EQUILIBRIUM STUDIES ON PURE COMPOUNDS:

NORMAL PROPYL ALCOHOL

by

THOMAS ARNOLD CROIL

Diploma in Chemical Engineering,
Royal Military College, 1956

B.A.Sc., University of British Columbia, 1957.

A THESIS SUBMITTED IN PARTIAL FULFILMENT
OF THE REQUIREMENT FOR THE DEGREE OF

MASTER OF APPLIED SCIENCE

in the Department

of

CHEMICAL ENGINEERING

We accept this thesis as conforming to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA
APRIL 1959.

ABSTRACT

Three grades of normal propyl alcohol have been purified
by several methods. The degree of purity has been established by
refractometric, ebulliometric, and viscometric measurements, the
best product being 99.65 volume % pure as measured by gas
chromatographic analysis.

A vapor-liquid equilibrium apparatus has been modified and
reconstructed in preparation for vapor pressure measurements of n-
propanol up to the critical point.

Several semi-empirical equations have been fitted to Young's
vapor pressure data for n-propanol with a view to their utilization
in presenting data on an homologous series or on a generalized basis.
In all cases the per cent difference between calculated and
experimental values was less than 2.0% with a maximum average
difference of 0.9%.

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Department of __Chemical Engineering__

The University of British Columbia,
Vancouver 8, Canada.

Date _____ __February, 1959.__ _____

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NOMENCLATURE

1. a, b, c, α, β = constants from the Biot Formula.

2. A, B, C, D = constants for the Riedel, Frost and Antoine Equations

T = temperature, $^{\circ}R$. (unless otherwise noted)

T_R = reduced temperature (T/T_C)

P = vapor pressure, p.s.i.a. (unless otherwise noted)

P_R = reduced pressure (P/P_C)

μ = viscosity, centipoise.

ACKNOWLEDGEMENT

The author wishes to express his appreciation for the financial assistance of the Dr. F. J. Nicholson Scholarship Fund and the National Research Council during the course of this research.

INTRODUCTION

Chemical engineering design requires an adequate knowledge of the physical properties of materials.

While accurate experimental data is desirable, its measurement is often difficult and time consuming. For this reason chemical engineering literature has recently emphasised methods of correlating and predicting such data, especially in the field of thermodynamic properties (1).

Because the thermodynamic properties of the normal alcohols, and their solutions, have been the subject of considerable interest in these laboratories (2,3), this investigation of the vapor pressure of normal propanol was undertaken.

Although Speers (4) has examined the thermodynamic network for n-propanol, his calculations were based primarily on the long standing data of Young (5). While these data are considered most reliable by all critical compilers, no measurements above the normal boiling point have been made since that time (fifty years ago).

In view of the increasing importance of highly accurate critical point measurements, it was considered worthwhile to re-explore the vapor-liquid relationship of pure normal propanol up to the critical point. This consideration was partly influenced by the availability of a high pressure apparatus designed for multi-component vapor-liquid equilibrium, but equally suitable for such a one component system.

The selection of normal propyl alcohol as the single component was also influenced by the fact that benzene-n-propanol had been selected as the first binary system to be studied in these laboratories (through a range of pressure). This made the purification, and hence, the physical properties of propanol of considerable interest. The need for such a study became even more apparent in light of the meagre data available in the literature on purification techniques. Moreover it was essential to ascertain to what extent impurities would affect the vapor pressure of normal propanol before confronting the more complex problem of their effect on a binary system. This consideration is particularly important near the critical point (5,6).

Vapor-liquid equilibrium data for one-component systems (vapor pressure data) have traditionally been correlated by theoretical, semi-empirical and

empirical equations in order to enhance their usefulness. While data on individual compounds is often considered separately, there is a growing tendency to consider families of compounds (7) and of course to determine a completely generalized approach (1, 8, 9). Re-evaluation of vapor pressure data on n-propanol can therefore be usefully considered in all of these categories.

This thesis, then, presents information on obtaining and measuring the purity of highly purified n-propanol, on the apparatus for making vapor pressure measurements up to the critical point, and on correlations for existing data on n-propanol that can be used for evaluation of new data that may be obtained.

LITERATURE REVIEW

1. Purification of Normal Propanol

According to Timmermans (10) and Speers (4) the only worker who has measured the vapor pressure of propanol above one atmosphere is Young (5). His first concern was with the purity of the liquid to be investigated.

> "The physical properties of a substance, especially at
> or near its critical point, may be seriously affected by
> the presence of even a very small quantity of impurity; it
> is therefore of the utmost importance that the
> purification of the substances investigated should be
> carried out with the greatest possible care." (5)

Almost all the purification methods for n-propanol involve some form of fractional distillation of a commercial grade.

There is, however, one method, as described by Timmermans and Delcourt (11), which is an exception. They stated that there are traces of isomers and homologues which cannot be removed by simple fractional distillation alone. In this case the purification was made by fractional crystallization of a solid propyl ester, like the acid phthalate. The ester was either reduced or hydrolysed back to the alcohol and the usual distillation carried out. However the purity of a Kahlbaum sample (as determined by density and the critical temperature of solution in petroleum (12)) was found to be the same before and after transformation into the phthalate.

Young's n-propyl alcohol (13, 14) was procured from Kahlbaum. It

was purified by fractional distillation and then distilled with benzene through a very efficient still head to remove the last traces of water. The specific gravity of this specimen at $0^o/4^o$ was 0.81923 and the boiling point 97.20^{o}C. at one atmosphere.

This requirement of high purity propanol for physical property measurements stimulated further experimentation with purification techniques in more recent years.

de Brouckers and Prigogine (15) purified technical grade propanol by refluxing over lime for five hours and then distilling through a one meter column.

Kretschmer (16) found that a commercial grade of n-propanol contained 1.5% allyl alcohol as its main impurity. He carefully purified the alcohol by treating one litre with 15 ml. of bromine. The alcohol was fractionally distilled with a small amount of potassium carbonate through a 75-plate column. The middle fraction of 600 ml. was dried with 1 gram of magnesium ribbon, freshly cleaned with steel wool, in a storage flask attached to a vacuum system. Before the flask was sealed, 1 gram of 2,4-dinitrophenyl hydrazine was added to react with any propionaldehyde formed by the bromine treatment that had not been removed by distillation.

Both Keyes and Winninghoff (17) and Kraus and Bishop (18) dried propyl alcohol with metallic sodium and fractionally distilled.

Goldschmidt and Thomas (19) dried 1-propanol with aluminum amalgam and, to remove basic impurities, distilled over sulfanilic or tartaric acid.

Berner (20) boiled n-propanol with lime for six hours and after distilling warmed the middle fraction with calcium hydride in a stream of hydrogen.

Other workers who purified propanol include Lund and Bjerrum (21) and Brunel, Crenshaw and Tobin (22).

The main criterion for purity is considered to be the constancy of vapour pressure (5, 6) when the liquid is evaporated, or the vapor condensed, since impurities usually divide themselves unequally between liquid and vapor.

Wullner and Grotrian (23) found appreciable differences in pressure in the interval between the condensation of the first drop of liquid from the vapours of several organic liquids and the disappearance of the last bubble

of vapor, and these were shown by Tammann (24) to be due to impurities.
Tammann found that 0.0001 part of benzene in water was enough to cause an
inconsistency in pressure during evaporation or liquifaction, the vapor
pressure depending on the volume of the vapor phase. Constancy of vapor
pressure is, therefore, an extremely sensitive test of purity, far exceeding
boiling point in delicacy (6). A test of purity is to evaporate the liquid
by pumping off vapour until only one twentieth the volume of liquid remains,
when the vapor pressure should be unchanged (25). Another test is the
constancy of temperature during freezing (26).

Young (5) embraced these principles of purity and added others.
Amongst these he required close agreement between physical constants of two
different specimens of the same liquid.

While Weissberger (27) makes no mention of any specific criteria,
Timmermans (10) states the criteria of purity to be the density to the fifth
place (28) and the critical temperature of solution in petroleum (12).

2. Apparatus

The high pressure apparatus available was designed by Whittle (29)
after apparatus described by Sage and Lacey (30). In general it can be
classed as a static or bomb equipment. The work by Young, longstanding and
still highly regarded for its accuracy, was carried out by a static method
also, and hence should be considered in more detail for comparison to the
method and apparatus intended here.

Young's apparatus consisted basically of a long wrought iron tube
having one end fitted with a screw plunger and the other end sealed. This
tube, firmly secured in the horizontal position, had three shorter tubes
running in a vertical direction from it. Three thickwalled glass tubes,
graduated in millimeters and carefully calibrated, had one end pressure
fitted into the iron tubes and the other end sealed. The first two served
as air manometers for different pressure ranges, and the third was the
experimental tube containing the liquid under investigation. The iron
apparatus was filled with mercury and pressures applied by means of the
plunger. The temperature around the experimental tube was controlled by
passing vapors from various boiling liquids through a jacket around the tube.

When the vapor in the jacketing tube was at the required temperature, readings of vapor pressure were taken with the liquid and vapor in the experimental tube occupying a series of different volumes.

Young corrected his calculated pressure, 1) for the difference in level of the mercury in the experimental tube and the manometer, 2) for the pressure of the column of unvaporized liquid, 3) for the expansion of the heated column of mercury, 4) if necessary, for capilliarity, 5) for the deviation of air in the manometer from Boyles Law.

He made no correction for the vapor pressure of mercury because he was of the opinion that evaporation through a long column of liquid was an exceedingly slow process.

The assumptions made by Young in this statement have been seriously studied in the past few years. Jepson and Rowlinson (31) have shown that a correction for the volatility of mercury should be applied to observed pressures of compressed gases where the confining fluid is mercury. The usual correction, when applied, was simply the substraction of the normal vapor pressure of mercury corrected for the hydrostatic pressure (the Poynting effect (32)). They showed that this is not an adequate treatment of the problem, as the mixture of mercury atoms and compressed gas cannot behave as an ideal mixture. An estimation of the intermolecular forces between mercury atoms and the added gas leads to values of the virial coefficients from which a revised correction can be computed, assuming that the system is at equilibrium. This revised correction can be considerably larger than the usual correction and is often of opposite sign.

While it is true that in most vapor pressure measurements liquid is present over the mercury surface, its density rapidly decreases as the critical point is approached. Young's theory may be quite valid for long columns of liquid over mercury but it seems that the height and density of the liquid would be quite important. Jepson and Rowlinson's correction would be particularly applicable near the critical point, in Young's type of measurement.

Kay (33) and later Bahlke and Kay (34) improved Young's apparatus and also carefully considered the corrections required. A similar method has also been employed previously in these laboratories for measurement of n-butanol (35).

The bomb apparatus of Whittle, described below, requires similar

corrections to those above. The correction having regard to mercury requires special notice since the mercury surface is many times larger than in the case of Young's apparatus.

3. Presentation of Vapor Pressure Data

Numerous equations, both empirical and theoretical, have been given relating vapor pressures, P, with absolute temperature, T (6, 36, 37, 38).

Young used the Biot Formula (39) to correlate his data on n-propanol.

$$\log P = a + b\alpha^t + c\beta^t \tag{1}$$

where $a = 4.479470$ $\quad\quad \log \alpha = 0.001641423$

$\quad\quad \log b = \bar{1}.3915059$ $\quad\quad \log \beta = \bar{1}.99657025$

$\quad\quad \log c = 0.5509601$ $\quad\quad t = T^{\circ}C - 20.$

The constants were calculated from pressures at 20, 80, 140, 200 and 260°C. (13). The agreement between calculated and experimental data was good, but the nature of the equation made it difficult to use. Other investigators (40) also found the formula inaccurate and it has subsequently fallen into dis-use.

Reid and Sherwood (38) have recently recommended the Riedel correlation (41) for most accurate work.

$$\log P_R = A - \frac{B}{T_R} + C \ln T_R + DT_R^6 \tag{2}$$

(Actually this is the relation that Riedel used as a basis for his single constant reduced vapor pressure equation). It has its disadvantage, however, in that the critical temperature and pressure must be known. In many cases the accuracy of these constants cannot be too heavily relied upon.

Thomson (36), in his well known review of 1946, recommends the use of two Antoine equations,

$$\log P = A - \frac{B}{T - C} \tag{3}$$

where P = vapor pressure, p.s.i.a.

T = temperature, $^{\circ}$R.

C = constant, $^{\circ}$R.

A,B = constants.

one up to $T_R = 0.8$ or 0.85 and the other from $T_R = 0.8$ to $T_R = 1.0$, for most accurate results. The disadvantage here, of course, is the necessity for two equations when only one is desired.

Among the more recent equations is that proposed by Frost and Kalkwarf (42),

$$\log P = A + \frac{B}{T} + C \log T + \frac{DP}{T^2} \tag{4}$$

in which they try to explain the reverse curvature of the plot of log P versus $\frac{1}{T}$ on the basis of the non-ideal behavior of the vapor together with the change in heat of vaporization with temperature.

This equation has been successfully used by Thodos (43) to consider the vapor pressures of a series of the normal paraffin hydrocarbons. Its usefulness here indicates the strong possibility of it playing a similar role for the n-alcohols. The Antoine equation has also been most successfully used for families of compounds, notably by Dreisbach (7).

From the large number of equations available, these three have therefore been selected to be used with the vapor pressure of n-propanol. Young's data are employed, and any later re-evaluation or re-determination could always be compared to these in the same fashion. The equations selected (Riedel, Antoine, and Frost) all have a semi-empirical basis, offer relative simplicity in calculation, and provide the possibility of interesting comparisons with other members of the normal alcohol series.

PURIFICATION

1. Materials

I Fisher Certified Grade n-Propanol

This material was supplied with the following stated specifications:

Acidity (CH₃ COOH)	0.002%
Boiling Range	96 – 97.5°C
Non-Volatile Matter	0.000%
Substances precipitated by H_2O	None

This n-propanol is one of the co-products produced from carbon monoxide and hydrogen in the high pressure catalytic synthesis of methanol (44). The chief method of separations of these co-products and final purification of the n-propyl alcohol is careful fractionation.

The higher alcohol mixture produced by this synthesis has been found to contain the following primary alcohols (45):

n-propanol	(b.p. 97.19°C.)
isobutanol	(b.p. 108.39°C.)
2 methyl-1-butanol	(b.p. 128°C.)
2 methyl-1-pentanol	(b.p. 148°C.)
2,4 dimethyl-1-pentanol	
4 methyl-1-hexanol	
iso-propanol	(b.p. 82.3°C.)
3 methyl 2-butanol	(b.p. 114°C.)
2,4 dimethyl 3-pentanol	(b.p. 140°C.)
2,4 dimethyl 1-hexanol	
4 or 5 methyl-1-heptanol	
3 pentanol	(b.p. 115.6°C.)
2 pentanol	(b.p. 119.28°C.)

II Canadian Chemical Company Technical Grade
Normal Propyl Alcohol

This material is stated to have the following specifications:

Specific gravity at 20/20°C max	0.8074
Distillation range °C max	2
Colour APHA max	5
Acidity as Acetic % by wt. max.	.003
Alkalinity as NH_3% by wt. max.	0.2
Water content % by wt. max.	0.2
Non-volatile materials gms/100 ml	0.001

Mass spectrometer analysis of the product stream gives (46):

	High	Low	Avg.
2-Butanol	4.4%	2.8%	3.5%
2-Propanol	traces	traces	–
n-Propanol	97.1	95.5	96
Methoxy-Methylal	0.1	0.0	0.05

for August 18-25, 1958.

This propanol is produced as a by-product of propane oxidation.

III Eastman n-Propyl Acetate

The highest grade Eastman n-propyl acetate obtainable commercially was used. The only manufacturer's specification is the boiling point: 97 - 102°C.

IV Auxiliary Materials

The following materials were used as available commercially:

Reagent Grade Bromine,
Reagent Grade Anhydrous Potassium Carbonate,
Magnesium ribbon (freshly cleaned with steel wool),
Cylinder nitrogen (purified grade).
Reagent Grade Sodium Hydroxide.

2. Apparatus

a. Distillation Apparatus

All distillations were done on a Todd Precise Fractionation Assembly, employing a 25 mm. I.D. column packed with single turn case hardened Pyrex brand glass helices 4 mm. in diameter. The length of the column gave a fractionation efficiency of up to 60 theoretical plates. The apparatus was equipped with jackets and a dual heating unit designed to enable the fractionation column to be operated under adiabatic conditions up to $360^{\circ}C$.

An automatic still head timer controlled the reflux ratio from 2: 1 to 50: 1 in five integral steps by means of a solenoid operated valve made of teflon and containing a soft iron core.

b. Refractometer

All refractive index readings were made on a Pulfrich refractometer using the light prism with a sodium lamp to provide D - line readings. A constant temperature apparatus maintained the prism at $20^{\circ}C \pm 0.1^{\circ}C$. The refractometer was read to the nearest 0.5 minutes.

The normally immersed thermometer well was equipped with a rubber gasket which sealed the top of the cylindrical sample container when the well was lowered into it.

c. Gas Chromatograph

A Beckmann GC-2 gas chromatograph was used consisting of the following elements: a chromatographic column, a carrier gas flow control, a heated sample inlet system, a thermal conductivity cell, an electronically controlled heater system, and an electronically regulated voltage supply.

The columns were flat spirals of $\frac{1}{4}$ inch copper or stainless steel tubing interchangeable with ones of different packing and different length. Cylinder helium was used as the carrier gas. The conductivity cell was an electrically balanced filament type giving a reproducibility of $\pm 0.1\%$ of full scale deflection (47). The instrument had a temperature range from 40° to $220^{\circ}C$, maintained by an internal full-proportional heater,

electronically controlled. Zero stability was 2% per hour or better, under normal operating conditions (47).

The liquid samples were injected into the chromatograph from a Beckmann 22400 liquid sampler. A syringe type instrument, it was designed for introduction of precisely measured small quantities of liquids (.005 cc to .05 cc). Uniform results were obtained with reproducibility of 0.1% to 0.5% (47).

d. Ebulliometer

Boiling points were determined by the comparative method as described by Swietoslawski (48).

Two differential ebulliometers constructed according to the standard specifications of Barr and Anhorn (49) were used. Ebulliometer A (50) contained the primary standard, and B (51) the sample to be studied. Both pieces of apparatus consisted basically of a boiler with a thermometer well and drop counter, a condensation temperature element with a thermometer well and drop counter, and a condenser. In addition, B had a rectifying element between the two thermometer wells and was equipped with a silica gel drying tube above the condenser. Both A and B were well insulated with asbestos. The thermometer wells were built up with cork and insulation so that the thermometer was immersed to the same level as it was during calibration. These wells were filled with mercury and covered with a light oil so that the liquid level would rise to the top of the well when the thermometer was immersed. The boiler sections were wrapped with nichrome heating wire and the heat input controlled with a variable auto transformer. In the case of A, the boiler tube was packed with pyrex glass wool to give undisturbed boiling during operation with the primary standard.

The Beckmann thermometer used in the ebulliometers had 100 divisions per degree. It was calibrated in a constant temperature oil bath against a Leeds and Northrup platinum resistance thermometer with a 1955 NBS certificate (52).

Distilled water having a specific conductivity greater than 800,000 ohms^{-1} cms^{-1} was used as the primary standard.

e. Viscometer

A routine Cannon-Fenske viscometer of the type recommended by the ASTM (54) for testing petroleum products, and as described by Cannon and Fenske (53), was used.

3. Procedure

I Fisher Certified Grade Normal Propyl Alcohol

The n-propanol was charged to the still pot in one litre lots with several grams of anhydrous potassium carbonate and a few boiling chips. The apparatus was then purged for several minutes with purified grade cylinder nitrogen to remove any air atmosphere. The system was closed and the vent on the distillate collecting vessel connected to a glass tube which dipped into a flask of propanol. The system was then opened at the vent stopcock allowing N_2 in excess of atmospheric pressure, to bubble out through the propanol.

The heater under the still pot was turned on and the charge brought to boiling. When refluxing was observed from the packing at the bottom of the column the heater was cut back and the two column heaters switched on. When distillate began condensing in the top condenser the temperature in the upper part of the column was adjusted to the column top temperature. Similarly the lower part was adjusted to the still pot temperature. The column packing was inspected for signs of local heating and then the apparatus was left to come to equilibrium.

When this point was reached, the reflux timer was set at 50: 1 and distillate was collected.

The first 500 mls. were drawn off and then a centre cut of 150 mls. was collected over freshly cleaned magnesium ribbon in a nitrogen purged flask. The flask was then sealed with a ground glass stopper and stored.

Additional runs were made, under exactly the same conditions, with 15 ml. of bromine per litre of propanol in the still pot, part of the purification procedure described by Kretschmer (16).
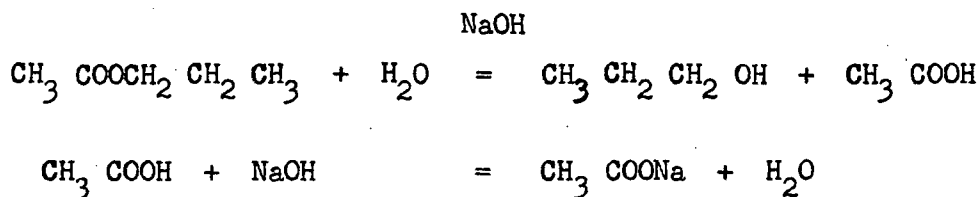
II Canadian Chemical Company Technical Grade Normal Propyl Alcohol

2 litres of n-propanol were distilled by similar procedure at

50: 1.reflux ratio.   The first 50 mls. were discarded and last 100 mls.
left in the boiler.   This distillation procedure was repeated twice more
and the final cut stored over Mg ribbon in a nitrogen atmosphere.

III Hydrolysis of Normal Propyl Acetate to Normal Propyl Alcohol

The production of high purity n-propyl alcohol by hydrolysis of
the acetate, as in the following reactions, was suggested (46):

$$NaOH$$
$$CH_3 COOCH_2 CH_2 CH_3 + H_2O = CH_3 CH_2 CH_2 OH + CH_3 COOH$$

$$CH_3 COOH + NaOH = CH_3 COONa + H_2O$$

1500 grams of Eastman white-label n-propyl acetate was fractionated on
the Todd still at 15: 1 reflux ratio, and a heart cut of the 101.6°C.
fraction taken.   About 1 litre of the rectified propyl acetate was
placed in a 2-litre flask with 200 ml. of water and 50 grams of sodium
hydroxide pellets, and the flask was closed with a rubber stopper.   The
contents were given vigorous and prolonged shaking by hand, with frequent
addition of more   sodium hydroxide in 10 to 20 gm. portions, until a
sudden generation of heat indicated the commencement of hydrolysis.   The
stopper was then loosened and agitation was reduced to a gentle swirling,
letting the flask cool undisturbed whenever it became uncomfortably hot
to the hand.   At this stage the ester odour had been replaced by the
alcohol odour.   Periods of gentle swirling and cooling were alternated
until further agitation produced no further heat.

The mixture was transferred to a 2-litre still flask, 200 mls. of
water added, and the n-propanol-water azeotrope was removed by
fractionation, collecting the 87.7°C. cut at 10: 1 reflux ratio.   The
azeotropic cut was treated with an excess of anhydrous potassium carbonate
to salt out the alcohol as an upper layer.   The upper layer was removed
in a separator funnel and dried by shaking with successive portions of
anhydrous potassium carbonate.   The final settling period was extended
overnight.   The dried alcohol was then filtered into a 1-litre flask,

and last traces of water removed by fractionating at 15:1 reflux ratio, collecting a heart cut, when the temperature had steadied near 97° (uncorrected still head temperature), as pure n-propanol.

4. Purity Determinations

a. Methods

1. Refractive Index

The refractometer was prepared for use by ensuring that the sample container was clean and dry and that the zero reading was correct.

The sample to be analysed was sealed in a serum bottle with a rubber serum bottle stopper, previously boiled in propanol. The sealed bottle was placed on a tray in the refractometer constant temperature bath and left for about twenty minutes. At the end of this period the bottle was removed from the bath and about 5 mls. of sample withdrawn into a hypodermic syringe. After the air was ejected from the syringe, the sample was run into the refractometer sample container and the thermometer well, (with rubber gasket) lowered into place as quickly as possible. The angle of refraction was read immediately and then at successive time intervals until the reading was constant within 0.5 minutes. This reading was recorded and then the procedure was repeated with new samples from the serum bottle until the readings were consistent within 0.5 minutes.

2. Chromatographic Analysis

Preliminary investigations were required for determining the optimum values for the variables connected with the chromatograph operation. In the case of flow rate, current and column length, the manufacturer's specified values were used (47). However sample size, column temperature and column composition were determined by a series of investigations.

The procedure involved finding a combination of these three variables which would give the best resolution, and hence, the clearest qualitative and quantitative indications of the sample composition.

Five recommended columns (46, 47, 54a) of $\frac{1}{4}$ inch copper tubing, each six feet long, were packed with 30 - 40 mesh brick dust. The dust was made by grinding up C - 22 Sil-o-cel brick, removing the 30 - 40 mesh cut, washing out the fines with water, and then drying in an oven. The brick for each column was treated with a different partitioning liquid in the following way. Six to eight mls. of partitioning liquid were made up to 40 mls. in a 100 ml. graduate with a dissolving solvent. Complete mixing was ensured by inserting a teflon piston into the graduate and pulling it back and forth. The piston was left at the bottom of the graduate and 50 mls. of brickdust pored slowly into the liquid mixture so that each particle fell independently through the fluid. After letting the particles settle for a few minutes, the coated brick dust was removed by extracting the piston. The dust was spread out on a tray to be air dried and subsequently packed into the copper tubing.

The five partitioning liquids used were:

1. Tricresol phosphate (reagent grade)
2. Flexol plasticizer - 8N8 (Carbide and Carbon Chemical Company)
3. Vacuum pump oil (Hyvac-Central Scientific Company)
4. Glycerine (reagent grade)
5. Polyethylene glycol di-2-ethylhexoate (Carbide and Carbon Chemical Company)

The optimum sample size and column temperature were determined with the best column of those listed above, following the procedure as outlined below.

The warm up period for the chromatograph was normally two hours. In this period the column was purged with helium at the operating pressure and was brought up to the operating temperature.

In order to check for zero drift and hence an indication of insufficient warm up period, the attentuator was set at its lowest value and the zero adjusted to the 50 millivolt position on the chart. If there was no perceptible shift in the zero position over a period of ten minutes, the apparatus was considered ready for use.

The sample to be injected into the column was drawn into and

rejected from the sampling syringe until it was obtained in an air free state. At the appropriate moment the chromatogram chart drive was switched on and the sample injected as quickly as possible into the column.

During the run the lowest attenuation was maintained to allow for maximum detection of the components. When no more peaks appeared after running at 0 millivolts for several minutes, the chart drive was switched off. However, in order to detect any possible additional components, the instruments were left running, with the recorder pen on the chart, for ten to twenty minutes after the chart drive had been stopped.

Identification of the unknown sample was traced again by a series of investigations. Suspected components were obtained in a fairly pure state and run separately on the chromatograph. When peaks appeared at the same position on the two chromatograms, it was generally accepted as positive identification. However, in cases where more than one suspected component coincided at the same position, known volumes of the suspected components were added to the unknown sample and the effect on the peak in question observed.

The peak height measurement technique was employed to obtain a quantitative analysis of the chromatograms. Only one calibration run (at 100%) was traced for each component, assuming a linear relationship between peak height and composition. The volume per cent of the components was determined as follows:

$$\text{Volume \%} = \frac{\text{component peak height}}{\text{component calibration peak height}} \times 100$$

In cases where the purest form of the component in question showed impurity peaks, the calibration peak height was substituted for what was considered a more accurately determined value (see Discussion, b) Results).

3. Boiling Point

Ebulliometer A (50) was filled with distilled water and the heat input set so that there was rapid boiling. The boiling rate was adjusted to give 5 - 10 drops/minute at the two drop counters. The temperature was measured in both thermowells to get an additional check on the purity of the primary standard.

Ebulliometer B (51) was filled with a sample of the n-propanol being studied and brought to a steady boil giving about 100 drops/minute at both drop counters. The temperature at each thermowell was measured to ascertain the purity (55).

A boiling point determination was begun by obtaining a steady temperature (within .002°C.) in the lower thermowell of A. The thermometer was then quickly transferred to the lower thermowell of B. This procedure was repeated until the temperatures were constant within .002°C. in both thermowells.

The temperature obtained in A was used in conjunction with the pressure-temperature relationships and the interpolation formulae for water, as recommended by the International Union of Chemistry, to obtain the atmospheric pressure.

Assuming a value of dT/dP for n-propanol at 760 mm. as 0.038°C/mm. (10), the actual boiling point of the sample in B at 760 mm. was calculated. The pressure range over which this correction had to be applied was a maximum of 10 mm.

4. Viscosity

The procedure for measuring the viscosity of n-propanol was described by de Verteuil (56) and his results are presented below.

b. Results

For the various starting materials, several "grades" of n-propanol were prepared, and determination of boiling point, refractive index, and viscosity, made as detailed above. The results are tabulated in Table 1 along with estimates of purity and water content.

In addition, the results obtained from the initial investigations

into suitable methods of purification of the available "grades" of n-propanol are presented in Table 2.

Two chromatograms, typical of those used to calculate the percent impurities of Table 1, are illustrated in Figure I.

For comparison purposes, the physical properties of n-propanol from the literature are tabulated in Tables 3a and 3b.

TABLE 1.

Physical Properties of Normal Propanol

		I	II	III
bp. °C. at 760 mm.	a	96.0-97.5[3]	96.1-98.1[3]	
	b		97.16	97.17[4]
n_D^{20}	a	1.38546	1.385[3]	
	b	1.38539	1.38524	1.38524
% Impurity[1,2] (by volume)	a	3.5	3.5	
	b	1.2	0.7	0.35
% Water[1] (by volume)	a	0.1	0.1	0.1
	b	0	0	0
μ (cp.)	b		15°C 2.486 25°C 1.946 30°C 1.718	

(See Page 21 for explanatory notes).

TABLE 2.

Initial Investigations

	Distillation Conditions		n_D^{20}	Impurity[1,2] (% by volume)
	Notes	Reflux Ratio		
	before distillation		1.38546	3.5
I	bromine added	25:1	1.38543	1.7
		25:1	1.38543	
		50:1	1.38539	1.2
	before distillation		–	3.5
II	1st distn.	50:1	–	1.2
	2nd distn.	50:1	–	0.7
	3rd distn.	50:1	–	0.5[5]
III	1st distn.	50:1	–	0.12[5]

(See Page 21 for explanatory notes).
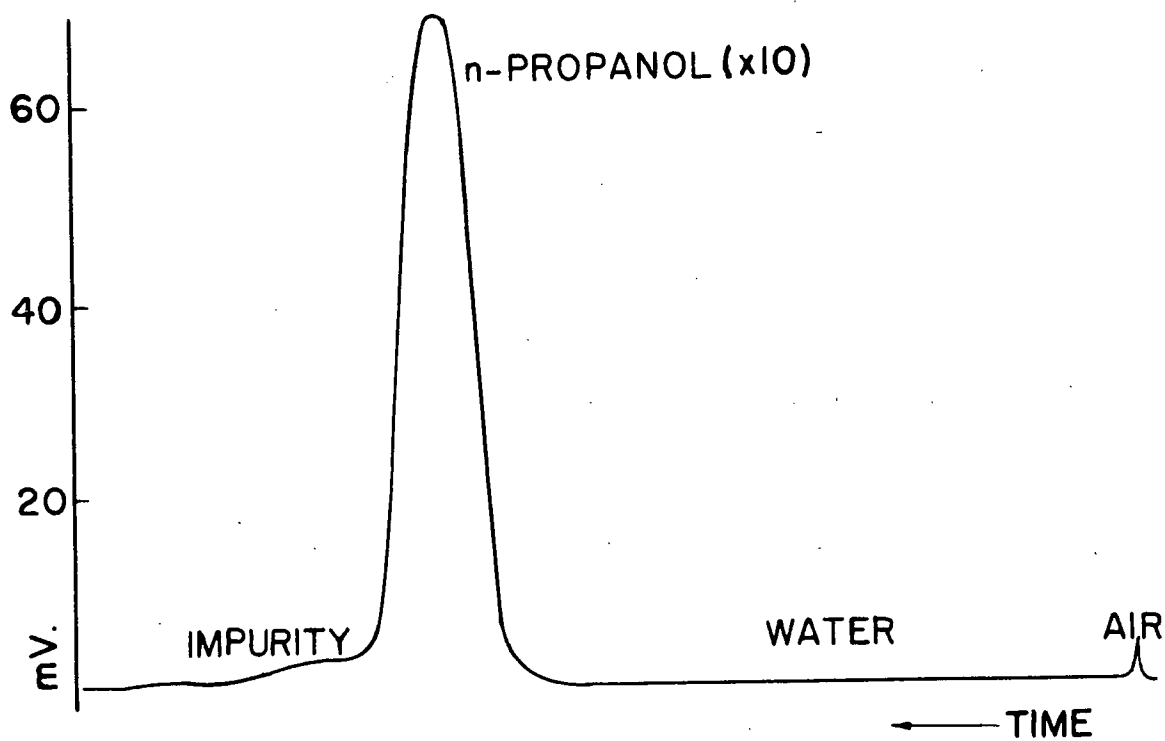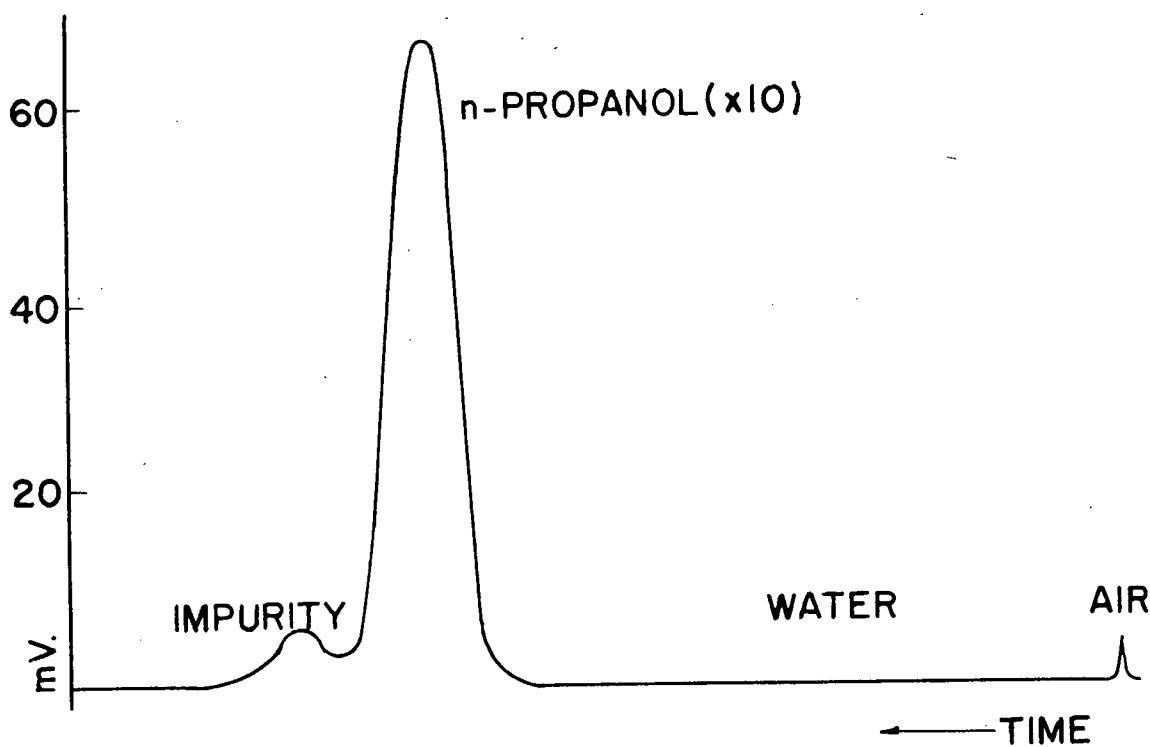
Figure I CHROMATOGRAMS OF NORMAL PROPANOL FROM A FLEXOL
PLASTICIZER COLUMN.

Notes for Tables 1 and 2.

I - Fisher Certified Normal Propyl Alcohol

II - Canadian Chemical Company Technical Grade Normal Propyl
       Alcohol

III - Normal Propyl Alcohol produced by hydrolysis of Normal
       Propyl Acetate

a - before purification

b - after purification

1. These volume percentages were calculated from the chromatograms obtained under the following conditions:

> Flow rate: 150 cc/min.
> Sample size: 0.005 cc.
> Current: 150 ma.
> Temperature: 70°C.
> Column Partitioning Liquid: Flexol Plasticizer-8N8
> Column Length: 6 feet.

2. The percentages here were calculated using 3.5 volume per cent sec-butanol impurity in n-propanol IIa as the standard. This is in accordance with the mass spectrometer analysis from Canadian Chemical Company (see Materials).

3. Manufacturer's specifications.

4. This reading was obtained using a Cenco U.S. Weather Bureau type standard mercurial barometer for the atmospheric pressure determination. The procedure for determining the boiling point was exactly as described above except that the barometer was substituted for ebulliometer A. Pressure readings were made to the nearest 0.1 mm.

and the brass scale correction applied at room temperature. Reduction of the barometer to latitude 45° was neglected.

Since the manufacturer considers this barometer "of the highest type of excellence", it was assumed accurate to 0.1 mm. Even an error of 0.1 mm., which corresponds to less than $0.005^{\circ}C$, would not affect the boiling point any more than the errors involved in the comparative method. For this reason the accuracy of the two methods is considered comparable.

5. This value was obtained using a 5 mm. I.D. column on the Todd Fractionation Assembly, rather than the 25 mm. I.D. column which was used for the final products, as described on p.19.

TABLE 3a.

Physical Data for Normal Propyl Alcohol from the Literature.

AUTHOR	DATE	b.p. °C. (760 mm.)	REFRACTIVE INDEX n_D^{20}	n_D^{25}	REF.
Young and Fortey	1903	97.19			(57)
Dorochewsky	1909	97.20			(58)
Dorochewsky	1911	97.26			(59)
Mundel	1913	97.1			(60)
Brunel, Crenshaw and Tobin	1921	97.19		1.3833	(61)
Brunel	1923	97.15		1.3833	(28)
Grimm and Patrick	1923	97.19			(62)
Trew and Watkins	1933			1.38343	(63)
Timmermanns and Delcourt	1934	97.15			(64)
Wojciechowski	1936	97.209			(65)
Zepalova-Mikhailova	1937	97.15			(66)
Addison	1945	98.0	1.3856		(67)
Vogel	1948		1.38556		(68)
Carley and Bertelsen	1949	97.19			(69)
Mumford and Phillip	1950	97.2	1.3862		(70)
Howey	1951	97.2	1.3858	1.3838	(71)
McKenna, Tartar and Lingafelter	1953			1.3837	(72)
Wetzel, Miller and Day	1953			1.3841	(73)
Purnell and Bowden	1954	97.2		1.3840	(74)
Croil I	1958		1.38539		This Research
II		97.16	1.38524		
III			1.38524		

TABLE 3b.

Physical Data for Normal Propyl Alcohol from the Literature.

AUTHOR	DATE	TEMP. °C.	DENSITY g./ml.	VISCOSITY cp.	REF.
Gartenmeister	1890	10	.8125	2.934	(75)
		20	.8052	2.273	
		30	.7973	1.791	
		40	.7890	1.416	
		50	.7802	1.148	
Thorpe and Rodger	1894	15.06		2.555	(76)
Thole	1910	25		1.990	(77)
Baker	1912	25	.8010	1.971	(78)
Dunstan & Thole	1913	25		1.962	(79)
English and Turner	1914	25	.7999	1.928	(80)
Herz	1918	25		1.915	(81)
Whitman	1930	25	.7957	1.962	(82)
Timmermanns and Delcourt	1934	15	.80749	2.522	(64)
		25	.79957	1.924(calc)	
		30	.79567	1.722	
Jones	1948	25	.8015	2.004	(83)
Mumford & Phillip	1950	20	.8053	2.29	(70)
		25	.8016	2.015	
de Verteuil and Croil n-propanol II	1958	15	.8075*	2.486	This research
		25	.7998*	1.946	
		30	.7957*	1.718	

* Assumed Values.

5. Discussion

a. Apparatus and Methods

1. Refractive Index

While the refractometer could only be read to the nearest 0.5 minutes, successive readings were sufficiently reproducible to give an average deviation from the mean of a group of readings of less than 0.25 minutes. This corresponds to a maximum error of about 4 in the fifth decimal place of the refractive index value.

The rubber gasket, sealing the sample container when the thermo-well was lowered into it, reduced the exposure of the sample to room air to a very small period of time. Thus any moisture pickup by the materials used was insufficient to cause detectable changes in refractive index. Similar precautions were taken with the liquid before analysis by storing it in a serum bottle and retracting samples, as required, with a hypodermic needle.

2. Chromatographic Analysis

The gas chromatographic analysis provided a most useful means of detecting impurities present. The selection of the best column and operating conditions was difficult, however. Of the six columns tested (silicon, tricresol phosphate, flexol plasticizer, vacuum pump oil, glycerine and polyethylene glycol 2-diethyl hexoate) the flexol plasticizer column alone gave clear distinct peaks for water, n-propanol and an unknown impurity. In the other columns the impurity was either hidden by the propanol peak or the peak was so flat it was difficult to analyze. As a result this column was selected and used for all the tests made to provide information on the purity of n-propanol.

According to the manufacturer's instructions (84) for determining volume %, a calibration curve should be obtained of composition versus peak height. The errors involved in taking this relationship to be linear are not likely to be significant here since the primary interest is not in absolute quantitative values but rather in relative ones. Failure

to exactly identify the main impurity makes the former impossible.

Other sources of error in this type of analysis are outlined by the manufacturer (84) but, in general, have not been considered relevant to these measurements.

3. Boiling Point

Difficulty was encountered in controlling the drop rate from ebulliometer A (50), containing the primary standard. The rate at the top of the apparatus always exceeded that at the bottom which is exactly the reverse of what was expected. It appeared that an error in construction permitted refluxing liquid from the top to return to the boiler section without passing through the bottom drop counter. Nevertheless this seemed to have no particular detrimental effect on the equilibration.

The measurement of the temperature in both thermowells of ebulliometer A gave the same value to within $0.001^{\circ}C$. indicating that the primary standard was of an acceptable purity. Similarly in the case of ebulliometer B (51), the two temperatures were within $.005^{\circ}C$. of each other. According to Swietoslawski (55) this places both liquids in the first degree of purity class.

Only one thermometer was used to eliminate the errors involved in using two or more, where the possibility of scale corrections is presented. On the other hand, it was almost impossible to measure the temperature in two ebulliometers with one thermometer, while the room pressure remained constant.

Nevertheless, corrections applied, as described previously, provided boiling points at 760 mm. pressure which are considered to have a maximum error of $.005^{\circ}C$. This error takes into account possible errors in calibration, lack of precise equilibrium conditions, and limitations in reading the thermometer and applying normal corrections to it.

4. Viscosity

The apparatus and procedure for making the viscosity measurements

tabulated above have been critically discussed by de Verteuil (56).

b. Purification

The purification of n-propanol presents a number of problems. The work described herein has clarified these problems, and proceeded towards their solution.

A significant problem is the vagueness of the literature already available, with its omissions, discrepancies and conflicting statements. A second important problem is the fact that the impurities and normal propanol are so close boiling that not only is it very difficult to separate them, but also to detect them by the measurement of physical properties.

The purification procedure adopted for n-propanol I was essentially that of Kretchmer (16), although details of the bromine treatment were lacking. Successive trials at brominating some n-propanol I, to assist in removing any allyl alcohol, showed little improvement over the original sample when measured by means of a gas chromatographic analysis. This initiated doubts about 1) the bromination method, 2) differences in the commercial grades of propanol used, 3) Kretchmer's conviction that the impurity was allyl alcohol. Further distillations at higher reflux ratios began to confirm the doubts about 2) or 3). The impurity peak decreased with distillation at higher reflux ratios even without any bromination.

The use of a nitrogen purge was found to be incidental since the product obtained from distillation in an air atmosphere was identical, within the limits of detecting differences in successive gas chromatograms, to that in a nitrogen atmosphere.

The n-propanol II, for which a mass spectrometer analysis was available, showed as its main impurity sec-butanol. The successive distillations at high reflux ratios gave a rate of decrease of the impurity peak on a chromatogram corresponding fairly well to that of n-propanol I. In addition the two impurity peaks appeared in the same positions on the chromatograms.

A sample of the n-propanol III, as produced from n-propyl acetate,

also gave a small impurity peak in the same position. This n-propanol III would have been more easily and efficiently prepared if potassium hydroxide had been used rather than sodium hydroxide, because of the much greater solubility of the latter. No difference in purity obtainable would be expected however.

On the basis that either allyl alcohol or sec-butanol was the main impurity indicated as being present, chromatograms were run on fairly pure ($\sim$ 90 - 95%) samples of each. These were used as standards for determining percentage impurity as described above. In addition allyl alcohol-propanol and sec-butanol-propanol mixtures were prepared and chromatograms obtained. In each case small concentrations of the suspected impurity (beginning at 1.0% by volume) were introduced in order to detect its effect on the impurity peak without completely masking it.

The essential aspects relating to the possible impurity identification as obtained from these chromatograms is illustrated schematically by Figure II.

Increasing proportions of allyl alcohol in the n-propanol caused distance "a" to decrease as peak A increased, i.e. shifting the impurity peak to the right. Conversely, addition of sec-butanol to the n-propanol caused the impurity peak to shift to the left.

This behavior make it impossible to attribute the impurity effect to either allyl alcohol (b.p. 97.08°C. (27)) or sec-butanol (b.p. 99.53°C. (27)), and could not, in itself, eliminate the possibility of another compound being present. The decrease in concentration of the impurity with continued distillation (see Results) would apparently be easier to achieve with sec-butanol having a boiling point difference of more than 2°C. However there is an azeotrope between allyl alcohol and n-propanol boiling at 96.73°C. (85) which should separate from propanol quite readily. At the same time, the failure of the bromination procedure to remove the impurity seems to indicate that allyl alcohol is not a major impurity.

None of the columns tested could cause separation of these peaks (A, B, C, Fig. II). It was therefore concluded that the impurity was

A - Allyl Alcohol
B - Impurity
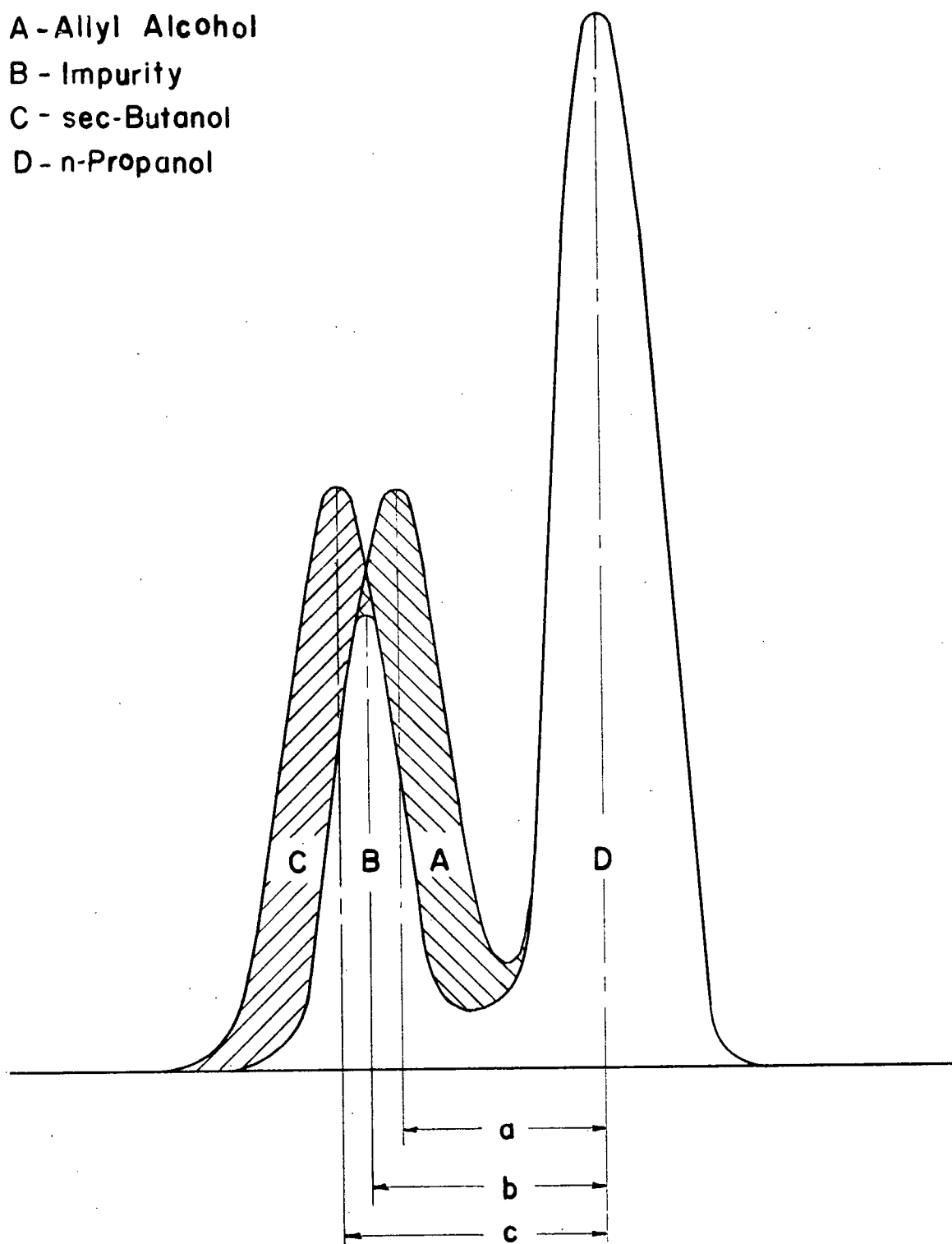C - sec-Butanol
D - n-Propanol

Figure II EFFECT OF SUSPECTED IMPURITIES ON
CHROMATOGRAM PEAKS

likely a single compound, and probably sec-butanol, although its amount could be determined as a percentage of either allyl alcohol or sec-butanol.

The percentage impurity, as determined from either of the two chromatograms run as standards, was 5.5 volume per cent. In each case the standard had unknown impurities whose percentage could not be determined exactly, thus making 5.5% an uncertain value. The mass spectrometer analysis of n-propanol II, with its average value of 3.5% sec-butanol, was therefore taken as representing the impurity peak in n-propanol I and II. All purified sample impurity concentrations were determined on this basis (84).

From the chromatographic analysis, Table 1 shows n-propanol III to be the purest of the three different samples, with a value of better than 99.65 volume %.

The boiling point was determined for n-propanol II and III. (97.16°C and 97.17°C. respectively). Although there is 0.01°C difference in the reported values, they are essentially the same within the accuracy obtained. Moreover any error introduced by using two different methods of obtaining the atmospheric pressure is considered negligible.

Considering the difference in impurity percentages for n-propanol II and III, the boiling point should probably not be taken as a primary criterion of purity in this case. However when compared with Weissberger's value, 97.15°C. (27), these boiling points both give further indication of the presence of higher boiling impurity.

The refractive indices decreased with decreasing per cent impurity. Since both sec-butanol (n_D^{20} = 1.39780 (27)) and allyl alcohol (n_D^{20} = 1.41266 (27)) have refractive indices higher than n-propanol (n_D^{20} = 1.38556 (27)), this is consistent with removal of either of these two compounds.

If plots of refractive index versus per cent composition of sec-butanol (in n-propanol) and allyl alcohol (in n-propanol) are considered linear, then the fact that n-propanol II (before purification) lies

closer to the former plot indicates that sec-butanol is more likely the impurity.

While water present as impurity lowers the refractive index of n-propanol, removal was clearly shown by the chromatograms. The best value obtained here is 1.38524 as compared to 1.38556 selected by Weissberger (27) and based on a determination by Vogel (68), using a simple fractional distillation for purification. From the experience of this investigation one distillation is not sufficient, and Vogel's result should be regarded dubiously.

The viscosity values were calculated by de Verteuil (56) assuming the density values as shown in Table 3b. The densities were carefully selected and agree well with several other investigators. There are large differences among reported viscosity values, however, and while the results reported here are self-consistent and considered to be accurate to 0.5%, they cannot be used as a means of purity comparison and are given only for completeness.

VAPOR PRESSURE APPARATUS

The apparatus designed by Whittle (29) for vapor-liquid equilibrium measurements can of course be employed for 1-component vapor pressure measurements, as mentioned above, and in so doing be simplified by eliminating the phase sampling section.

Basically the apparatus consists of a glass purification train connected to an equilibrium bomb (in a constant temperature bath) and a mercury storage bomb. The two bombs, of stainless steel, are identical and are connected in a vertical position by a movable rod used for measuring levels in the equilibrium bomb. They are also connected by high pressure tubing so that mercury can be transferred from one bomb to the other, thus enabling the rod to be moved without changing the mercury level in the equilibrium bomb. The temperature and pressure of the sample are varied by means of the constant temperature bath, and nitrogen pressure on the mercury in the mercury storage bomb, respectively. A schematic representation of the bomb assembly, revised from that of Whittle (29), is shown in Figure III.

The revisions that have been required may be listed as follows:

1. The synthetic rubber O-ring between the bottom bomb face and the pressure closure assembly was replaced with a teflon O-ring.

2. The level indicator, an N.R.C. design as described by Whittle (29), was replaced by a Pemberthy reflex type level gauge (Model No. V - 905), pressure tested from 0 to 3000 psi. at 100°F.

3. The previously silver soldered joint between the measuring head and the connecting rod was welded to eliminate the possibility of mercury attack on the solder.

4. For the purposes of vapor pressure measurements the position of the liquid vapor interface is not essential. For this reason the hot wire anemometer was not installed.

5.   Instead of using a resistance bridge for measuring the
       mercury level, an ordinary relay circuit with an indicating
       light was found to be satisfactory.   The circuit was
       opened or closed by raising or lowering the measuring head
       out of or into the mercury.   The level could be ascertained
       to within 1.0 mm.   This error was partially eliminated by
       consistently measuring from above the mercury surface.

Pressure tests were initially made on the entire system,
excluding the glass purification train and the level gauge, using
nitrogen from a regular storage cylinder up to 1000 p.s.i. and soap
solution as a leak detector.   Subsequently the system was filled with
S.A.E. 10 oil and the pressure raised to 4500 p.s.i. at room
temperature then reduced to 2000 p.s.i.   This pressure was held for
three days with no evident sign of leakage.

In order to transfer a sample into the equilibrium bomb, the
purification train and equilibrium bomb had to be vacuum tight.   A
vacuum of better than 10^{-3} mm. of mercury was obtained using a mercury
diffusion pump in conjunction with a Cenco Megavac vacuum pump.   The
rate of leakage caused a pressure change of approximately 0.001 mm./
minute.

To facilitate cleaning of the system, technical grades of
benzene, toluene, and n-propanol were circulated through the apparatus,
cold.   Once the exit solvents became clean, some n-propanol was pumped
into the bomb (leaving sufficient room for expansion) and the bomb
temperature raised to about 250°C.   As the exit solvent from this
treatment contained dirt particles and a considerable amount of
discoloration, further batches of n-propanol were introduced.   As the
number increased, the solvent became cleaner and apparently clearer.
However, on standing, the discoloration appeared, similar to the first
batch.   This was attributed to the air in contact with the n-propanol
causing an aldol condensation reaction which formed a coloured polymer
(54a).

It was then noted, after the above heating and cooling process,

that the equilibrium bomb was no longer vacuum or pressure tight, due to the apparent failure of the teflon V-rings in the packing gland above gland nut A (Figure III).   Increasing the pressure on the rings, by means of the gland nut and inserted split steel washers, had no apparent effect on the leak.

The failure was ascribed to teflon's lack of geometric stability with respect to the heating and cooling cycle, possibly with some extrusion at the high temperatures.   However, the manufacturer's specifications (86) state that teflon is flexible to 260°C.   Above 335°C. it loses strength and around 400°C. it decomposes slowly.   . Further examination of the packing will have to be made in order to ascertain whether a major change in design is required.

Other aspects of the apparatus design appear satisfactory for such measurements as that of the vapor pressure of n-propanol which has a critical temperature of 263°C. and a critical pressure of about 735 p.s.i.

VAPOR PRESSURE CORRELATIONS

1. Methods

Vapor-pressure-temperature correlations have been made using the data of Young and the selected equations discussed in the Literature Review.

In addition to Riedel's reduced vapor pressure equation,

$$\log P_R = A - \frac{B}{T_R} + C \ln T_R + DT_R^6 \tag{2}$$

it was considered of interest to check his equation using actual temperatures and pressures; i.e.

$$\log P = A - \frac{B}{T} + C \ln T + DT^6 \tag{5}$$

The two Antoine equations, of the form

$$\log P = A - \frac{B}{T-C} \tag{3}$$

were evaluated on the basis of the selection of the constant C. Thomson's graphical method for estimating C (36) was used, taking $T_o = 97.17^{\circ}C$. and $P_o = 760$ mm. as the point assumed free from error. A plot of $\log P$ versus $\dfrac{\log P - \log P_o}{T - T_o}$ is linear if the Antoine equation holds. When this present data was plotted two straight lines were drawn through the points. The slopes for these two lines, $-(T_o - C)$, and hence the values of C, $-230^{\circ}C$. (below the b.p.) and $-176^{\circ}C$. (above the boiling point), were used in the equations. On conversion to engineering units they became 77.5 and $175^{\circ}R$. respectively.

The third equation, proposed by Frost and Kalkwarf,

$$\log P = A - \frac{B}{T} + C \log T + \frac{DP}{T^2} \qquad (4)$$

was applied directly to the data.

In each case the best fit for the data was obtained by the method of least squares. The regression coefficients were calculated on the U.B.C. electronic digital computer, Alwac III E, programmed with Routine S-3 (87) for correlation and regression. In all cases at least six significant figures were carried through the computation, reducing the possible error to less than 0.05%.

The constants determined for these equations are tabulated in Table 4.

TABLE 4.

Constants for Vapor Pressure Correlations.

Name	Equation	A	B	C	D
Riedel	5	6.5592	6.5984	-3.4819	.0348
Riedel	2	32.694	6323.4	-3.3916	3.0×10^{20}
Antoine below b.p.	3	6.7282	3276.4	77.5	-
Antoine above b.p.	3	5.6444	2200.0	175	-
Frost	4	32.233	6288.6	-7.6641	18.31

The per cent deviation of the values of P calculated from these equations is compared in Table 5 and Figure IV with those obtained by Young using the Biot Formula.

$$\log P = a + b\alpha^t + c\beta^t \qquad (1)$$

TABLE 5

CORRELATION DEVIATIONS

$T^o R.$	$P_{exp.}$ p.s.i.a.	Biot	Riedel (2)	Riedel (5)	Antoine	Frost
			% Deviation of P_{Calc} from $P_{exp.}$			
491.688	.066519	+1.45	-0.69	-1.10	+1.10	-1.97
509.688	.140386	+1.79	-0.39	-1.03	-0.01	-0.24
527.688	.280385	+1.93	+0.94	+0.79	+0.60	+0.89
545.688	.533701	+1.92	+1.30	+1.24	+0.25	+1.35
563.688	.970717	+1.83	+1.37	+1.14	+0.49	+1.39
581.688	1.68619	+2.06	+1.60	+1.26	+0.67	+1.60
599.688	2.84254	+1.34	+0.73	+1.09	+0.03	+0.30
617.688	4.62154	+0.60	-0.13	+0.09	-0.43	-0.17
635.688	7.27071	-0.18	-1.21	-0.99	-0.69	-1.10
653.688	11.0994	-1.02	-2.00	-2.06	-0.79	-2.00
671.688	16.2915	-0.78	-1.81	-1.80	+0.50	-1.80
689.688	23.3204	-0.65	-1.63	-1.70	+0.51	-1.60
707.688	32.5442	-0.35	-1.24	-1.30	+0.46	-1.20
725.688	44.3397	+0.12	-0.66	-0.75	+0.58	-0.60
743.688	59.4419	+0.20	-0.38	-0.51	+0.40	-0.32
761.688	78.3535	+0.12	-0.23	-0.64	+0.10	-0.04
779.688	101.790	-0.20	-0.32	-0.49	-0.35	-0.14
797.688	129.461	+0.04	+0.19	-0.22	-0.18	+0.35
815.688	162.102	+0.42	+0.83	+0.58	+0.18	+1.00
832.688	202.381	-0.20	+0.40	+0.15	=0.40	+0.60
851.688	247.533	+0.06	+0.80	+0.55	-0.08	+1.40
869.688	301.174	-0.23	+0.59	+0.36	-0.30	+0.45
887.688	361.196	-0.06	+0.76	+0.78	-0.06	+0.93
905.688	428.392	+0.34	+1.06	+1.04	+0.40	+1.16
923.688	506.513	+0.26	+0.73	+0.63	+0.30	+0.78
941.688	595.290	+0.07	+0.17	+0.12	+0.04	+0.13
959.688	698.124	-0.54	-0.97	-0.90	-0.73	-1.10
966.348	737.126	-0.45	-1.32	-1.13	-0.46	-1.56
Average Deviation		0.69	0.87	0.87	0.40	0.93
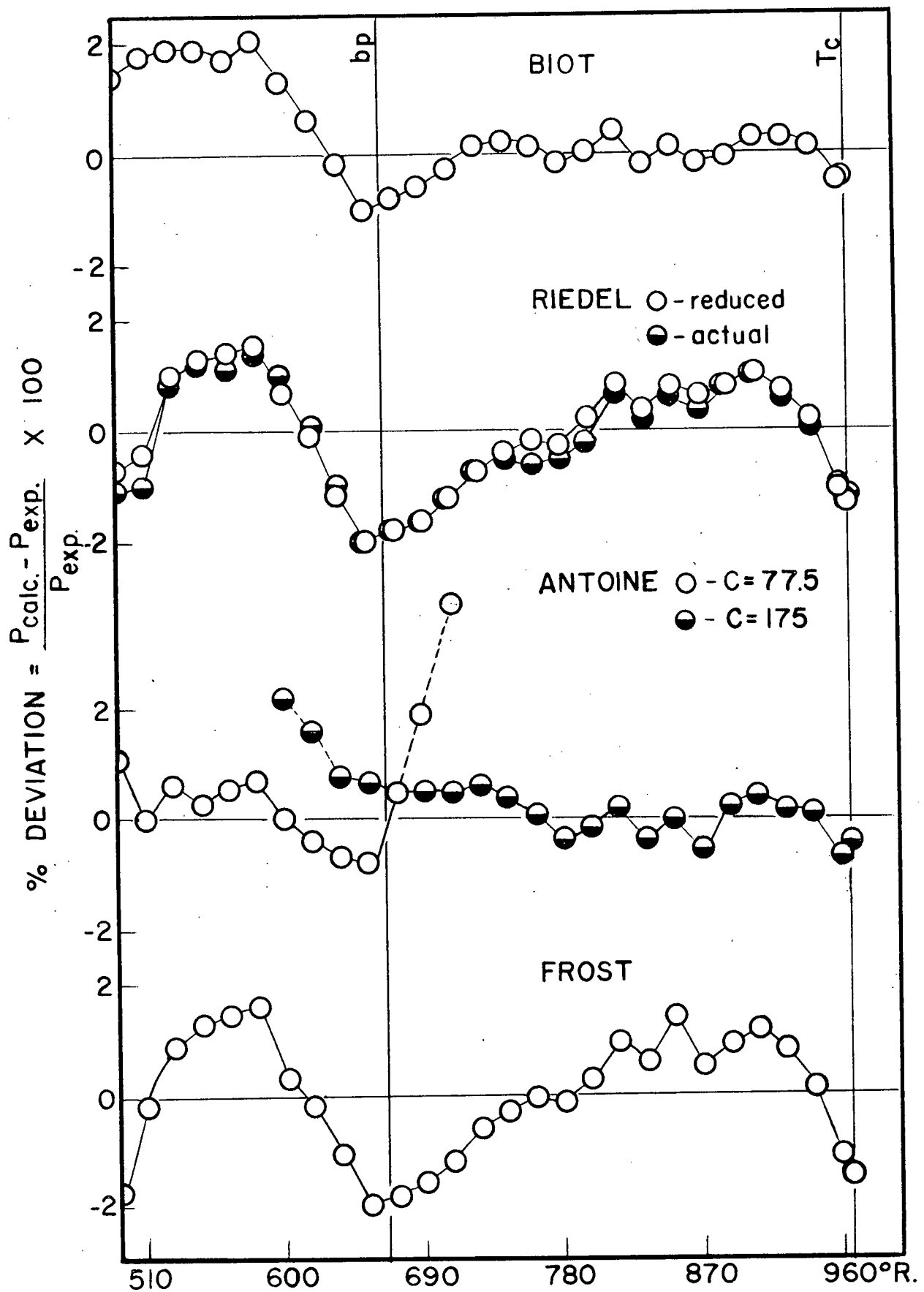
Figure IV   CORRELATION DEVIATIONS

2. Discussion

In general, all the plots of Figure IV show the same tendencies. Positive peaks occur at 581.7, 815.7, 851.7, 905.7 °R. and negative ones at 653.7, 833.7, 869.7 °R. in nearly all cases. The large negative peak near the boiling point is of particular interest. This occurs for Frost, Riedel, and Biot equations but is eliminated by the use of two Antoine equations.

Of the four equations compared, the Antoine correlation appears to give the best fit. However, as was mentioned previously, the disadvantage of using two equations must be taken into consideration. Although Thomson (36) recommends $T_R = 0.8$ as the intersection point of the equations, $T_R = 0.45$ was used here for the best results. The extension of the equations beyond the intersection point results in increased deviations, as is shown by the dashed lines in Figure IV. This tends to support the choice of $T_R = 0.45$ as the intersection point.

The next best fit for the data is given by the Biot formula. Although the deviations are quite large in the low temperature regions they become considerably less significant above the boiling point. Biot's formula does have the advantage of covering the full range of data, but it is questionable whether it is any better in the low temperature region than the extension of the high temperature range Antoine equation. However this consideration becomes insignificant when the evaluation of the Biot constants is taken into account. The solution of this five constant equation, following Prony's Method of Interpolation by Expotentials (88), requires much computation and almost excludes the possibility of using the method of least squares.

The fit of the two Riedel equations appear to be almost identical indicating that the critical data have been carefully measured. Both equations fit this data well enough to consider applying them to other members of the n-alcohol series. However

there is a greater possibility of chain length relationships between the constants of a reduced form of the equation used for a homologous series. On the other hand, the equation using actual temperatures and pressures is not dependent on the critical data for its correlation. This would be an advantage where critical constants have not been accurately determined or where available data is fragmentary.

The deviations of the Frost equation are very similar to those of the Riedel equations. These are, of course, identical except for the last term and the graphs indicate that this difference is not very significant. It would appear that the Frost equation does not account for the reverse "s" shaped curve in the plot of log P versus $1/T$, as Thodos (43) found it did for the normal hydrocarbons.

In the final analysis, the Antoine equations are the simplest to use. Although they fit the data very well, there is the disadvantage of two equations. The Biot equation should not be considered because of the difficulty involved in calculating the constants. There is little to choose between the Frost and two Riedel equations. Possibly the reduced form of the Riedel equation is most useful because of its applicability to the theorem of corresponding states.

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