 pore compounds, using an existing apparatus designed and constructed by Diab (4). Poor results were obtained for M.T.B.E., n-heptane, and n-octane due to the in efficiency of the vacuum pump. Good results were obtained for 1, 2-propanediol when the vacuum pump was changed.

Table VIII gives a summary of abs average deviations from the published literature. And it also gives extrapolated normal boiling points calculated thru the use of straight line equations developed for each compound by statistical means. These normal boiling points were compared to what have been reported in the literature.

Recommendations

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

1. For below atm pressure measurements the higher degree of vaccum one can achieve, the less deviation. As a result a periodic change of pump oil is recommended a long with the use of ice traps to condense the volatile vapors before they contaminate the oil.

2.   No attempt should be made to flash mixtures in the apparatus, since this can alter the compositions.

3.   A more accurate pressure measuring device with insulator to prevent liquid from entering the gauge which results in difficulty as far as cleaning the system. This is recommended especially for below atm pressure measurements.

4.   Purity of chemicals has to be somehow checked before starting to determine the magnitude of any impurity and its contribution to the overall systamatic error associated with the use of the apparatus.

TABLE VIII

SUMMARY OF ABS AVERAGE PERCENT DEVIATION AND NORMAL BOILING
POINTS OBTAINED IN THIS WORK

Chemical or Compound Name	abs-avg Percent Dev.	N.B.P. of This Work	N.B.P. of Literature	Ref. No.
Methyl-tert-Butyl Ether	2.02	124.5[4]	131.2	(1)
N-Heptane	4.7-6.4	201.9[4]	209.2	(21), (7)
N-Octane	4.6-6.4	247.8[4]	258.3	(12), (7)
1, 2-Propanediol	1.14-1.22	370.2[4]	370.8	(7), (14)
Tri-propylene Glycol[1]	131	475.0	512.9[3]	(7)
Tri-propylene Glycol[2]	69	486.9	512.9	(7)

[1] Before pump was changed

[2] After pump was changed

[3] $487.9^{\circ}F$ was determined in the lab

[4] Extrapolated

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APPENDIX A

EQUIPMENT CALIBRATION

TABLE IX

"CALIBRATION OF MATHESON" 0-760 "MM HG USING HG MANOMETER"

Manom High In Hg	Manom Low In Hg	Total In Hg	ΔP Atmos. Press Total In Hg	ΔP In P.S.I.	Gauge Abs. mm Hg	Gauge P.S.I.	Dev.
+14.45	-14.25	28.70	0.190	0.0933	21.50	0.4157	+0.3224
+12.765	-12.585	25.35	3.540	1.7388	104.00	2.0110	+0.2722
+11.800	-11.620	23.42	5.470	2.6867	151.50	2.9295	+0.2428
+10.725	-10.550	21.275	7.615	3.7403	206.00	3.9834	+0.2431
+ 8.850	- 8.675	17.525	11.365	5.5822	301.50	5.8301	+0.2478
+ 6.900	- 6.705	13.650	15.24	7.4855	398.50	7.7057	+0.2202
+ 4.900	- 4.750	9.650	19.24	9.4502	501.50	9.6974	+0.2472
+ 2.950	- 2.825	5.7750	23.115	11.3535	597.50	11.5538	+0.2002
+ 1.870	- 1.750	3.6200	25.2700	12.4120	653.50	12.6366	+0.2246
+ 0.950	- 0.850	1.800	27.0900	13.3060	702.00	13.5745	+0.2685
+ 0.05	+ 0.05	0.000	28.89	14.1901	747.50	14.4543	+0.2642

Atmoshperic pressure = 28.89" Hg

Slope = 1.00285

Average Deviation = -.2503

Intercept = 0.2722

$$P_{actual}(P.S.I.) = (0.019392) \, P_{EXP}(mm \, Hg) - 0.2722$$

TABLE X

"CALIBRATION OF 60 PSIG ROYLYN PRESSURE
GAUGE USING DEAD WT TESTER"

Dead Wt lbs	Gauge Reading PSIG	Dev.
0.0	0.00	0.00
10.00	10.03	+0.03
14.00	14.12	+0.12
20.00	20.10	+0.10
24.00	24.07	+0.07
30.00	30.03	+0.03
36.00	36.05	+0.05
40.00	40.00	0.00
50.00	49.97	-0.03
60.00	60.00	0.00

Abs average deviation = 0.043 psi

$$P_{act}(psi) = (1.001172) \, P_{IND}(psi) - 0.07033$$

TABLE XI

"CALIBRATION OF THE VACUUM REGION SCALE OF THE ROYLYN "60" PSI" GAUGE USING HG MANOMETER

Manom High In Hg	Mandom Low In Hg	Total In Hg	ΔP Atmos. Total In Hg	ΔP In P.S.I.	Gauge Reading "Hg	Gauge "Hg Atm-Reading	Gauge P.S.I.	Dev.
14.57	-14.30	28.87	0.2200	0.1081	28.95	0.140	0.0688	-0.0393
12.75	-12.55	25.30	3.790	1.8616	25.65	3.44	1.6897	-0.1720
10.48	-10.30	20.78	8.31	4.0817	21.10	7.98	3.9196	-0.1621
8.95	- 8.78	17.73	11.36	5.5798	18.00	11.09	5.4472	-0.1326
7.08	- 6.90	13.98	15.11	7.4217	14.35	14.74	7.2399	-0.1818
6.04	- 5.88	11.92	17.17	8.4335	12.30	16.79	8.2469	-0.1867
5.05	- 4.88	9.93	19.16	9.4109	10.50	18.59	9.1310	-0.2799
4.15	- 4.00	8.15	20.94	10.2852	8.65	20.44	10.0397	-0.2456
3.04	- 2.90	5.94	23.15	11.3707	6.50	22.59	11.0957	-0.2751
1.91	- 1.80	3.71	25.38	12.4661	4.20	24.89	12.2254	-0.2407
0.05	+ 0.05	0.00	29.09	14.2883	0.750	28.34	13.9200	-0.3684

Atmospheric pressure = 29.09" Hg

Slope = 1.01775

Average Deviation = -0.2076 psi

Intercept = 0.0737

$$P_{actual} \text{ (P.S.I.)} - (0.4999) \ [P_{atm}(Hg) - P_{IND}(\text{"Hg})] + 0.0737$$

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TABLE XII

"CALIBRATION OF (0-1000 PSI) ROYLYN AGAINST MANSFIELD D. GREEN D.W.G"

Applied Pressure Lbs	Indicated Pressure	Dev.
0.00	0.00	0.00
100.00	99.80	-0.20
200.00	200.00	0.00
300.00	298.00	-2.00
400.00	398.50	-1.50
500.00	498.50	-1.50
600.00	598.00	-2.00
700.00	697.50	-2.50
800.00	798.00	-2.00
900.00	898.25	-1.750
1000.00	1000.00	0.00

Abs average deviation = 1.2227 psi

$$P_{act}(psi) = 1.00124 \ (P_{IND}(psi) + 0.60425$$

TABLE XIII

"CALIBRATION OF CHROMEL-ALUMEL THERMOCOUPLE USING THE NBS-CALIBRATED PLATINUM RESISTANCE THERMOMETER" "°F-SCALE"

No	Temp. °F Indicated T_{IND}	Temp. °F Actual T_{actual}	Temp. °F FIT	Percent Dev. *
1	125.0000	124.6087	124.6800	0.06
2	198.8478	198.0591	197.6100	0.22
3	282.1364	279.6116	280.5500	0.34
4	341.9091	340.7884	340.5200	0.08
5	375.3044	374.7860	374.1900	0.16
6	440.1304	439.5816	439.8800	0.07

* Average abs percent deviation = 0.15

$$T_{act}(°F) = 2.5416 + (0.97060) T_{IND} + (5.2364 \times 10^{-5}) T_{IND}^2$$

TABLE XIV

CALIBRATION OF CHROMEL-ALUMEL THERMOCOUPLE USING THE NBS CALIBRATED PLATINUM RESISTANCE THERMOMETER "$^\circ$C -SCALE"

No	Temp. $^\circ$C Indicated T_{IND}	Temp. $^\circ$C Actual T_{act}	Temp. $^\circ$C FIT	Percent Dev.*
1	51.6667	51.4493	51.4920	0.08
2	92.6932	92.25504	92.0080	0.27
3	138.9647	134.56199	138.0800	0.38
4	172.1717	171.5491	171.4000	0.09
5	190.7246	190.4366	190.1000	0.17
6	226.7391	226.4342	226.6000	0.07

* Average abs percent deviation = 0.18

$$T_{act}(^\circ C) = 0.92006 + (0.97393)\, T_{IND} + (9.4321 \times 10^{-5})\, T_{IND}^{2}$$

APPENDIX B

EXPERIMENTAL DATA

TABLE XV

VAPOR PRESSURE DATA FOR METHYL-TERTIARY-BUTYL-ETHER

Temp. °F	Exp. P "PSIA"	Temp. °R	$\frac{10^3}{T}$	Log P
216.570	58.310	676.240	1.4788	1.7657
250.740	86.310	710.410	1.4076	1.9361
269.430	109.810	729.100	1.3716	2.0406
311.610	170.310	771.280	1.2966	2.2312
339.610	224.310	799.280	1.2511	2.3509
375.000	304.310	834.670	1.1981	2.4833
413.000	412.310	872.670	1.1459	2.6152
448.320	534.310	907.990	1.1013	2.7278
470.000	620.310	929.670	1.0757	2.7926

Slope = -2.55878

Intercept = 5.54733

$$\text{Log } P = 5.54733 - \frac{2558.78}{T}$$

TABLE XVI

VAPOR PRESSURE DATA FOR N-OCTANE

Temp. $^\circ F$	Exp. P "PSIA"	Temp. $^\circ R$	$\dfrac{10^3}{T(R)}$	Log P
276.700	22.570	736.370	1.3580	1.3535
312.000	34.370	771.670	1.2959	1.5362
347.000	50.970	806.670	1.2397	1.7073
376.000	68.870	835.670	1.1967	1.8380
421.550	109.870	881.220	1.1348	2.0409
460.230	156.370	919.900	1.0871	2.1942
497.680	214.370	957.350	1.0446	2.3312
521.200	259.370	980.870	1.0195	2.4139

Slope = 3.147012   Corr-Coefficient = 0.9998

Intercept = 5.61532

$$\log P = 5.61532 - \frac{3147.012}{T}$$

TABLE XVII

VAPOR PRESSURE DATA FOR N-HEPTANE ABOVE
ATM. PRESSURE

Temp. °F	Exp. P "PSIA"	Temp. °R	$\frac{10^3}{T}$	Log. P
207.870	16.095	667.540	1.4980	1.2067
230.478	22.195	690.148	1.4490	1.3463
264.609	35.015	724.279	1.3807	1.5443
290.304	47.795	749.974	1.3334	1.6794
308.652	59.095	768.322	1.3015	1.7716
326.870	72.395	786.540	1.2714	1.8597

Slope = 2.880864   Corr-Coefficient = -0.9999

Intercept = +5.52151

$$\text{Log } P = 5.52151 - \frac{2880.864}{T}$$

TABLE XVIII

VAPOR PRESSURE DATA FOR TRIPROPYLENE GLYCOL AFTER PUMP WAS CHANGED

Temp. °F	Exp. P "PSIA"	Temp. °R	$\frac{10^3}{T}$	Log. P
327.174	1.512	786.844	1.2709	0.1795
365.318	2.947	824.988	1.2120	0.4694
439.273	8.047	898.943	1.1124	0.9056
458.41	10.355	918.079	1.0892	1.015
474.296	12.740	933.966	1.0707	1.105

Slope = -4.569065   Corr-Coefficient = -0.9998

Intercept = +5.9941

$$Log\ P = 5.9941 - \frac{4569.07}{T}$$

TABLE XIX

VAPOR PRESSURE DATA FOR "TRIPROPYLENE GLYCOL"
BEFORE PUMP WAS CHANGED

Temp. $°F$	Exp. P "PSIA"	Temp. $°R$	$\dfrac{10^3}{T}$	Log. P
356.304	3.6344	815.974	1.2255	0.56043
408.000	6.8762	867.670	1.1525	0.83735
431.682	8.9390	891.352	1.1219	0.95129
448.68	10.904	908.352	1.1009	1.0376
479.000	15.460	938.670	1.0653	1.1892
494.091	18.2600	953.761	1.0485	1.2615

Slope = -3.95385   Corr-Coefficient = -0.9995

Intercept = +5.39765

$$Log\ P = 5.39765 - \frac{3953.85}{T}$$

TABLE XX

VAPOR PRESSURE DATA FOR (1-2) PROPANEDIOL AFTER
PUMP WAS CHANGED

Temp. ^{O}F	Exp. P "PSIA"	Temp. ^{O}R	$\dfrac{10^3}{T}$	Log. P
208.087	0.4065	667.757	1.4976	-0.3909
275.864	2.224	735.531	1.3596	+0.2918
311.773	4.721	771.443	1.2963	+0.6740
342.609	8.910	802.279	1.2464	+0.9499
356.261	11.576	815.931	1.2256	+1.0636
366.273	13.932	825.943	1.2107	+1.1440

Slope = -5.39453   Corr-Coefficient = -0.9993

Intercept = +7.6675

$$\text{Log P} = 7.6675 - \frac{5394.53}{T}$$

APPENDIX C

DATA REPORTED IN LITERATURE

TABLE XXI

VAPOR PRESSURE DATA FOR TRIPROPYLENE GLYCOL REPORTED
BY JORDAN (7)

Temp. OF	Temp. OR	$\frac{10^3}{T}$	P^* "psia"	Log. P
364.280	823.950	1.2137	1.1602	0.0645
390.200	849.870	1.1767	1.9337	0.2864
428.360	888.030	1.1261	3.8674	0.5874
471.740	931.410	1.0736	7.7347	0.8884
512.960	972.630	1.0281	14.696	1.1672

Slope = -5.917342

Intercept = +7.2774

$$\text{Log } P^* = 7.2478 - \frac{5917.342}{T}$$

TABLE XXII

VAPOR PRESSURE DATA FOR (1-2) PROPANEDIOL REPORTED
BY JORDAN (7)

Temp. $^\circ$F	Temp. $^\circ$R	$\dfrac{10^3}{T}$	P^*"psia"	Log. P
181.760	641.430	1.5590	0.19337	-0.7136
205.52	665.190	1.5033	0.3867	-0.4126
269.60	729.27	1.3712	1.9337	0.2864
301.46	761.13	1.3138	3.8674	0.5874
334.58	794.25	1.2590	7.7347	0.8884
370.760	830.430	1.2042	14.696	1.1672

Slope = -5.30681   Corr. = -0.9999

Intercept = +7.5625

$$\text{Log. } P = 7.5625 - \frac{5306.81}{T}$$

TABLE XXIII

VAPOR PRESSURE DATA REPORTED BY JORDAN, FOR N-OCTANE

Temp. °F	Temp. °R	$\frac{10^3}{T}$	P^*"psia"	Log. P^*
258.260	717.930	1.3929	14.696	1.1672
306.860	766.530	1.3046	29.392	1.4682
385.160	844.830	1.1837	73.4800	1.8662
456.440	916.110	1.0916	146.96	2.1672
538.520	998.190	1.0018	293.920	2.4682

Slope = -3.31647   Corr-Coefficient = -0.9999

Intercept = +5.7903

$$\text{Log. } P^* = 5.7903 - \frac{3316.47}{T}$$

TABLE XXIV

VAPOR PRESSURE DATA REPORTED BY JORDAN (7) ABOVE ATMOSPHERIC PRESSURE FOR N-HEPTANE

Temp. $^\circ$F	Temp. $^\circ$R	$\dfrac{10^3}{T}$	P^*"psia"	Log. P
209.170	668.840	1.4951	14.696	1.1672
256.640	716.310	1.3960	29.3920	1.4682
330.260	789.930	1.2659	73.480	1.8662
397.040	856.710	1.1673	146.960	2.1672
477.500	937.170	1.0670	293.920	2.4682

Slope = -3.04302   Corr-Coefficient = -0.9999

Intercept = +5.7172

$$\text{Log. } P^* = 5.7172 - \frac{3043.02}{T}$$

APPENDIX D

CALCULATED DATA USING A.P.I.

TABLE XXV

A.P.I. CALCULATED VAPOR PRESSURE DATA FOR N-HEPTANE

Temp. (°F)	Temp. (°R)	T_r	A	B	C	P* Calcid "psia"
207.870	667.540	0.68654	1.53282	-0.21913	-1.32421	14.433
230.478	690.148	0.70979	1.19112	-0.19223	-1.18264	20.531
264.609	724.279	0.74489	0.78588	-0.17126	-0.98809	32.981
290.304	749.974	0.77132	0.55485	-0.13296	-0.85483	47.005
308.652	768.322	0.790191	0.42279	-0.11766	-0.76576	58.810
326.870	786.540	0.80893	0.31527	-0.10356	-0.68183	72.605

TABLE XXVI

A.P.I. CALCULATED VAPOR PRESSURE DATA FOR N-OCTANE

Temp. (°F) Exp.	Temp. °R	T_r	A	B	C	P^* Calcid "psia"
276.700	736.370	0.71922	1.07001	-0.18209	-1.12823	19.566
312.000	771.670	0.75370	0.70245	-0.14837	-0.94250	31.807
347.000	806.670	0.78789	0.43758	-0.11946	-0.77638	49.016
376.000	835.670	0.81621	0.27921	-0.09836	-0.65033	67.955
421.550	881.220	0.86070	0.11809	-0.06945	-0.46997	108.21
460.230	919.900	0.89848	0.04446	-0.04811	-0.33069	154.73
497.680	957.350	0.93506	0.01111	-0.02956	-0.20543	213.18
521.200	980.870	0.95803	0.00274	-0.01872	-0.13017	258.02

APPENDIX E

SAMPLE CALCULATIONS

SAMPLE CALCULATIONS

A.P.I. Generlized Method

One point sample calculation for n-heptane will be outlined here in detail, as follows:

Critical Properties of N-Heptane

$$T_c = 972.324 \ ^\circ R$$

$$P_c = 396.792 \ psia$$

$$W = 0.351$$

Evaluation of Constants

Let us take as an example:

$$T_{EXP} = 290.304 \ ^\circ F$$

$$\therefore T_{abs} = 290.304 + 459.67 = 749.974 \ ^\circ R$$

$$\therefore T_r = \frac{T_{abs}}{T_c} = \frac{749.974}{972.324} = 0.77132$$

$$A = \frac{36}{T_r} - 35.0 \ (T_r)^6 + 96.73 \ Log \ T_r$$

$$\therefore A = \frac{36}{0.77132} - 35.0 - (0.77132)^6 + 96.73 \ Log \ (0.77132)$$

$$\therefore A = 0.55485$$

$$\therefore B = \text{Log } T_r - (0.0364)(A)$$

$$B = \text{Log } (0.77132) - (0.0364)(0.86858)$$

$$B = -0.13296$$

$$\therefore C = 7 \text{ Log } T_r - 0.118 \text{ A}$$

$$C = 7 \text{ Log } (0.77132) - (0.118)(0.55485)$$

$$C = -0.85483$$

$$\therefore (\text{Log } P_r^*)^0 = C - 1.192 \text{ B}$$

$$(\text{Log } P_r^*)^0 = -0.85483 - (1.192)(-0.13296)$$

$$(\text{Log } P_r^*)^0 = -0.69634$$

$$\therefore (\text{Log } P_r^*)^1 = (4.93)(B)$$

$$(\text{Log } P_r^*)^1 = -0.65549$$

$$\therefore \text{Log } P_r^* = (\text{Log } P_r^*)^0 + W(\text{Log } P_r^*)^1 \quad \text{at const } T_r$$

$$\text{Log } P_r^* = -0.69634 + (0.351)(-0.65549)$$

$$\text{Log } P_r^* = -0.92642$$

$$P_r^* = 0.11846$$

$$\therefore P = (P_c)(P_r^*)$$

$$P_{calcid} = (396.792)(0.11846) = 47.005 \text{ psia}$$

$$\therefore \text{ Dev. } \% = \frac{P_{EXP} - P_{calcid}}{P_{calcid}} \times 100$$

$$\text{Dev. } \% = \frac{47.795 - 47.005}{47.005} \times 100 = 41.68\%$$

Nomenclature

$^\circ C$	Degrees centigrade
$^\circ F$	Degrees fehrnheit
"Hg	Inches of mercury
N.B.P.	Normal boiling point
P_{act}	Actual pressure (psia)
P_{atm}	Atmoshperic pressure (psia)
P_c	Critical pressure (psia)
P_{EXP}	Experimental vapor pressure (psia)
P_{IND}	Indicated pressure
P_r^*	Reduced vapor pressure
psia	Pounds per square inches absolute
psig	Pounds per square inches gauge
$^\circ R$	Degrees rankine
T_{abs}	Absolute temp. ($^\circ R$)
T_{act}	Actual temp. ($^\circ F$, $^\circ R$, $^\circ C$)
T_c'	Critical temp. ($^\circ R$)
T_{IND}'	Indicated temp. ($^\circ F$, $^\circ R$, $^\circ C$)
T_r'	Reduced temp.
W	Acentric factor (dimensionless)

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