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DENSITIES OF POLAR AND NON-POLAR COMPOUNDS AND THEIR MIXTURES

BY

PETER NORMAN NOTWICK, JUNIOR

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PETER NORMAN NOTWICK, JUNIOR

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DEPARTMENT OF CHEMICAL ENGINEERING
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ABSTRACT

Two principal studies were conducted as part of this thesis: evaluation of existing correlations for predicting densities of polar and non-polar liquids and their mixtures and experimentally measuring the densities of certain liquid systems.

Utilizing a modification of the simple picnometer experimental method, data were obtained for both pure compounds and liquid mixtures. Comparison of the pure compound data with available literature sources established the reliability of the technique.

The results of the correlation comparison indicate that the Riedel equation, is the most generally reliable for predicting the densities of pure "normal" compounds. Lydersen, et al., prepared tables for the solution of this equation, however, these have been found to be unreliable for application to compounds with low critical compressibility factors.

By modifying the Riedel equation with the variable third parameter of Joffe and Zudkevitch, its applicability is extended to some non-normal compounds. It was also found to be reliable for many binary systems when used in conjunction with Kay's mixing rule.

Attempts were made to fit the Riedel equation to the data for non-normal compounds by least squares regression. Many of these were successfully fitted indicating that only the choice of constants prevents their being predicted by that equation. Some of these compounds, however, could not be made to conform to the Riedel form (e.g., water, ethanol, and methanol).

Experimentation with different equation forms showed that a more parabolic form was more successful in predicting the behavior of the non-conforming non-normal compounds.

ACKNOWLEDGEMENT

The author wishes to express his appreciation to some of the numerous parties whose considerations made this work possible.

Appreciation is extended to the personnel of the Corporate Engineering and Corporate Research Departments of Allied Chemical Corporation which underwrote the experimental work. Particular among these were Mr. E. W. Hofer and Dr. D. Shirer.

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INTRODUCTION

Over the past two decades, the increase in the use of digital computers has made available to engineering designers the ability to not only perform laborious design calculations but also to simulate integrated chemical plant systems.

The development of sophisticated algorithims by chemical industry technologists, however, has greatly out-stripped the production of complete and reliable physical property data to form the input. As a result, the existing mathematical systems suffer not only because their otherwise excellent reliability is impaired, but also because the justification for using the complicated correlations included in them is wanting. Paradoxially, therefore, the situation perpetrates that which it was originally conceived to avoid: the use of conservative (hence, costly in plant constructions capital) short-cut and "rule-of-thumb" design techniques.

As a remedy, generating the required quantities of physical property data would be both costly and impractical. For this reason, generalized equations of state seem the most promising and practical solution. Ideally, such useful relationships would require minimal input data to generate a complete profile of the physical behavior of a chemical system.

The theorem of corresponding states is one of the oldest and simplest conceptual approaches to developing this ultimate predictive tool. Originally proposed in the latter part of the nineteenth century, it has undergone numerous attempts at refinement since then.

Employing this theorem, then, it is the object of the present project to refine existing correlations for predicting one specific physical property: liquid density. Consideration will be given to not only pure compounds but also mixtures of both normal and non-normal liquids.

At the same time, in order to broaden the scope of available data for testing, new experimental measurements were generated for binary liquid mixtures in the low critical compressibility range. This area has been somewhat neglected to date.

LITERATURE REVIEW

Correlation of Densities of Pure Compounds

The theorem of corresponding states as originally proposed by van der Waals propounded that all pure gases would manifest the same compressibility factor magnitude, z, at a given set of corresponding conditions. The criterion of correspondence was equality of reduced temperature and pressure between two or more compounds. In its two parameter form the theorem is symbolically represented as:

$$P_{r1} = \frac{P_1}{P_{c1}} = P_{r2} = \frac{P_2}{P_{c2}} \text{ and } T_{r1} = \frac{T_1}{T_{c1}} = T_{r2} = \frac{T_2}{T_{c2}}$$

Subscripts "1" and "2" denote each of the two arbitrary pure compounds, the subscript "c" identifies the critical conditions of the respective compounds, the subscript "r" indicates reduced conditions and T and P represent absolute values of temperature and pressure, respectively.

Since z, as defined (i.e., $z = \frac{PV}{RT}$), represents the deviation of the behavior of a real system from the predictions of ideality, the theorem may be generalized thus:

Pure substances in corresponding states will experience quantitatively identical deviations of their thermodynamic properties from ideality.

Although Young extended the theorem to liquids, it was found that even though the principle held more or less well for discreet groups of compounds, it failed to prove true in general.

Much later Watson[49] proposed the liquid density relationship

$$\frac{\rho_1}{\rho_{r1}} = \frac{\rho_2}{\rho_{r2}} \tag{1}$$

which will be applied later. This set of ratios is ofter referred to as the "Watson proportionality".

This two parameter approach, however, failed to predict the behavior of many liquids. As a result the need for a third parameter which would characterize the compounds seemed to be indicated.

Riedel[38, 39] developed a criterion for distinguishing compounds which lend themselves to the simple treatment requiring only reduced temperature, pressure and a constant third parameter. "Normal compounds", as these conforming substances are called, agree within 5% with the relationship:

$$\frac{\sigma \, Vo^{2/3}}{T_c} = 1.86 + 1.18\omega \tag{2}$$

in which σ is the hypothetical surface tension of the liquid at 0° K,

Vo is the hypothetical partial molal volume of the liquid at 0° K,

ω is the Pitzer acentric factor to be discussed later and

T_c is as previously defined.

Riedel defined the required third parameter as the slope of the vapor pressure curve at the critical temperature, i.e.,

$$\alpha = \left(\frac{d \ln P}{d \ln T}\right)_{Tc} \tag{3}$$

He then proposed an equation for predicting the reduced density, ρ_r, of a saturated liquid:

$$\rho_r = 1 + 0.85 \, (1-T_r) + (0.53 + 0.2\alpha)(1-T_r)^{1/3} \tag{4}$$

As a simpler alternative, Pitzer et al.[34] proposed the acentric factor, ω, as a third parameter. This constant measures the deviation of the intermolecular potential function from that of a perfectly spherical molecule. It is defined as:

$$\omega = - \log\left(P_r\right)_{0.7} - 1.0 \qquad (5)$$

where $\left(P_r\right)_{0.7}$ is the reduced vapor pressure at $T_r = 0.7$. Although published in a tabular form, the gaps between Pitzer's entries for correlating the reduced densities of saturated liquids were too large and too numerous to be deemed sufficient for general use.

The best known of the third parameters, however, is z_c. Its popularity rests largely on the extensive charts prepared by Lydersen et al.[30] to facilitate evaluation of the then available correlations for predicting individual property deviations from ideal gas behavior. It should be noted that in preparing his tables and charts, Lydersen employed the Riedel equation (equation 4) to obtain the reported values. This was possible because the three proposed third parameters (α, ω and z_c) assumed to be interrelated by:

$$z_c = \frac{1}{1.28\,\omega + 3.41} = \frac{1}{0.26\,\alpha + 1.90} \qquad (6)$$

Francis[12] noted that the plot of the liquid density of a compound versus temperature (or reduced density versus reduced temperature) adopted an increasingly parabolic shape as it approached the critical temperature. However, recognizing that the curves are steeper and more linear at lower values of T_r, he adopted a two region approach (i.e., one equation for the parabolic region and another for the linear) whose equations were of the form:

$$\rho_s = A - BT_s - C/(E - T_s) \text{ for } T_s > (T_c - 20^\circ C) \qquad (7a)$$

$$(\rho_c - \rho_s) = K(T_c - T_s) \text{ for } T_s \leq (T_c - 50^\circ C) \qquad (7b)$$

in which ρ_s and T_s are the saturation density and temperature, respectively, ρ_c and T_c are the critical values of density and temperature, and n, K, A, B, C, and E are empirical constants determined for each individual compound.

Although the accuracy of predictions of liquid densities using Francis formulas is reasonably good, the awkwardness of the two-region approach is disadvantageous. Furthermore, most other equations enjoy the advantage that either a smaller number of constants must be determined for every compound or their constants are given in terms of z_c (or α, ω) or T_r.

Other investigators followed the familiar route of adding to the number of terms and, hence, constants employed. This usually has the effect of improving the fit of a given form of any equation but at the sacrifice of simplicity and ease of calculation.

A few of the representatives of this approach are:

Martin[31] proposed the relationship:

$$\rho_r = 1 + A(1-T_r)^{1/3} + B(1-T_r)^{2/3} + C(1-T_r) + D(1-T_r)^{4/3} \qquad (8)$$

Yen and Woods[51], in further development, determined that Lydersen's tables could be represented by Equation 8 but that the fourth term, D, could be eliminated and the remaining constants defined in terms of z_c as follows:

$$A = 17.4425 - 214.578\, z_c + 989.625\, z_c^2 - 1522.06\, z_c^3$$

$$B = \begin{cases} 3.28257 + 13.6377\, z_c + 107.4844\, z_c^2 - 384.211\, z_c^3 \\ \qquad \text{if } z_c \leq 0.26, \\ 60.2091 - 402.063\, z_c + 501.0\, z_c^2 + 641.0\, z_c^3 \\ \qquad \text{if } z_c > 0.26, \end{cases}$$

$$D = 0.93 - B$$

These authors reported an accuracy of ± 2% for most pure compounds but indications are that the equation yields less satisfactory predictions than the Riedel equation and some others especially for mixture

Stiel[42] proposed that a fourth parameter is required to improve the applicability of the theorem of corresponding states to polar compounds. He defined χ , a parameter established in a manner similar to Pitzer's ω at $T_r = 0.6$.

Halm and Stiel[14] in further work on Stiel's concept produced a complicated relationship composed of a six-member series whose terms were lengthly functions of T_r, ω and χ .

Rackett[35] developed an equation which is claimed to include in its realm of applicability non-normal liquids. Its form is:

$$\log V_r = (1-T)^{2/7} \log z_c \qquad (9)$$

which was unusual in that it was solved for reduced specific volume instead of density. More important, except for the exponent, it contained no arbitrary constants.

Spencer and Danner's investigation[41] suggested that the Rackett equation's accuracy could be improved. They therefore tested

Rackett's suggestion that z_c should be replaced by an empirical factor, which is a modified critical compressibility factor, z_{ra}. This characteristic constant is evaluated by regression of experimental data.

Obviously, this approach would improve the fit of any equation but the presupposition of the existence of sufficient data to perform a curve fit eliminates the need for a predictive correlation. The value of this contribution, therefore, must be regarded skeptically.

Gunn and Yamada[13] proposed a relationship which was also solved for the specific volume and had the form:

$$\frac{V}{V_{sc}} = V_r^o(1.0 - \omega V^1_r) \qquad (10)$$

where V^o_r and V_r^1 are lengthly equations explicit in T_r,

V is the absolute specific volume,

ω is as previously defined and

V_{sc} is the scaling volume defined as:

$$V_{sc} = \frac{V_{0.6}}{0.3862 - 0.0866} \qquad (10b)$$

in which $V_{0.6}$ is the specific volume at $T_r = 0.6$. While most of the foregoing relationships require only the value of z_c to permit evaluation, it is noteworthy that this last equation requires a data point at $T_r = 0.6$ as does Halm and Stiel.

Correlation of Densities of Liquid Mixtures

Although all of the foregoing discussion has concerned itself with predicting the properties of pure substances, mixtures can be treated in a similar manner. The adaptation requires the calculation of "pseudo-critical" properties; i.e., the mixture is treated as a pure substance with unique physical constants.

Procedurally, a mixing rule such as that proposed by Kay[19], Joffe[18] or some later modification[27], is applied to produce the pseudo-critical temperature. Kay's Rule, the simplest, is usually satisfactory for temperature calculations and is represented thus:

$$T_{cm} = \sum_{i}^{n} x_i T_{ci} \tag{11}$$

in which T_{cm} is the pseudo-critical temperature of the mixture,

X_i is the mole fraction of a given component i, and

T_{ci} is the critical temperature of a given component i.

Similarly, simple mixing rules can also be applied to third parameters (α, ω or Z_c) with good reliability. Usually, however, Kay's Rule will prove unsatisfactory for calculating pseudo-critical pressure and some other method (such as those mentioned above) should be utilized for better accuracy.

One general word of caution remains to be offered when applying any of the foregoing correlations. Hougen et al. in their widely-used text[16] pointed out that reported values for the critical density are often unreliable. Consequently, simply multiplying the calculated reduced density by the critical will not necessarily yield an accurate absolute value. The recommended procedure is to apply Watson's proportionality (Equation 1). This requires an absolute density measurement (hopefully reasonably close to the area of interest), use of the desired correlation from among the foregoing to calculate the reduced density, and employment of the ratio of the two as a reference. Subsequently, when the reduced density for the desired point is calculated, the magnitude of the absolute density may be more reliably obtained by multiplying it by the reference ratio.

This procedure is represented by the equation:

$$\rho_1 = \rho_{r1} \frac{\rho_{ref}}{\rho_{rref}} \tag{12}$$

When this method is applied to mixtures, it becomes:

$$\rho_m = \rho_{rm} \frac{\rho^o_m}{\rho^o_{rm}} \tag{13}$$

where ρ^o_{rm} is the theoretical mixture reduced density at 0^oK; given by

$$\rho^o_{rm} = 2.38 + 0.2\,\alpha_m, \tag{14}$$

and

ρ_{rm} is the mixture reduced density at $T_{rm} = T/T_{cm}$, $P_{rm} = P/P_{cm}$, and ρ^o_m is calculated per the proposal of Hougen and Watson[16] (1st edition);

$$\rho^o_m = \frac{M_m}{V^o_m} \tag{15}$$

where M_m is the average molecular weight of the mixture,

$$V^o_m = \sum_i^n x_i V^o_i \text{ and} \tag{16}$$

$$V^o_i = \frac{M_i}{\rho^o_i} \text{ and, in turn}$$

$$\rho^o_i = \rho^o_{r_i} \frac{\rho_{ref}}{\rho_{rref}} \tag{17}$$

In proposing this procedure Hougen and Watson implied the assumption of additivity of specific volumes at absolute zero.

Definition of Non-Normal Liquids

Since much has been made of the distinction between normal and non-normal compounds with respect to the predictability of their liquid densities, identification of each of these types of compounds is in order.

"Non-normal" in this context is usually synonymous with "polar" or "hydrogen bonded". That is, most of these compounds contain a lone hydrogen chemically bonded to a highly electronegative atom such as oxygen, nitrogen or fluorine. In the liquid state such compounds form non-chemical bonds between the hydrogen of one and the electronegative atom of an adjacent similar molecule.

The resulting behavior of these compounds differs from that of their chemical analogues containing less electronegative atoms by exhibiting higher melting and boiling points and sharply differing entropies of vaporization. In short, a hydrogen bonded compound behaves in a manner one would associate with a higher molecular weight, less volatile substance.

Examples of hydrogen bonded organics include alcohols and acids. To a lesser extent ethers, nitriles and amines will also exhibit this behavior. Hydrogen bonded inorganics include water and hydrogen fluoride as well as ammonia to a lesser degree.

PART I - COMPARISON OF AVAILABLE CORRELATIONS

PURE COMPOUND CORRELATIONS

Because a large number of the equations presented in the Literature Review section proved too complicated and unwieldy for practical application, they were eliminated from consideration at the outset of the project. Some others, such as the Spencer and Danner modification of the Rackett equation, had no value as predictive tools and were likewise rejected. Remaining, then, were the Riedel equation, the Rackett equation and the variable third parameter approach of Joffe and Zudkevitch.

Evaluation of the Riedel Equation

Riedel's correlation, as is true with most other proposed methods, works very well for non-polar, non-associating compounds such as hydrocarbons but exhibits appreciable inaccuracies when applied to "non-normal" liquids. In light of this fact, it seemed worthwhile to explore the nature of the non-conformance of some compounds to the Riedel formula.

It was reasoned that if the constant and the exponent of the third term were fitted by least squares regression instead of in the normal manner, it would serve as a test as to whether or not the Riedel form is a universally applicable equation (given proper constant values) or has no value except for certain non-normal compounds.

The results of attempted curve fits on nine common normal and non-normal substances showed that the data of several of the latter did indeed follow a trend which could be predicted by the Riedel form. Examples of this group are acetic acid and acetonitrile.

However, density data of some other non-normal substances described curves which were distinctly different from the Riedel equation. Methanol, ethanol and water's reduced density vs. reduced temperature plot formed a curve which more nearly resembled a parabola rather than a Riedelian shape.

The obvious conclusion to be drawn is that the Riedel equation form cannot be made universally applicable regardless of how the constants and exponents are defined.

Table I contains the results of this study involving three classes of compounds: "normal" liquids (ethane, propane, pentane), non-normal liquids which can be made to conform (acetonitrile, n-propanol and acetic acid) and non-conforming compounds (ethanol, methanol, and water). The term "conforming compounds" is used to designate those substances whose average percent error and error bias between actual data and the curve-fitted Riedel equation is appreciably less than 1%.

Figures I, II and III each depict a typical and normal, non-normal conforming, and non-conforming compound, respectively. Note that the conventional Riedel curve is shown along with the experimental data and the curves representing the least squares fit to the Riedel equation.

TABLE I

REDUCED DENSITY DATA CURVE FIT TO THE RIEDEL EQUATION

COMPOUND	MOL. WEIGHT	Z_c	RANGE OF T_r DATA	NO. PTS.	RIEDEL CONSTANT FOR n = 0.3333...	PERCENT ERROR			RIEDEL CONSTANT AND EXPONENT	PERCENT ERROR			DATA REFERENCE
						HIGH	AVG.	LOW		HIGH	AVG.	LOW	
Methanol	32.042	0.2202	0.5323 to 0.9971	30	K = 2.1326	2.76	1.69	0.007	K = 0.7305 n = 0.3118	2.00	0.92	0.03	47
Ethanol	46.069	0.2491	0.5291 to 0.9988	28	K = 2.0596	2.62	1.49	0.16	K = 0.7051 n = 0.3175	2.32	1.01	.006	47
N-Propanol	60.096	0.2496	0.6578 to 0.9996	20	K = 2.1741	6.25	1.01	0.015	K = 0.6956 n = 0.2900	3.45	1.01	.002	47
Acetonitrile	41.053	0.1815	0.4986 to 0.9931	21	K = 2.3302	4.12	2.33	0.04	K = 0.9317 n = 0.3380	1.95	0.49	0.027	47
Acetic Acid	60.052	0.2005	0.4929 to 0.9973	31	K = 1.9809	2.80	.46	.006	K = 0.6602 n = 0.3155	1.97	0.26	.01	47
Water	18.015	0.2294	0.4220 to 0.9996	29	K = 2.2414	5.98	2.30	.18	K = 0.8197 n = 0.3339	6.70	2.04	0.14	7
Ethane	30.070	0.2793	0.8127 to 0.9997	12	K = 1.7958	1.28	0.56	.14	K = 0.6334 n = 0.3519	.56	0.25	.05	10
Propane	44.097	0.2765	0.6249 to 0.9991	26	K = 1.8353	1.03	0.45	.005	K = 0.6294 n = 0.3445	.61	0.17	.01	11
N-Pentane	72.151	0.2685	0.6582 to 0.9930	30	K = 1.9099	1.60	0.27	.016	K = 0.6582 n = 0.3393	1.11	0.37	.003	28

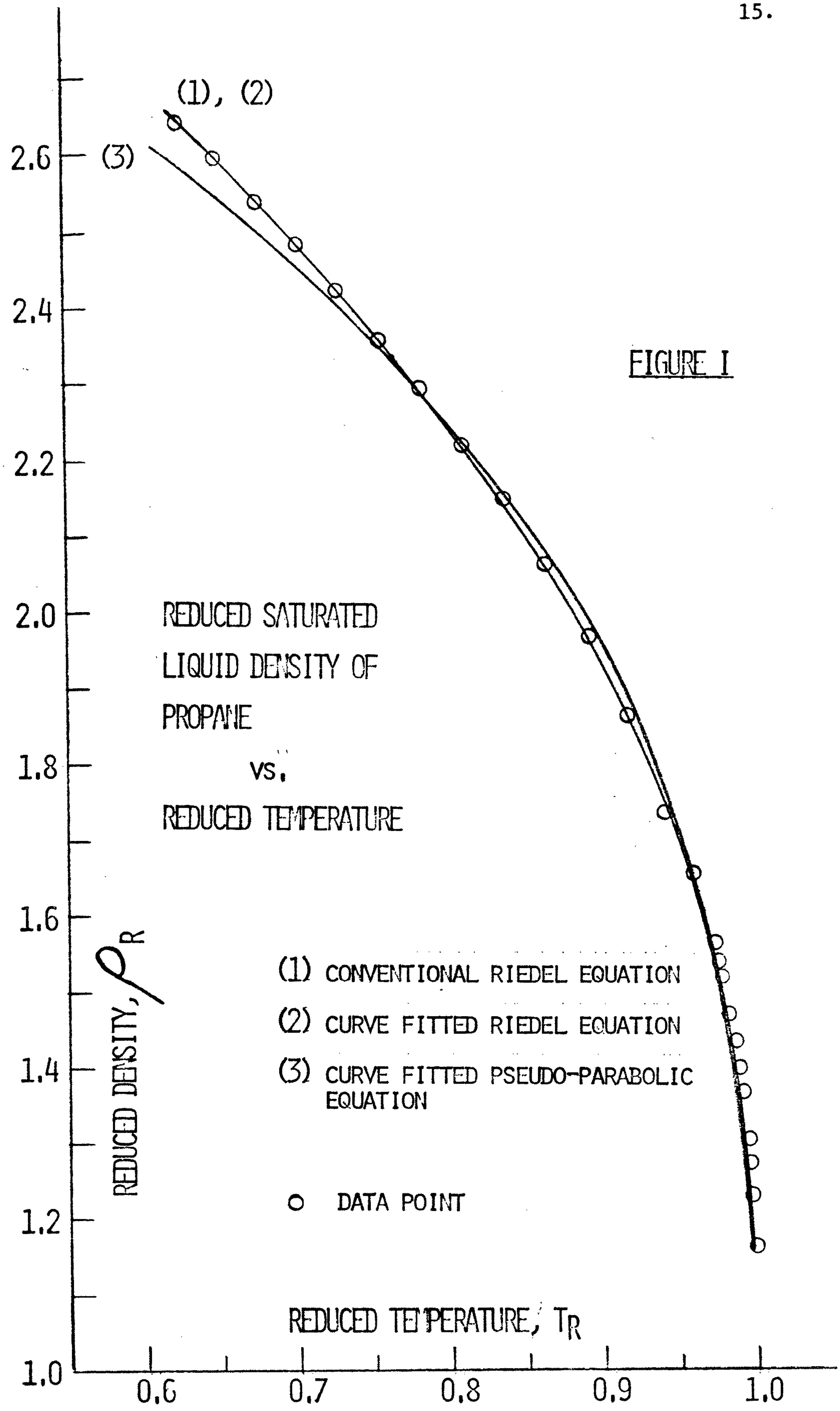

FIGURE I

REDUCED SATURATED LIQUID DENSITY OF PROPANE
vs.
REDUCED TEMPERATURE
(1), (2)
(3)
(1) CONVENTIONAL RIEDEL EQUATION
(2) CURVE FITTED RIEDEL EQUATION
(3) CURVE FITTED PSEUDO-PARABOLIC EQUATION
○ DATA POINT
REDUCED DENSITY, ρ_R
REDUCED TEMPERATURE, T_R
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
0.6
0.7
0.8
0.9
1.0

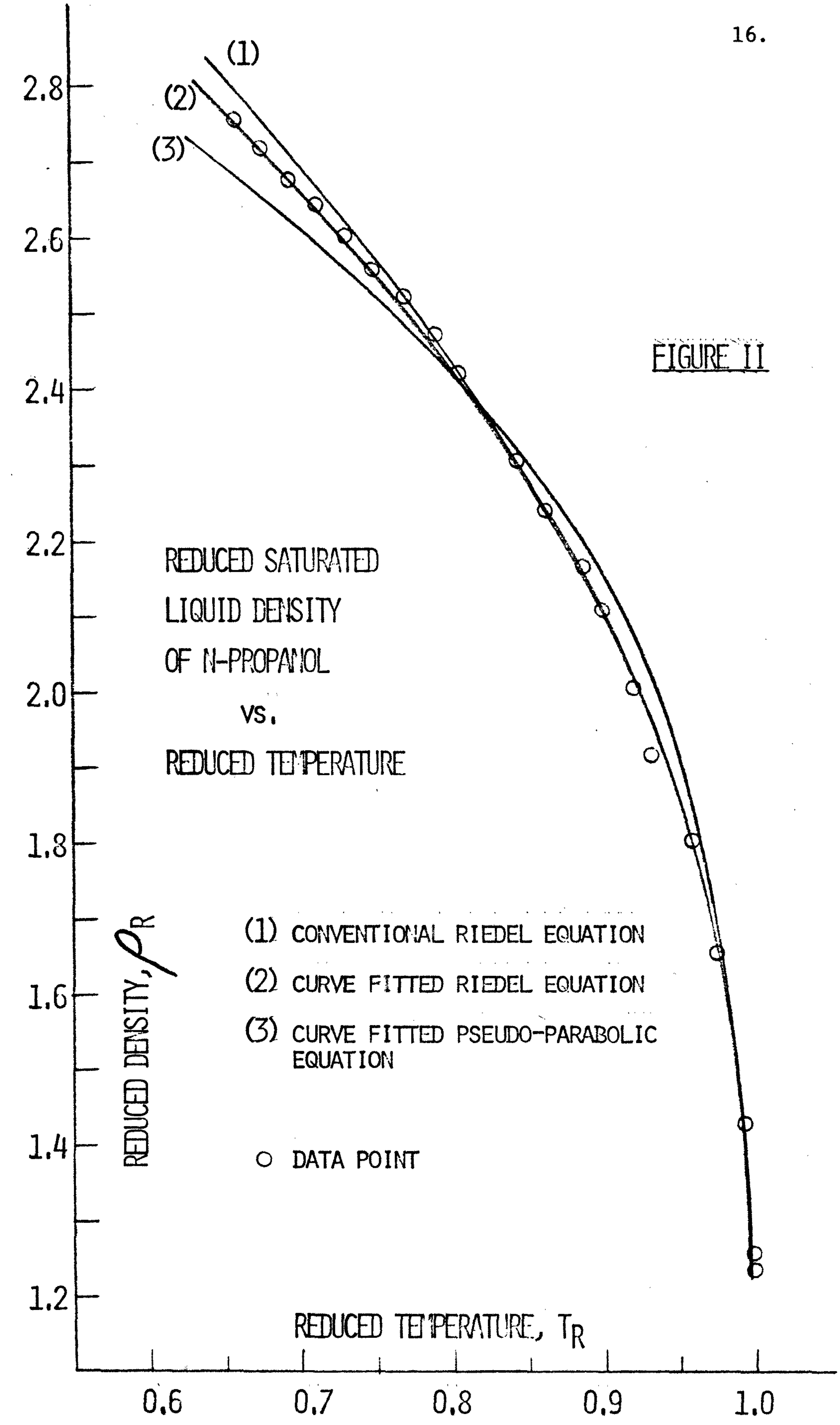

FIGURE II

REDUCED SATURATED LIQUID DENSITY OF N-PROPANOL vs. REDUCED TEMPERATURE

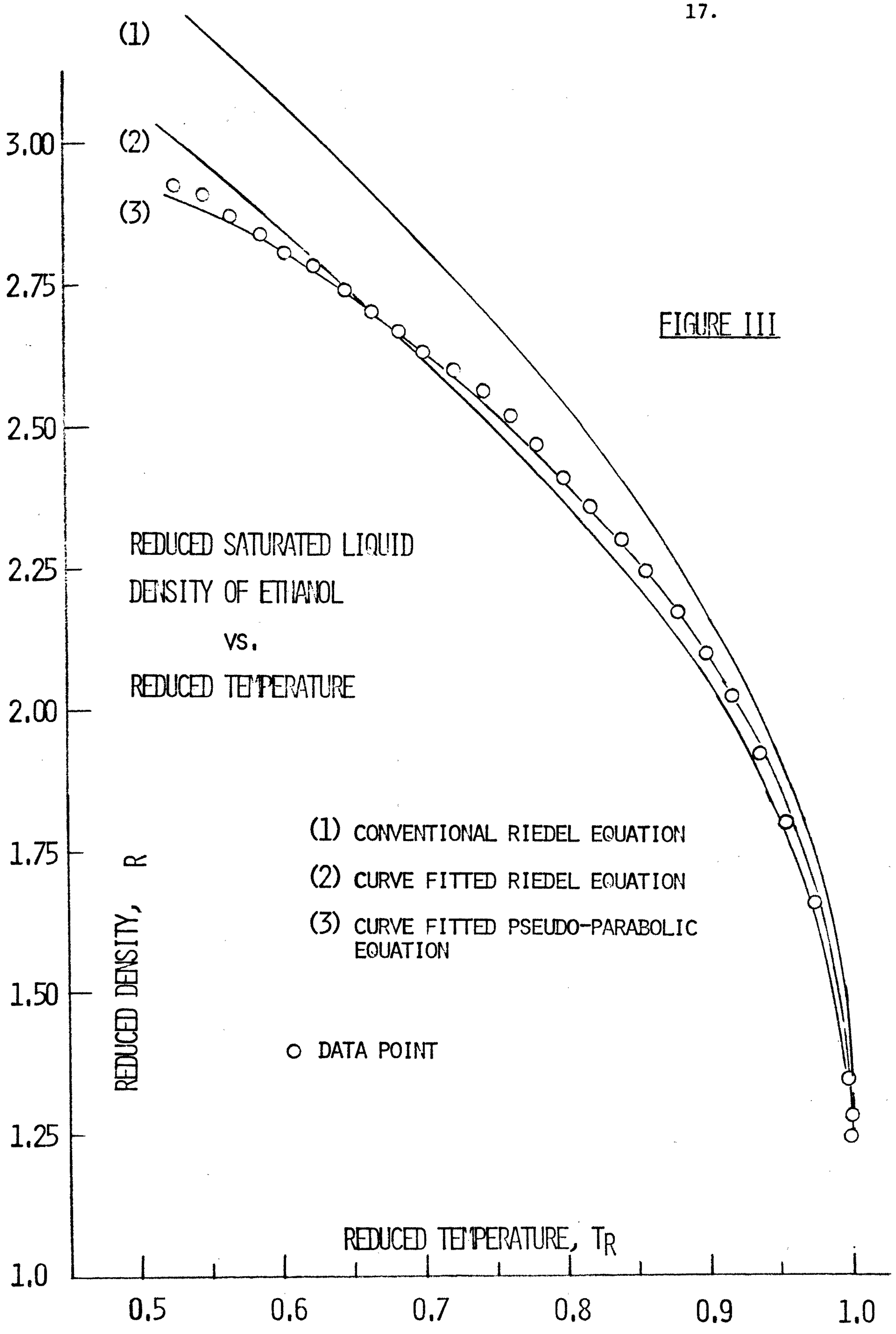

FIGURE III

REDUCED SATURATED LIQUID DENSITY OF ETHANOL
vs.
REDUCED TEMPERATURE

Although Riedel recognized the lack of validity of this correlation for compounds which associate due to hydrogen bonding in his definition of normality, Lydersen et al.[30] apparently ignored this fact when they employed the Riedel equation to generate their chart for saturated liquid density. In this chart, the values presented for $z_c = 0.23$ were those for water. The lack of validity of this choice can be graphically demonstrated by plotting values for reduced density (generated from the Riedel equation) vs. reduced temperature for various levels of critical compressibility. If the actual data for water were plotted on the same graph, it would be seen that, as stated before, a more parabolic curve will result. This curve actually crosses the other z_c lines at low values of reduced temperature. It is for this reason that Lydersen's charts should not be employed to calculate the saturated liquid densities of compounds whose critical compressibilities are less than 0.25.

Evaluation of the Rackett Equation

As a recent innovation, it was felt that the Rackett correlation should justify its usefulness by proving itself a superior liquid density model compared with its predecessors. This, of course, refers to the Riedel equation, the only prior equation of appreciable merit.

These two equations were tested on experimental data of several common compounds representing both normal and non-normal liquids. The results of this comparison are tabulated in Table II. The detailed computer print-out is included in Appendix C.

TABLE II

COMPARISON OF RIEDEL AND RACKETT EQUATIONS

COMPOUND	NUMBER OF POINTS	DATA REDUCED TEMPERATURE RANGE	RACKETT PERCENT ERROR			RIEDEL PERCENT ERROR			DATA REFERENCE
			HIGH	AVG.	LOW	HIGH	AVG.	LOW	
Hexadecane	6	0.4081 to 0.5015	0.07	0.06	0.01	0.63	0.30	0.05	*
Ethane	13	0.8127 to 1.000	1.13	0.60	0.00^{+}	0.74	0.36	0.00^{+}	10
Propane	26	0.6249 to 0.9991	1.68	0.64	0.00^{+}	0.98	0.47	0.00^{+}	11
Acetic Acid	30	0.4929 to 0.9805	13.21	5.61	0.00^{+}	7.15	2.16	0.00^{+}	47
Methanol	30	0.5323 to 0.9971	11.66	6.19	0.00^{+}	9.58	4.26	0.00^{+}	47
Ethanol	28	0.5291 to 0.9988	5.90	3.48	0.00^{+}	5.44	2.96	0.00^{+}	47
Acetonitrile	21	0.4986 to 0.9931	7.80	2.30	0.00^{+}	3.57	0.88	0.00^{+}	47
Dodecane	7	0.4413 to 0.5514	0.25	0.12	0.06	0.27	0.15	0.07	*
n-Pentane	30	0.6583 to 0.9930	1.64	0.29	0.00^{+}	1.26	0.30	0.00^{+}	28
n-Propanol	21	0.6578 to 0.9996	6.71	1.84	0.00^{+}	7.51	1.50	0.00^{+}	47
Water	23	0.4220 to 0.8923	11.13	6.64	0.00^{+}	8.23	5.38	0.00^{+}	7

* Experimental data measured in Part II.

Of the eleven species tested, five (ethane, propane, n-pentane, dodecane and hexadecane) are normal liquids. As might be expected, all of these were accurately predicted by both equations. For the Riedel correlation, all had average errors below 0.5% (all but one were below 0.4%) with maximum errors below 1%. By comparison, the Rackett formula performed better for only one compound (hexadecane: average error = 0.06%; maximum error = 0.7%) but was noticeable poorer for two others (ethane and propane). In spite of these findings, it cannot be disputed that either equation could be regarded as highly reliable for normal compounds in this category.

It should be noted that the data for dodecane and hexadecane were actual experimental measurements produced for Part II of the present work. Except for these two, whose reduced temperature range spanned only 0.1 (about 70^{o}C), all of the data covered a 0.2 to 0.4 variation in reduced temperature and included the critical point.

Six non-normal compounds (acetic acid, methanol, ethanol, acetonitrile, n-pentanol and water) were also tested with more conclusive results. Although neither equation predicted the behavior of this group of substances as well as it did the normals, the Riedel showed a slight superiority to the Rackett (from the point of view of average and maximum percent error) for five compounds (acetic acid, acetonitrile, methanol, ethanol and water). At best, the Rackett only matched the former's reliability on the sixth (n-propanol).

Acetonitrile, it will be noted, conformed to the Riedel formula exceedingly well with an average error of only 0.88% and a maximum of 3.57% for a reduced temperature data range of about 0.4. The other four organics conformed to the Riedel with average errors between 1.50 and 4.26% compared with 1.84 to 6.19% error using the Rackett correlation.

In spite of the foregoing, one general qualification should be made about the results of the non-normal compounds: simply comparing the errors is quite misleading. Examination of the detailed results included in Appendix C reveals that for five of the compounds, the error increases steadily with reduced temperature for both equations, e.e., a distinct, large bias exists. The conclusion to be drawn is that any near-conformity of the non-normals to either equation is coincidental. Both correlations trace curves which are a pronouncedly different shape from the trend of the data.

A word about acetonitrile's conformity should also be offered. It will be recalled that in the previous discussion concerning the nature of non-normal compounds, hydrogen bonding was held responsible for most non-normality. In the case of acetonitrile, since it has no hydrogen bonded directly to the electronegative nitrogen, this effect is not possible although molecular polarity does exist. For this reason, acetonitrile's behavior with respect to the Riedel and Rackett formulas is more like that of a straight-chain hydrocarbon than, say, an alcohol.

Conclusion: Overall, a slight advantage may be assigned to the Riedel equation for both normal and non-normal compounds below $z_c = 0.25$.

Joffe-Zudkevitch Adaptation of the Riedel Equation

This new adaptation of the Riedel equation is being formally described in this thesis as a hitherto virtually unpublished innovation.[52]

Simply stated, the proponents of this method contend that no simple coefficient derived from a constant third parameter can characterize a given compound over a broad range of reduced temperature values. Accordingly, it was hypothesized that the third parameter should be a function of reduced temperature.

To test this supposition, the Riedel equation was rearranged thus:

$$\psi = \frac{\rho_r - 1 - 0.85\,(1-T_r) - 1.692\,(1-T_r)^{1/3}}{0.985\,(1-T_r)^{1/3}}$$

ρ_r vs. T_r data were then introduced into the expression to generate a plot of ψ vs. T_r.

Inspection showed that the loci of data for most compounds was a straight line up to at least $T_r = 0.8$. However, beyond this determination no generalization seemed possible. While most slopes were relatively shallow (absolute value less than 1.0) both compounds with positive and others with negative slopes existed among non-normal substances. Some of the tested liquids maintained a constant trend up to the critical temperature while others showed a marked tendency to level off or even pass through a maximum after $T_r = 0.8$.

Naturally, normal compounds were very nearly horizontal in slope --- a circumstance which validates the Riedel assumption of a constant, temperature - independent third parameter for these substances.

As a result of these determinations, two alternate procedures were evolved:

1. If a density data point is available, (It is rare that a handbook value or good estimate of a compound's density at some temperature is not available.) an empirical third parameter could be obtained which would be more reliable than the parameter calculated by the classical Riedel approach. (Note, However, that using this single value over a broad range of T_r implies acceptance of the basic Riedelian assumption of a constant third parameter and could still result in substantial error.)

2. If more than one data point is available, the slope of the ψ vs. T_r function could be determined. In that case, the behavior of the saturated liquid density over a broad range of T_r could be determined with considerable confidence.

For cases in which the trend of the ψ vs. T_r function changes sharply after $T_r = 0.8$, it was decided that above this point the coefficient at $T_r = 0.8$ would be used. This approach has been found to be accurate both for compounds which maintain a constant slope up to criticality and for those which do not. An example calculation employing this method is included as Appendix D.

Obviously, the varying third parameter correlation is most accurate when used with compounds previously designated "non-normal conforming" in the discussion of the conventional Riedel equation. Note that the Joffe-Zudkevitch procedure is similar in effect to the curve-fitting analysis undertaken on the original correlation (see Evaluation of the Riedel Equation).

However, this modification's major utility is not due so much to its value as a predictive tool for pure compound liquid densities as to its utility for liquid mixture densities in which individual pure component data are available. This will be further discussed in the section devoted to mixtures.

Treatment of Non-Conforming Compounds

While the Joffe-Zudkevitch modification brings a number of non-normal compounds within the Riedel equation's predictive ability, many common compounds still elude correlation. Accordingly, attempts were made to define an applicable equation form.

Recognizing the parabolic properties of the data for water, ethanol, methanol, etc., an equation of that type was tested.

Its form was:

$$\rho_r = 1 + \left[4K\ (1-T_r)\right]^n$$

which resembles the rearranged general parabolic equation:

$$y = a + \left[4K\ (x + b)\right]^{1/2}$$

Linear regression of the density data for non-conforming compounds showed that this equation modeled compounds such as methanol and ethanol almost as well as the Riedel predicted the hydrocarbons. Unfortunately, as might have been expected, normal and non-normal compounds which conformed to the Riedel equation fit this expression rather poorly by comparison. (See Table III)

Ethanol, for instance, was one of the compounds which was considered non-conforming even when curve fitted to the Riedel equation (Table I). Examination of Figure III illustrates how the experimental data fell well below the conventional Riedel curve and crossed the curve of the fitted Riedel. However, it conformed excellently to the shape of the pseudo-parabolic form. From an error profile of 2.32, 1.01 and 0.006 (the high, average and low percent error, respectively) for the fitted Riedel, ethanol exhibited a profile of 1.44, 0.56 and 0.03.

On the other hand, n-propanol, a conforming non-normal substance, experienced an unfavorable error profile change from 3.45, 1.01 and 0.002 for the fitted Riedel to 5.03, 2.19 and 0.14 (Figure II).

Still worse was propane, a normal compound, where an error profile of 0.61, 0.17 and 0.01 deteriorated to 2.07, 0.77 and 0.05.

TABLE III

LIQUID DENSITY DATA CURVE FIT TO THE PSEUDO-PARABOLIC FORM

COMPOUND	NUMBER OF POINTS	DATA REDUCED TEMPERATURE RANGE	PERCENT ERROR			DATA REFERENCE
			HIGH	AVG.	LOW	
Water	28	0.4220 to 0.9996	3.04	0.67	0.03	7
Ethanol	28	0.5291 to 0.9988	1.44	0.57	0.03	47
Methanol	30	0.5323 to 0.9971	1.04	0.26	0.03	47
Acetonitrile	20	0.5351 to 0.9931	1.64	0.97	0.31	47
n-Pentane	30	0.6582 to 0.9930	1.11	0.34	0.02	28
Acetic Acid	31	0.4929 to 0.9973	2.87	1.21	0.02	47
n-Propanol	20	0.6578 to 0.9996	5.03	2.19	0.14	47
Propane	26	0.6249 to 0.9991	2.07	0.77	0.05	11

It is nevertheless interesting that the pseudo-parabolic equation, which is little more than the classical Riedel correlation with the center term deleted, can be made to fit hitherto unpredictable data. One might conclude that if some coefficient were devised for the second term of the Riedel expression which would greatly decrease its contribution for certain non-normal compounds, that equation might become universally applicable. Speculation suggests that this coefficient might measure the absolute value of the slope of Joffe and Zudkevitch's ψ vs. T_r line and decrease the coefficient's magnitude as the slope increases. Obviously, a considerable amount of testing would be required to determine the viability of this proposal.

LIQUID MIXTURE CORRELATIONS

The only widely-accredited approach to predicting the densities of liquids is the pseudo-critical property method described in the Literature Review section. Of the mixing rules available, Kay's[19] is the simplest and is found to be reasonably effective for critical properties other than pressure.

Accordingly, Kay's Rule was used to calculate the third parameter for the mixture from individual component parameters. The third parameter of interest was, of course, the ψ of the Joffe-Zudkevitch method.

Test data for this evaluation consisted of nine binary systems whose individual component physical property data were well established by literature sources. Mixture density data included four systems whose solution densities were measured experimentally as part of the present project. The rest consisted of various aqueous binaries obtained from the literature.

The results of this evaluation are presented in Table IV.

A major problem with available data on the density of liquid mixtures is the relatively narrow temperature ranges covered. In most cases, the range of reduced temperatures tabulated for a particular system was only 0.1.

As might be expected, systems containing water, the compound least correspondent with the Riedel equation, exhibited the poorest accuracy. Still, except for the binary containing acetic acid, the disagreement between predicted and experimental data for nearly all systems was less than 2% over the range tested. The poor performance of aqueous acetic acid might be ascribed to the unique tendency of this compound to dimerize (due to hydrogen bonding) in both the liquid and vapor phase. Also, the excursion from predicted values increased steadily with increasing acid concentration.

The excellent results of the dodecane - hexadecane (normal-normal) binary were as expected while the agreement of the methanol-acetonitrile, the methanol - water and ethanol - water binaries was encouraging. The magnitude of the errors observed is well within the uncertainty acceptable for use in chemical engineering design calculations, confirming the usefulness of this correlation.

TABLE IV

TEST OF DATA AGREEMENT WITH THE JOFFE-ZUDKEVITCH METHOD

SOLUTE	SOLVENT	SOLUTE CONCENTRATIONS (WEIGHT FRACTION)	TEMPERATURE RANGE(°C)	PERCENT ERROR			DATA REFERENCE
				HIGH	AVG.	LOW	
Acetic Acid	Water	0.10, 0.30, 0.50, 0.75	0 to 30	11.20	6.38	0.64	5
Ethyl Ether	Ethanol	0.4858	50 to 210	2.81	1.40	0.25	+
Dodecane	Hexadecane	0.361, 0.651	17.2 to 89.7	0.35	0.21	0.02	*
Methanol	Acetonitrile	0.336, 0.650, 0.899	15.4 to 50.1	1.14	0.44	0.02	*
Ethanol	Water	0.10, 0.25, 0.50, 0.75	10.0 to 40.0	1.88	0.41	0.20	5
Isopropanol	Water	0.10, 0.25, 0.50	0.0 to 30.0	7.03	2.10	0.11	5
Methanol	Water	0.10, 0.25, 0.50, 0.75	0.0 to 20.0	1.24	0.89	0.06	5
Hexadecane	Isopropanol	0.3040, 0.616	17.20 to 70.0	2.66	2.19	1.49	*
Acetonitrile	Isopropanol	0.293, 0.493	17.20 to 70.0	0.78	0.48	0.14	*

* Experimental data from Part II

\+ Personal Correspondence

Only the hexadecane - isopropanol mixture was inexplicably non-conforming. One might have expected this combination of a normal and a conforming non-normal substance to yield better agreement than a mixture of two non-conformers such as the ethanol - water system.

Although not attempted as part of the present program, the testing of other mixing rules might be undertaken to determine if the correlational disagreements observed might be resolved without resorting to other correlation methods.

PART II -- EXPERIMENTAL MEASUREMENTS

INTRODUCTION

Although it was originally planned to measure the saturated liquid densities of representative systems for broad ranges of reduced temperature, the cost of apparatus suitable for making these determinations above the normal boiling point proved prohibitive. For reasons of availability as well as economy, therefore, the liquid pycnometer method was chosen. Since system pressure was atmospheric and temperatures were below the normal boiling point in all cases, the difference between the measured values and those expected under truly saturated conditions would be negligible.

EXPERIMENTAL METHOD CRITIQUE

Two major attributes of the liquid pycnometer test method impaired its qualifications for use in the present program.

1. Inherent in the underlying assumptions of this method is the condition which requires that the bath, the laboratory and the mass balance all be at the same temperature. This immediately restricts the experiments to a temperature range relatively close to ambient conditions. If these conditions are not maintained, errors would result due to the insertion of a capillary top whose temperature (and, hence, dimensions) were dissimilar to the vial. Also, generation of convective air currents by a comparatively warm pycnometer in the balance chamber might also prove a source of error.

2. At certain points in the testing procedure, the sample is necessarily exposed to the surroundings allowing free evaporation for several minutes. Volatile liquids might escape at this time in sufficient quantities to either prevent filling the capillary when it is replaced or alter the composition of a mixture by selective evaporation. Because of this possibility, testing at or very near the boiling point of the sample or one of its components would be inadvisable.

As a result of these considerations, a modified experimental procedure was evolved.

APPARATUS DESCRIPTION

Equipment employed in the pycnometer method of density measurement consisted of three major systems depicted in the diagram of Figure IX (Appendix A):

1. Constant Temperature Bath -- This included a 4-liter Dewar flask filled with white mineral oil, a cooling water coil of 3/8-inch copper tubing, a thermocap-type automatic temperature controller and a slave electric heater.

2. Sample Vessels -- These consisted of two pairs of Pyrex glass pycnometers whose volume was known in each case.

3. Monitoring Apparatus -- This category included the thermometer which recorded the bath temperature and the electronic balance by which each sample's mass was determined.

A detailed equipment specification list is included in Appendix A.

EXPERIMENTAL PROCEDURE AND DATA TREATMENT

1. With the temperature controller adjusted to the desired level, the pycnometers are filled to the brim with the sample solution. (Note that the classical experimental procedure requires filling only half way up the neck. This would not allow for evaporation and leakage in subsequent steps.)

2. After capping, the pycnometers are immersed in the bath up to their necks. Deeper immersion causes the oil of the bath to wick up the ground-glass joint and could cause contamination of the fluid.

3. In order to avoid the inaccuracies inherent in inserting a capillary top whose temperature is dissimilar to that of the vial, the capillaries are placed in a large test tube filled with the test liquid. The test tube is then likewise immersed in the bath and allowed to equilibrate with the samples.

4. After equilibration, the removal sequence begins with the removal of the pycnometer caps. These are hand dried with lintless tissue and placed in a drying chamber (i.e., a large heating mantle set at a high temperature) for a few minutes.

5. When the dry caps have cooled sufficiently to be easily handled, the capillaries are extracted from the test tube one at a time and placed on their respective pycnometers. This operation is

carried out employing a pair of long tweezers. The dual advantage of this instrument is that it prevents both finger-oil contamination as well as capillary heating/cooling resulting from skin contact. When inserting the capillaries, it is important to ram them home fairly briskly. This forces the excess liquid up the tube rather than out the neck of the vial around the capillary cap.

6. Wiping the excess liquid from the exterior of the capillary and cap seat is accomplished as quickly as possible using a lintless tissue. The cap is then set in place to prevent evaporation of the liquid from the tip of the capillary.

7. The pycnometer must be allowed to cool/warm to room temperature to prevent convective air currents during weighing. Giving the cap a slight twist when it is placed on the vial makes a reliably air-tight seal to prevent the escape of vapors.

8. The exterior of the entire pycnometer is wiped several times to remove both oil and debris before weighing.

Note that when the cap is removed for drying, the pycnometer is standing open for at least 5 minutes under the best of conditions. This can be a source of error, not only because of evaporation losses per se, but because the sample mixture has established an equilibrium vapor phase in the void space of the cap. This single stage evaporation could alter the composition of the liquid gradually over several measurements when the sample is recovered for reuse.

Practical maximum temperature for any system is 10°C below the boiling point of the more volatile component. Practical minimum for this study was about 15°C absolute -- set by the available cooling water temperature.

Speed and dexterity are of the utmost importance in obtaining reliable and consistant results.

For each test, two pycnometers are run at a time (both filled with the identical solution). If the results are suitably consistent (±0.001 g/cc combined uncertainty) the point is taken as reliable; otherwise it is rerun.

Data analysis was a simple matter of dividing the sample mass obtained from the procedure described above by the volume of the pycnometer at the testing temperature. This latter value was obtained by prior calibration of the vial with distilled water (see Error Analysis section).

EXPERIMENTAL DATA PRESENTATION AND DISCUSSION

Five types of liquid systems were identified within the critical compressibility range of interest (i.e., Z_c 0.25):

Group 1. pure non-associating compounds (e.g., normal hydrocarbons),

Group 2. pure associating (i.e., hydrogen bonding) compounds (e.g., methanol, ethanol and acetic acid),

Group 3. mixtures of associating compounds,

Group 4. mixtures of non-associating compounds and

Group 5. mixtures of associating with non-associating compounds.

Two requirements dominated the choice of the actual compounds used in these determinations. One was the desirability of a sufficiently high boiling point (at least 80°C) to insure a broad temperature range for investigation (see Experimental Procedure section). Also, the compound of choice should be readily and economically available in a suitably pure form (at least 99 weight percent).

The data obtained during this investigation are presented below according to category.

<u>Group 1.</u> Data obtained for pure dodecane (C_{12}) and for pure hexadecane (C_{16}) are presented in Table V and represented in Figure IV. The high boiling points of these two hydrocarbons (215.3°C and 287°C, respectively) made it possible to measure densities up to 90°C (the practical maximum set by handling considerations) with relatively small uncertainties. Note that the measured values of 0.7479 gm/cc for dodecane and 0.7715 gm/cc for hexadecane, both at 22.0°C, are suitably consistent with literature[15] values of 0.7487 and 0.77331, respectively, at 20°C. These latter points are also included on the graph.

It will be noted that one point, that of dodecane at 17.1°C, is noticeably at variance with the trend of the other data points. Examination of the data measured during the entire program shows that 5 out of 11 points measured at temperatures less than 20°C exhibited unaccountably high experimental errors. Apparently, a large potential for experimental error exists at sub-room levels which is not as intuitively discernible as that encountered at elevated temperatures. It could be concluded that although potential error increases with temperature both above and below the 20-25°C room level, the condition worsens more rapidly with decreased temperature.

This source of error, however, apparently diminished with practice. Of the five erroneous points, three were generated in the first (chronologically) series of experiments (water - dimethoxyethane systems), one in the second group (methanol-acetonitrile mixtures) and one in the third (pure hydrocarbons). No spurious data points were generated in any of the four systems measured subsequently.

Group 2. Measurement of the properties of compounds in this category was considered largely unnecessary because of the mass of literature data available for substances such as the primary alcohols, acetonitrile, acetic acid, etc. One commercial compound, however, has received recent attention in the literature[22] insofar as measurement of its critical properties but virtually no attempt has been made to measure the liquid density. Dimethoxyethane density data was, therefore, measured. Results are tabulated in Table VIII and plotted on Figure VI.

As noted before, the sub-room temperature measurement suffered a slight failure to conform but the 19.9°C data point's 0.8679 value compared reasonably well with a literature value[15] of 0.8665 at 20°C.

This latter result, taken with the good conformity of the dodecane and hexadecane measurements to the literature, gives confidence in the inherent reliability of this experimental method.

It will be noted that, unlike the rest of the experimental measurements, the data collected for pure dimethoxyethane and for its aqueous mixtures are not utilized in Part I of this thesis. This was due to the fact that the reported critical properties for this compound were found to be inconsistent with the density data.

Kobe, et al.[22] reported critical properties for DME which resulted in a critical compressibility of 0.2345. When, however, the reduced densities derived from experimental and literature data are plotted against the reduced temperature, the loci of the points corresponded to the Riedel curve for a compound in which $z_c > 0.29$.

Since the data of even the most non-normal compounds lie at least partially along the proper Riedel z_c curve, one might conclude that this eccentric behavior is due to erroneous critical constants.

Group 3. Methanol - acetonitrile, dimethoxyethane - water and isopropanol - acetonitrile solutions of various concentrations were measured. Results are tabulated in Tables VII, VIII & IX and represented in Figures V, VI & VIII, respectively. The methanol-acetonitrile series was naturally limited by the low boiling point of methanol (64.96°C) to temperatures below 55°C (see the Experimental Procedure section). Note that the uncertainties of this system and for the dimethoxyethane - water mixtures are comparatively greater than for any other system investigated. (This is particularly true in the latter systems where sub-room temperature measurements were particularly unreliable.)

This fact points up the generally observed trend of worsening data scatter with increased temperature, with more volatile components and with increased concentration of the more volatile compound in a mixture. The fact that the third system of this group (which was measured chronologically later in the program) exhibited this behavior to a markedly lesser degree is probably attributable to the improvement in experimental technique more than any other factor.

Group 4. For the sake of comparison, various dodecane - hexadecane mixtures were measured and are presented in Table V and Figure IV. This provided a test system of two compounds whose pure state density behavior followed the Riedel - Lydersen predictions faithfully.

Due to the low volatility of these hydrocarbons, uncertainties were quite low. Also, the data points indicated a consistent trend both along each of the constant composition curves and among the curves themselves forming a uniform family.

Group 5. When a polar associating compound is mixed with a non-polar, the question becomes which is the dominant effect: will the associator induce a non-normalizing effect or will the non-associator dampen molecular interaction?

To answer this question, a system composed of hexadecane and isopropanol was offered as representative of this group. Results are found in Table X and Figure VIII. It will be noted that uncertainties for this body of data are the lowest of all systems tested, even though it does not contain the two least volatile compounds. (Note that the dodecane - hexadecane system, which was run simultaneously with this set of mixtures, possesses larger uncertainties.) This anomaly, although possibly coincidental, may indicate a strong surpression effect by the hexadecane on the isopropanol's volatility providing a closer agreement of experimental results.

With respect to an answer to the question posed above, there is evidence of unusual molecular interaction in the hexadecane - isopropanol system as already suggested by the fact that these data could not be predicted reliably by the Joffe-Zudkevitch method of Part I.

This non-normality is underscored when pure isopropanol data from the literature and hexadecane data from Table V is plotted on Figure VIII. Although pure isopropanol data appear consistent with the mixture curves, hexadecane's trend actually crosses these curves. The internal consistency of the hydrocarbon curves of Tables V & VI and their agreement with literature data, however, diminishes the possibility that the hexadecane data is erroneous. Assuming the presence of some unexpected interaction between hexadecane and isopropanol, therefore, seems to be the only viable conclusion.

TABLE V

MEASURED LIQUID DENSITIES OF PURE HYDROCARBONS

Temperature	gm/cc	
°C	Dodecane	Hexadecane
17.1	0.7489 ± 0.0008	
21.3		0.7729 ± 0.0004
22.0	0.7479 ± 0.0003	0.7715 ± 0.0017
40.5	0.73435 ± 0.00025	0.75965 ± 0.00015
59.7	0.72075 ± 0.00015	0.74635 ± 0.00045
	0.72045 ± 0.00025	
75.0	0.7089 ± 0.0004	0.73545 ± 0.00055
89.5	0.69815 ± 0.00075	0.7255 ± 0.0006

TABLE VI

MEASURED LIQUID DENSITIES OF HYDROCARBON MIXTURES

	gm/cc	
Temperature	Percent Dodecane in Hexadecane	
°C	36.09	65.13
17.2	0.76605 ± 0.00015	0.7595 ± 0.0003
31.2	0.7576 ± 0.0004	0.74935 ± 0.00015
49.7	0.7437 ± 0.0002	0.7361 ± 0.0004
70.0	0.7288 ± 0.0010	0.7214 ± 0.0004
89.7	0.71565 ± 0.00055	0.7080 ± 0.0005

TABLE VII

MEASURED LIQUID DENSITIES OF METHANOL - ACETONITRILE SOLUTIONS

Temperature	gm/cc Percent Methanol		
°C	33.63	65.02	89.93
15.4	0.79095 ± 0.00065	0.79525 ± 0.00045	0.79595 ± 0.00085
25.0	0.7826 ± 0.0014	0.7851 ± 0.0018	0.7853 ± 0.0014
	0.7826 ± 0.0004	0.7856 ± 0.00055	
40.3	0.76885 ± 0.00085	0.7724 ± 0.0006	0.7749 ± 0.0003
50.1	0.7590 ± 0.0008	0.7615 ± 0.0003	0.7659 ± 0.0008

TABLE VIII

MEASURED LIQUID DENSITIES OF DIMETHOXYETHANE - WATER SOLUTIONS

Temperature	gm/cc Percent DME		
°C	19.37	49.18	100.0
15.4	0.99395 ± 0.00025	0.98255 ± 0.00065	0.8685 ± 0.0009
19.9			0.8679 ± 0.0002
35.2	0.9858 ± 0.0005	0.9623 ± 0.0007	0.8513 ± 0.0002
55.0	0.9748 ± 0.0006	0.9479 ± 0.0019	0.83025 ± 0.00025
70.5	0.9660 ± 0.0013	0.9374 ± 0.0011	0.8129 ± 0.0005

TABLE IX

MEASURED LIQUID DENSITIES OF ACETONITRILE - ISOPROPANOL SOLUTION

Temperature °C	gm/cc Percent Acetonitrile 29.32	 49.27
17.2	0.7861 ± 0.0003	0.7851 ± 0.0006
31.2	0.77335 ± 0.00035	0.7716 ± 0.0002
49.7	0.7550 ± 0.0003	0.7526 ± 0.0004
70.0	0.73415 ± 0.00085	0.73125 ± 0.00095

TABLE X

MEASURED LIQUID DENSITIES OF HEXADECANE - ISOPROPANOL SOLUTION

Temperature °C	gm/cc Percent Hexadecane 34.04	 61.60
17.2	0.78095 ± 0.00025	0.7774 ± 0.0002
31.2	0.77025 ± 0.00035	0.76645 ± 0.00015
49.7	0.7538 ± 0.0003	0.75155 ± 0.00025
70.0	0.73515 ± 0.00035	0.73385 ± 0.00025

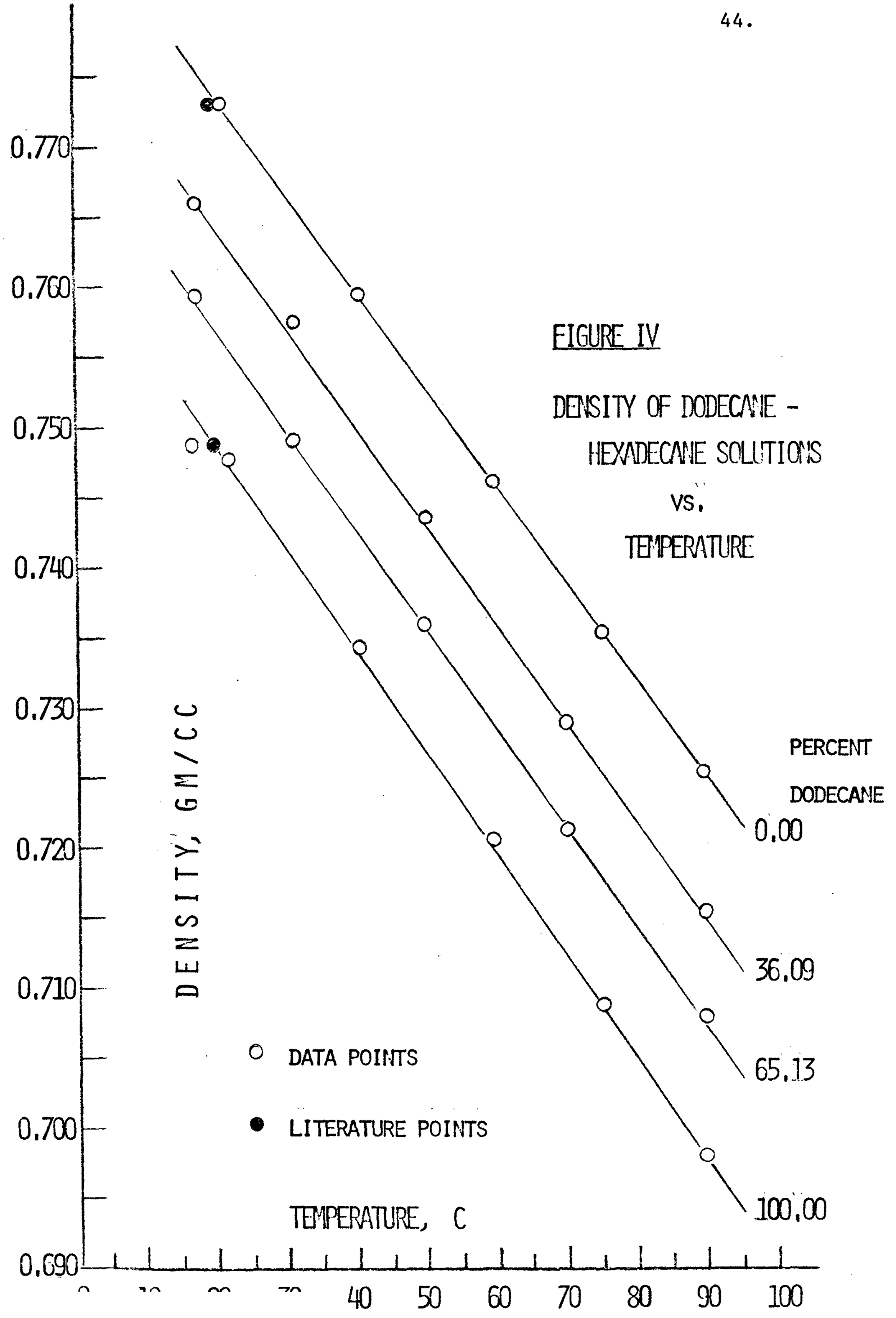

FIGURE IV

DENSITY OF DODECANE -
HEXADECANE SOLUTIONS
VS.
TEMPERATURE

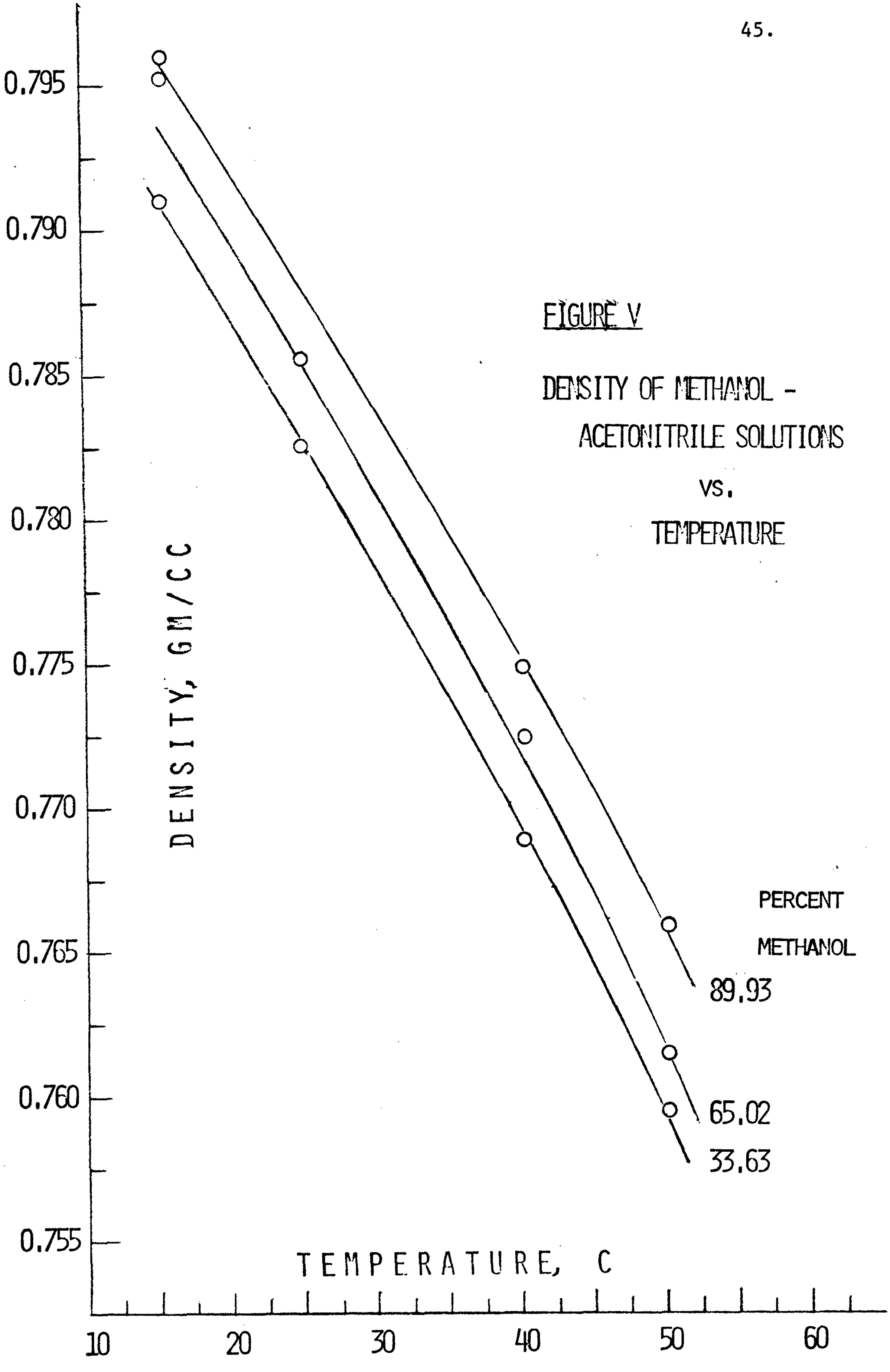
FIGURE V

DENSITY OF METHANOL - ACETONITRILE SOLUTIONS VS. TEMPERATURE

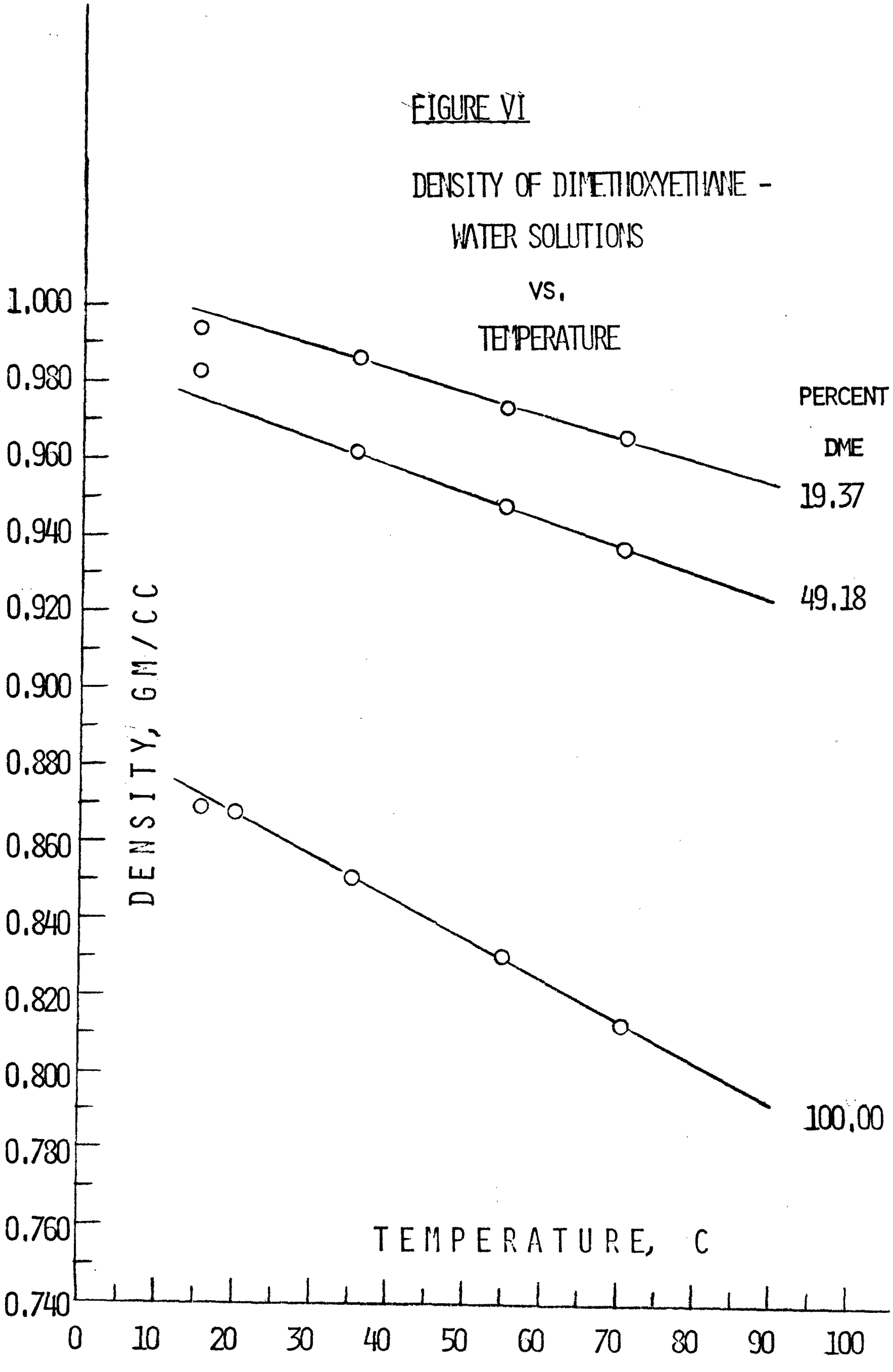
FIGURE VI
DENSITY OF DIMETHOXYETHANE - WATER SOLUTIONS
VS.
TEMPERATURE
PERCENT
DME
19.37
49.18
100.00
DENSITY, GM/CC
TEMPERATURE, C
1.000
0.980
0.960
0.940
0.920
0.900
0.880
0.860
0.840
0.820
0.800
0.780
0.760
0.740
0
10
20
30
40
50
60
70
80
90
100

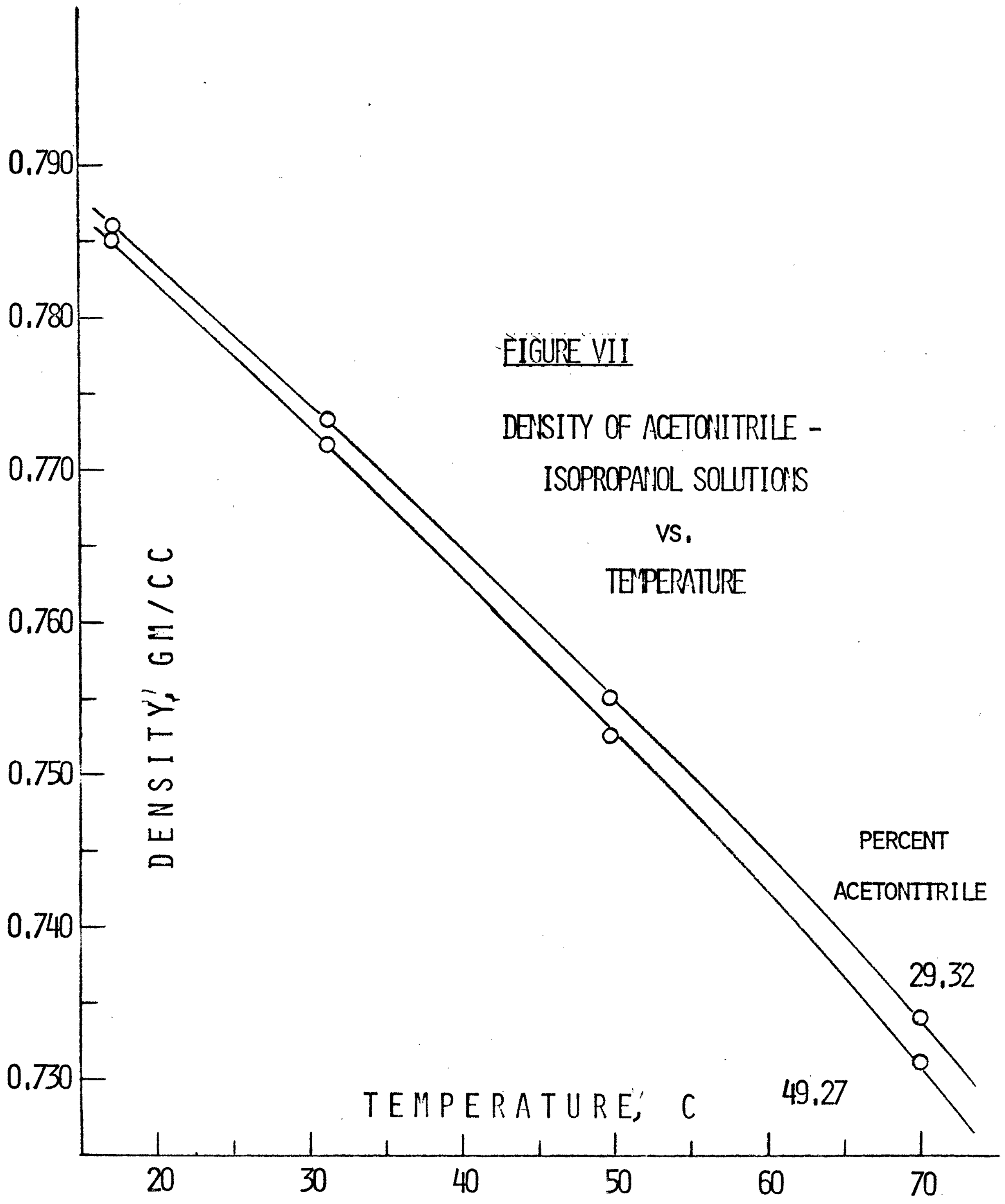

FIGURE VII

DENSITY OF ACETONITRILE - ISOPROPANOL SOLUTIONS VS. TEMPERATURE

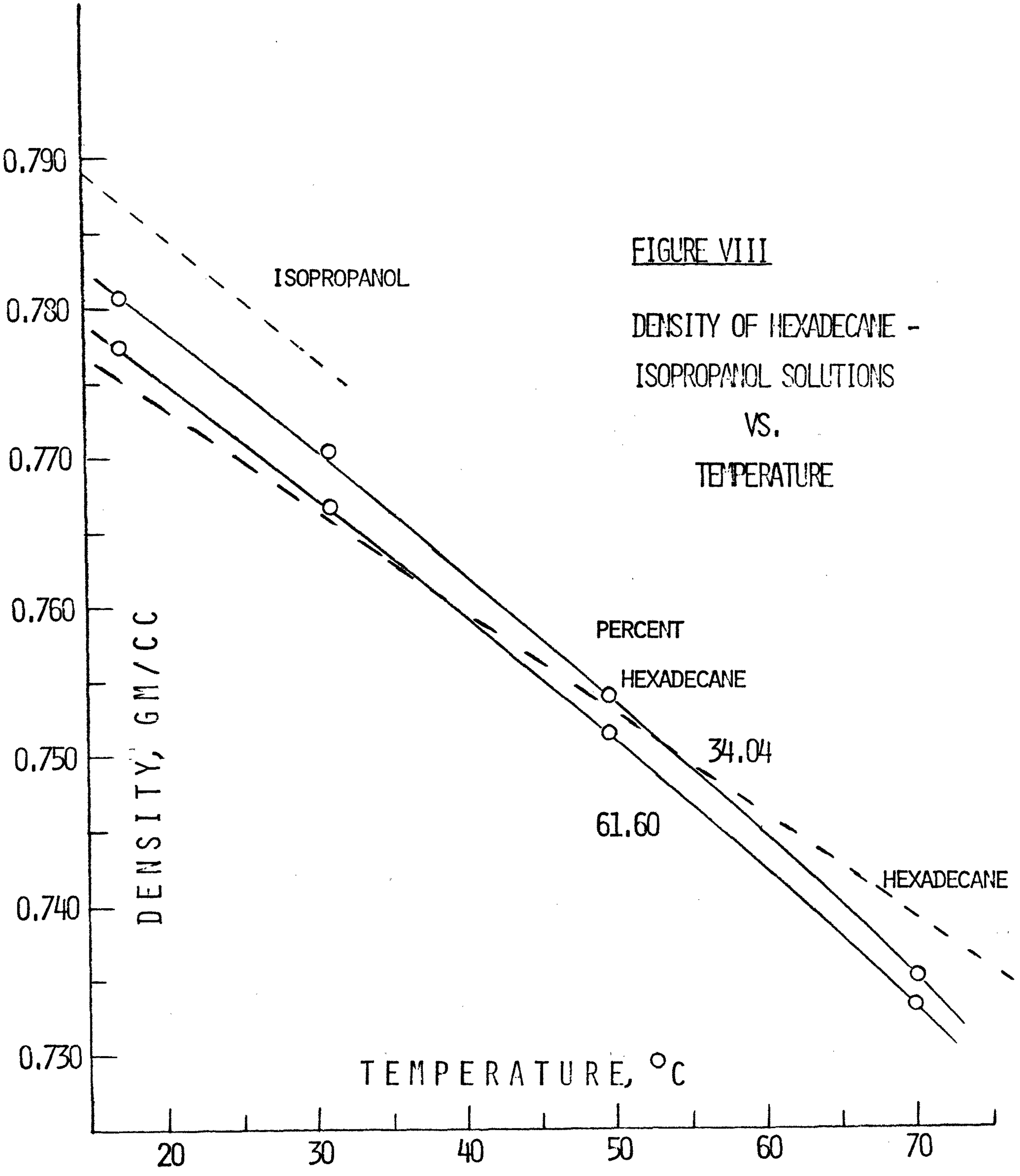
FIGURE VIII
DENSITY OF HEXADECANE - ISOPROPANOL SOLUTIONS VS. TEMPERATURE
ISOPROPANOL
PERCENT HEXADECANE
34.04
61.60
HEXADECANE
DENSITY, GM/CC
0.790
0.780
0.770
0.760
0.750
0.740
0.730
TEMPERATURE, °C
20
30
40
50
60
70

ERROR ANALYSIS

Sources of Uncertainties

1. Temperature - The mercury-in-glass thermometer employed could be read to an uncertainty of about ± 0.2°C. It was graduated in 1°C increments.

Because the minimum required thermometer immersion was 3 inches while the pycnometer could be immersed only up to its cap (less than 2 inches), the possibility of error due to a temperature gradient with bath depth existed. It was therefore necessary to keep the agitator motor controller running at least 60% of its full scale speed. With this precaution taken, measurements indicated that the temperature of the bath was uniform and independent of depth. The uncertainty was, therefore, only as great as that of the thermometer reading itself.

The thermometer was calibrated in the standard manner, noting its actual readings when immersed in a distilled water ice bath and boiling distilled water. Because of the relatively small scale of the thermometer, no more elaborate calibration method was deemed necessary.

2. Pycnometer Volume - As previously mentioned, the sample vials were calibrated using distilled water employing the same methods described in the Experimental Procedure section. By dividing the resulting sample mass by the density of the water obtained from some standard literature source[15], the actual volume of the nominal

10 ml pycnometer as a function of temperature was determined. This test was run at least three times for a given vial at a given temperature and the standard deviation of the data points calculated by the formula:

$$s^2 = \frac{\sum_{i}^{n} (x_i - \bar{x})^2}{n}$$

where S = the standard deviation,

n = the number of data points,

x_i = an individual data point and

$\bar{x}_i$ = the arithemetic mean of all the data points.

As might be deduced from previous discussion, the calibration point scatter and, hence, the standard deviation increased markedly with temperature. As a result, the plotted calibration curve for a single vial formed two straight lines of positive slope whose relative vertical (ordinate) displacement increased steadily with temperature.

This temperature effect is quantified in the table below:

Pycnometer No.	% Uncertainty	
	@ 20°C	@ 80°C
1	0.026	0.040
2	0.008	0.031
3	0.016	0.046
4	0.012	0.024

Note that the relative uncertainty increased by a factor of 1.5 to 4.0 over a range of 60°C.

3. <u>Sample Mass Uncertainty</u> - Least consequential of the sources of experimental error was the mass of the sample.

A recently-calibrated electronic balance was employed whose scalar uncertainty was 0.0001 gm. Since two mass readings are required per sample (tar and final), the total sample mass uncertainty is 0.0002 gm.

Considering that nearly all samples were 7 to 8 gms, the uncertainty due to this source of error is 0.0025 to 0.0029% a factor of only 0.05 to 0.3 of the potential error due to pycnometer calibration.

Experimental Error

As noted previously, each data point was the average of two pycnometer tests run simultaneously. The uncertainties shown in Tables IV through IX represent the sum of the density uncertainty due to the volumetric error. For example, if two results were 0.7596 0.0002 gm/cc and 0.7583 ± 0.0001 gm/cc, the reported result would be the mean between the lowest possible result (i.e., 0.7583 - 0.0001 = 0.7582) and the highest (i.e., 0.7596 + 0.0002 = 0.7598) or 0.7590. The uncertainty would then be half the range between the two extremes or ± 0.0008.

Note that the weighing error has been ignored in this calculation since its effect is negligible in the number of significant figures carried.

The total error, then, for each data point would be given by:

$$\Delta E_T = \sqrt{(\Delta x)^2 + (\Delta y)^2}$$

where Δy is the uncertainty in the ordinate direction (density),

Δx is the uncertainty in the abcissa direction (temperature), and

ΔE_T is the resulting total error for each mixture.

Note that Δx is fixed for all data (the temperature reading is uncertain in the same amount for each point) but Δy varies from data point to data point but should generally increase with temperature (given that the same pycnometer is employed throughout).

CONCLUSIONS AND RECOMMENDATIONS

As a result of the foregoing work, several conclusions have been reached with regard to available correlations, data sources and experimental findings. These were as follows:

1. The simple picnometer density measurement technique can be adapted to temperature ranges significantly above and below room temperature with excellent results.

2. Certain associating compounds such as water, ethanol and methanol cannot be made to conform to the Riedel equation no matter how the constants are defined.

3. The Rackett equation is inferior to the Riedel correlation in accuracy and breath of application to chemical systems.

4. The Joffe-Zudkevitch modification of the Riedel equation increases that correlation's ability to predict the behavior of some non-normal liquids.

5. The Joffe-Zudkevitch method is reasonably reliable (maximum error $<$ 3% for most systems) for predicting binary liquid mixture densities for all systems tested except aqueous acetic acid.

6. The Lydersen generalized physical property charts are erroneous and should not be used to calculate saturated liquid densities for compounds whose critical compressibility is below 0.25.

7. Eliminating the third term and redefining the coefficient and exponent of the Riedel equation shows promise as a correlation for non-normal compounds.

8. The critical properties reported by Kobe, et al.[22] for dimethoxyethane appear inconsistent with the density data obtained both from other literature sources[15] and from the data measured in this work.

From these and other observations, the following suggestions are offered to further the investigations undertaken in this thesis:

1. Attempts should be made to find a mathematical device to diminish the effect of the second term of the Riedel equation with a view of making that equation universally applicable.

2. Other pseudo-critical property mixing rules besides Kay's Rule should be tested for predicting liquid mixture densities.

3. Attempts should be made to experimentally generate more binary liquid mixture data for compounds whose critical compressibility is below 0.25. Equipment capable of measuring saturated liquid densities at elevated pressures will be required to permit study of a sufficiently broad temperature range.

4. Saturated liquid density data should be generated for 1, 2 - dimethoxyethane with a view to resolving the contradiction between presently available critical property and liquid density data.

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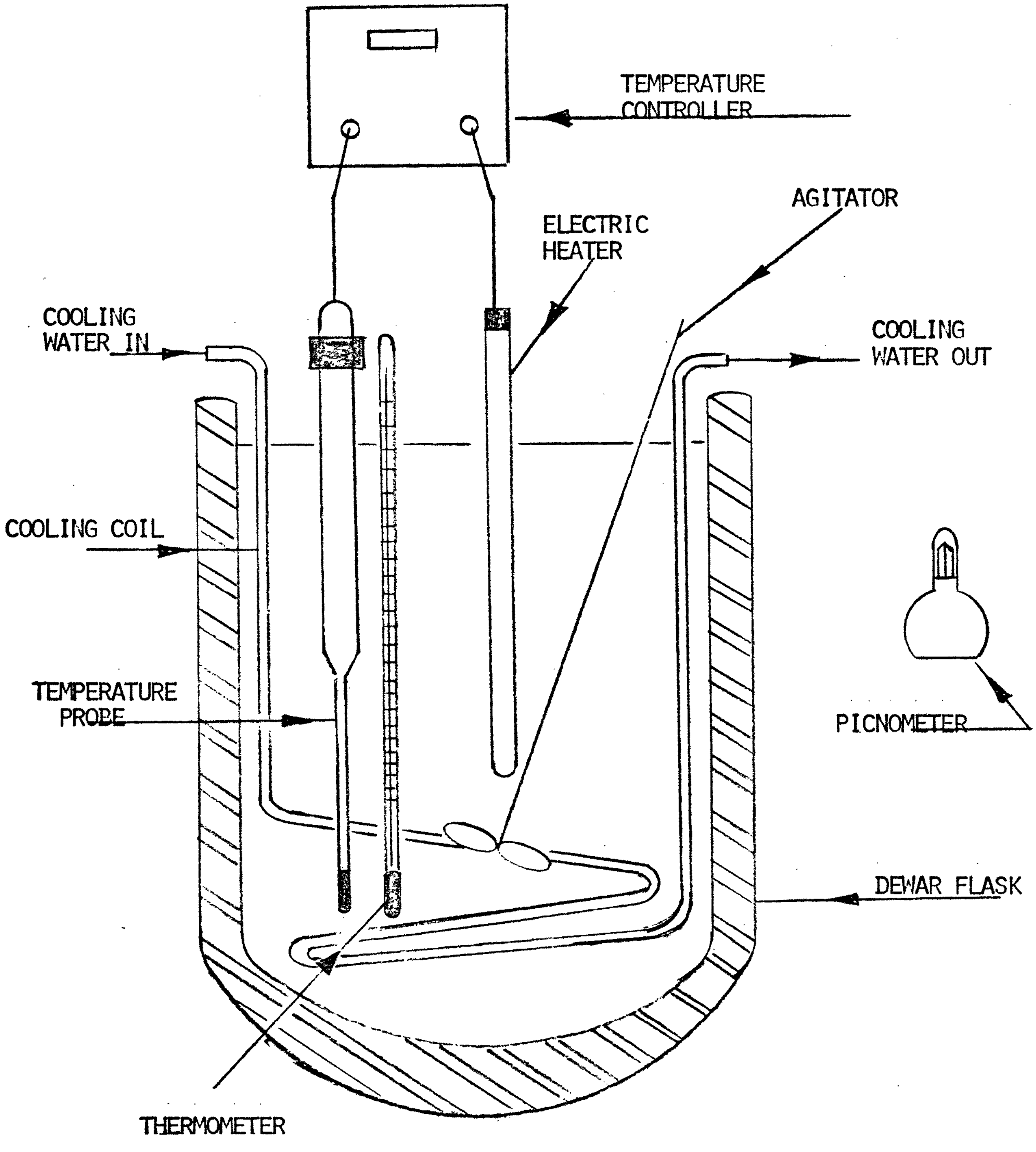
APPENDIX

A

EXPERIMENTAL EQUIPMENT

FIGURE IX

EQUIPMENT DIAGRAM



APPARATUS SPECIFICATIONS

"Electronic Relay" Temperature Controller

Manufacturer: Precision Scientific Company, Chicago, Illinois

Catalogue Number: 62690

Serial Number: 10-S-8

Maximum Load: 1650 watts

Agitator

Type: 3-inch diameter stainless steel propeller

Agitator Motor

Manufacturer: Gerald K. Heller Company, Baltimore, Maryland

Model Number: 2T60 variable speed motor

Type: NSH-12R

Serial Number: 1606974

Maximum Torque: 5.4 in-lbs

Motor Controller

Manufacturer: Gerald K. Heller Company, Baltimore, Maryland

Model Number: 2T60

Type: Reversible, chromatic (vacuum tube)

"Powerstat" Variable Automatic Transformer

Manufacturer: Superior Electric Company, Bristol, Connecticut

Type: "Powerstat"

Model Number: 3PN116B

0-140 V output, 50-60 Hz single phase

Pyrex Dewar Flask (approximately 1 gallon)

Thermometer (Mercury-in-Glass)

Manufacturer: Walter H. Kessler Company, Inc.

Immersion: 3 inches

Range: 10 to 150°C

Graduation: 1°C

Electronic Balance

Manufacturer: Mettler Instrument Corp., Hightstown, New Jersey

Serial Number: 172242

Type: H15

Capacity: 160 gm

Pycnometers

Manufacturer: Scientific Glass Apparatus Company, Bloomfield, New Jersey

Size: 10 ml nominal

Catalogue Number: JB2530

Type: Pyrex glass with cap

APPENDIX

B

COMPUTER RESULTS FOR THE COMPARISON OF THE RIEDEL AND RACKETT EQUATIONS

```
00101       1*             DIMENSION TITLE(20)
00103       2*          10 FORMAT(6F10.0)
00104       3*          15 FORMAT(20A4)
00105       4*          25 FORMAT(2F10.0)
00106       5*          60 FORMAT('1'//1X,20A4//)
00107       6*          75 FORMAT(2X,'TEMP',2X,'EXP DEN',5X,'RACKETT',2X,'ERROR',5X,'RIEDEL',
00107       7*            12X,'ERROR',4X,'TEM RED'/)
00110       8*         750 FORMAT(1X///1X,'***PROGRAM END***')
00111       9*          80 FORMAT(1X,F6.2,2X,F6.4,5X,F6.4,3X,F6.2,4X,F6.4,2X,F6.2,4X,F6.4)
00112      10*             R=82.05
00113      11*          20 READ 15,TITLE
00116      12*             READ 10,TC,PC,RHOC,WGTM,RHOR,TEMPR
00126      13*             IF(TC)1000,1000,50
00131      14*          50 TCAB=TC+273.15
00132      15*             ZC=PC*WGTM/R/TCAB/RHOC
00133      16*             TEMRR=TEMPR+273.15
00134      17*             TRR=TEMRR/TCAB
00135      18*             PROD=(1.0-TRR)**(2.0/7.0)*ALOG(ZC)/2.303
00136      19*             RHORED=1.0/(10.0**PROD)
00137      20*             REFRAT=RHOR/RHORED
00140      21*             ALPH=3.8462/ZC-7.3076
00141      22*             CONST=0.53+0.2*ALPH
00142      23*             FAC=1.0-TRR
```

DATE 042574

```
00143      24*             RRR=1.0+0.85*FAC+CONST*FAC**(1.0/3.0)
00144      25*             REFR=RHOR/RRR
00145      26*             PRINT 60,TITLE
00150      27*             PRINT 75
00152      28*         500 READ 25,TEMP,RHO
00156      29*             IF(RHO)20,20,100
00161      30*         100 TEMAB=TEMP+273.15
00162      31*             TR=TRMAB/TCAB
00163      32*             PROD=(1.0-TR)**(2.0/7.0)*ALOG(ZC)/2.303
00164      33*             APROD=1.0/(10.0**PROD)
00165      34*             RHORAK=APROD*REFRAT
00166      35*             PDIF1=(RHO-RHORAK)/RHO*100.0
00167      36*             FAC=1.0-TR
00170      37*             RIEDEL=1.0+0.85*FAC+CONST*FAC**(1.0/3.0)
00171      38*             RHORIE=RIEDEL*REFR
00172      39*             PDIF2=(RHO-RHORIE)/RHO*100.0
00173      40*             PRINT 80,TEMP,RHO,RHORAK,PDIF1,RHORIE,PDIF2,TR
00204      41*             GO TO 500
00205      42*        1000 PRINT 750
00207      43*             STOP
00210      44*             END

          END OF COMPILATION:        NO  DIAGNOSTICS.
```

```
  ETHANE LITERATURE DATA***

  TEMP  EXP DEN     RACKETT  ERROR     RIEDEL  ERROR    TEM RED

  32.18   .2066      .2044    1.06      .2051    .74    1.0000
  32.10   .2285      .2307    -.95      .2290   -.23     .9997
  32.00   .2354      .2381   -1.13      .2365   -.47     .9994
  31.00   .2627      .2653    -.99      .2644   -.64     .9961
  30.00   .2770      .2789    -.68      .2783   -.46     .9929
  29.00   .2870      .2889    -.68      .2885   -.52     .9896
  25.00   .3157      .3164    -.21      .3162   -.17     .9765
  20.00   .3397      .3397     .00      .3397    .00     .9601
  10.00   .3746      .3735     .29      .3736    .25     .9274
    .00   .4012      .3996     .39      .3999    .31     .8946
 -10.00   .4237      .4218     .46      .4223    .33     .8619
 -20.00   .4436      .4414     .51      .4422    .31     .8291
 -25.00   .4528      .4504     .52      .4515    .29     .8127
```

```
PROPANE DENSITY DATA FROM LITERATURE***

 TEMP   EXP DEN      RACKETT  ERROR       RIEDEL  ERROR     TEM RED

-42.05   .5821       .5815      .11       .5840   -.33       .6249
-33.15   .5720       .5710      .18       .5731   -.20       .6490
-23.15   .5600       .5588      .22       .5605   -.09       .6760
-13.15   .5471       .5461      .18       .5474   -.06       .7030
 -3.15   .5337       .5329      .14       .5338   -.03       .7301
  6.85   .5196       .5191      .09       .5197   -.02       .7571
 16.85   .5048       .5046      .05       .5048   -.00       .7842
 26.85   .4891       .4891      .00       .4891    .00       .8112
 36.85   .4722       .4725     -.07       .4723   -.02       .8382
 46.85   .4539       .4545     -.13       .4541   -.05       .8653
 56.85   .4336       .4345     -.21       .4340   -.10       .8923
 66.85   .4102       .4117     -.37       .4112   -.24       .9194
 76.85   .3821       .3843     -.57       .3837   -.42       .9464
 81.85   .3650       .3676     -.71       .3670   -.55       .9599
 86.85   .3442       .3473     -.89       .3466   -.70       .9734
 87.85   .3395       .3425     -.89       .3418   -.69       .9762
 88.85   .3343       .3374     -.94       .3367   -.72       .9789
 89.85   .3286       .3320    -1.02       .3312   -.79       .9816
 90.85   .3226       .3260    -1.05       .3251   -.79       .9843
 91.85   .3157       .3193    -1.15       .3184   -.86       .9870
 92.85   .3079       .3118    -1.27       .3108   -.93       .9897
 93.85   .2990       .3029    -1.31       .3017   -.91       .9924
 94.85   .2875       .2918    -1.48       .2903   -.98       .9951
 95.35   .2803       .2846    -1.55       .2830   -.98       .9964
 95.85   .2710       .2755    -1.66       .2737   -.98       .9978
 96.35   .2570       .2613    -1.68       .2591   -.82       .9991
```

```
N-PENTANE DENSITY DATA FROM LITERATURE***

TEMP  EXP DEN     RACKETT  ERROR     RIEDEL  ERROR     TEM RED

 36.08   .6095     .6085      .17     .6086     .15     .6583
 37.79   .6072     .6067      .09     .6068     .07     .6619
 43.34   .6008     .6008      .00     .6008     .00     .6737
 48.90   .5944     .5948     -.07     .5947    -.06     .6855
 54.45   .5876     .5887     -.19     .5886    -.17     .6973
 60.01   .5814     .5825     -.20     .5823    -.16     .7092
 65.56   .5753     .5762     -.16     .5760    -.11     .7210
 71.12   .5684     .5698     -.25     .5695    -.19     .7328
 76.68   .5624     .5632     -.15     .5628    -.08     .7447
 82.23   .5556     .5566     -.17     .5561    -.09     .7565
 87.79   .5495     .5497     -.04     .5492     .05     .7683
 93.34   .5424     .5427     -.05     .5422     .04     .7801
 98.90   .5351     .5355     -.07     .5349     .03     .7920
104.46   .5280     .5281     -.02     .5275     .09     .8038
110.01   .5208     .5205      .06     .5199     .17     .8156
115.57   .5128     .5126      .04     .5121     .14     .8275
121.12   .5047     .5045      .04     .5040     .15     .8393
126.68   .4969     .4961      .16     .4956     .27     .8511
132.23   .4885     .4873      .24     .4868     .34     .8629
137.79   .4805     .4782      .48     .4777     .58     .8747
143.34   .4709     .4686      .49     .4682     .58     .8866
148.90   .4611     .4585      .57     .4581     .66     .8984
154.46   .4507     .4477      .66     .4474     .74     .9102
160.01   .4396     .4362      .78     .4359     .84     .9220
165.57   .4267     .4237      .71     .4234     .77     .9339
171.12   .4113     .4099      .34     .4097     .39     .9457
176.68   .3956     .3943      .33     .3941     .38     .9575
182.23   .3765     .3761      .11     .3758     .18     .9693
187.79   .3516     .3531     -.41     .3526    -.28     .9812
193.34   .3131     .3182    -1.64     .3171   -1.26     .9930
```

```
DODECANE EXPERIMENTAL DATA***

TEMP  EXP DEN      RACKETT  ERROR      RIEDEL  ERROR    TEM RED

17.10   .7489       .7508   -.25       .7506   -.23      .4413
22.00   .7479       .7473    .08       .7474    .07      .4488
40.50   .7344       .7339    .06       .7348   -.05      .4769
59.70   .7207       .7198    .13       .7214   -.09      .5061
59.70   .7204       .7198    .09       .7214   -.13      .5061
75.00   .7089       .7083    .08       .7105   -.23      .5293
89.50   .6982       .6972    .13       .7000   -.27      .5514
```

```
HEXADECANE EXPERIMENTAL DATA***

TEMP   EXP DEN       RACKETT  ERROR       RIEDEL  ERROR     TEM RED

22.00    .7715        .7720     -.06       .7721    -.08      .4081
21.30    .7729        .7724      .06       .7725     .05      .4072
40.50    .7596        .7596      .01       .7609    -.16      .4337
59.70    .7463        .7466     -.03       .7490    -.35      .4603
75.00    .7354        .7360     -.07       .7394    -.53      .4814
89.50    .7255        .7258     -.05       .7301    -.63      .5015
```

```
METHANOL DATA FROM LITERATURE***

TEMP   EXP DEN      RACKETT  ERROR      RIEDEL  ERROR     TEM RED

   .00   .8100      .8155    -.68      .8131    -.38      .5323
 10.00   .8008      .8036    -.35      .8024    -.20      .5518
 20.00   .7915      .7915     .00      .7915     .00      .5713
 30.00   .7825      .7792     .42      .7804     .27      .5908
 40.00   .7740      .7666     .95      .7690     .64      .6103
 50.00   .7650      .7539    1.46      .7574     .99      .6297
 60.00   .7555      .7408    1.94      .7456    1.31      .6492
 70.00   .7460      .7275    2.48      .7334    1.69      .6687
 80.00   .7355      .7138    2.95      .7209    1.98      .6882
 90.00   .7250      .6998    3.47      .7081    2.34      .7077
100.00   .7140      .6854    4.00      .6948    2.69      .7272
110.00   .7020      .6706    4.47      .6811    2.98      .7467
120.00   .6900      .6553    5.03      .6669    3.35      .7662
130.00   .6770      .6394    5.55      .6521    3.69      .7856
140.00   .6640      .6229    6.19      .6366    4.13      .8051
150.00   .6495      .6056    6.76      .6203    4.50      .8246
160.00   .6340      .5874    7.34      .6030    4.88      .8441
170.00   .6160      .5682    7.76      .5846    5.09      .8636
180.00   .5980      .5476    8.42      .5648    5.55      .8831
190.00   .5770      .5253    8.96      .5431    5.88      .9026
200.00   .5530      .5007    9.46      .5188    6.18      .9221
210.00   .5255      .4727   10.06      .4908    6.60      .9415
220.00   .4900      .4391   10.38      .4567    6.80      .9610
225.00   .4675      .4189   10.40      .4356    6.82      .9708
230.00   .4410      .3944   10.58      .4096    7.11      .9805
232.00   .4295      .3826   10.93      .3970    7.57      .9844
234.00   .4145      .3689   11.00      .3821    7.81      .9883
236.00   .3955      .3522   10.95      .3637    8.04      .9922
238.00   .3705      .3291   11.19      .3377    8.84      .9961
238.50   .3635      .3211   11.66      .3287    9.58      .9971
```

```
ETHANOL DATA FROM LITERATURE***

TEMP   EXP DEN      RACKETT  ERROR      RIEDEL  ERROR      TEM RED

   .00   .8062       .8111    -.61       .8105   -.53       .5291
 10.00   .7979       .8004    -.31       .8001   -.27       .5485
 20.00   .7894       .7894     .00       .7894    .00       .5678
 30.00   .7810       .7782     .35       .7786    .31       .5872
 40.00   .7722       .7669     .69       .7675    .61       .6066
 50.00   .7633       .7553    1.05       .7562    .93       .6260
 60.00   .7541       .7434    1.42       .7447   1.25       .6453
 70.00   .7436       .7313    1.66       .7329   1.44       .6647
 80.00   .7348       .7189    2.17       .7208   1.90       .6841
 90.00   .7251       .7061    2.62       .7084   2.30       .7034
100.00   .7157       .6930    3.18       .6956   2.80       .7228
110.00   .7057       .6794    3.72       .6825   3.29       .7422
120.00   .6925       .6654    3.91       .6688   3.42       .7615
130.00   .6789       .6509    4.12       .6547   3.56       .7809
140.00   .6631       .6358    4.12       .6400   3.49       .8003
150.00   .6489       .6200    4.46       .6245   3.76       .8197
160.00   .6329       .6033    4.67       .6083   3.89       .8390
170.00   .6165       .5857    5.00       .5910   4.13       .8584
180.00   .5984       .5668    5.28       .5725   4.33       .8778
190.00   .5782       .5464    5.50       .5524   4.46       .8971
200.00   .5568       .5240    5.90       .5302   4.77       .9165
210.00   .5291       .4986    5.77       .5050   4.56       .9359
220.00   .4958       .4686    5.48       .4750   4.20       .9553
230.00   .4550       .4302    5.45       .4359   4.20       .9746
240.00   .3825       .3651    4.56       .3679   3.82       .9940
241.00   .3705       .3529    4.76       .3549   4.21       .9959
242.00   .3546       .3361    5.21       .3369   5.00       .9979
242.50   .3419       .3236    5.36       .3233   5.44       .9988
```

```
ACETONITRILE DATA FROM LITERATURE***

 TEMP   EXP DEN      RACKETT  ERROR      RIEDEL  ERROR     TEM RED

212.34    .5340       .5340      .00      .5340     .00      .8862
213.46    .5301       .5315    -.26       .5317    -.31      .8882
218.83    .5147       .5191    -.85       .5206   -1.15      .8980
223.15    .5066       .5087    -.41       .5112    -.91      .9059
227.72    .4983       .4973     .21       .5007    -.49      .9142
232.61    .4863       .4844     .38       .4888    -.52      .9232
236.52    .4756       .4736     .41       .4788    -.66      .9303
240.50    .4637       .4621     .35       .4678    -.89      .9376
243.04    .4594       .4544    1.09       .4605    -.23      .9422
245.77    .4527       .4457    1.54       .4521     .12      .9472
249.02    .4403       .4349    1.23       .4416    -.29      .9531
252.01    .4291       .4243    1.13       .4311    -.47      .9586
262.00    .3932       .3820    2.85       .3883    1.26      .9768
264.17    .3796       .3706    2.38       .3763     .87      .9808
266.61    .3654       .3560    2.56       .3608    1.26      .9852
269.00    .3502       .3391    3.17       .3424    2.23      .9896
269.98    .3425       .3310    3.37       .3334    2.66      .9914
270.92    .3355       .3222    3.97       .3235    3.57      .9931
 20.00    .7856       .8407   -7.01       .7828     .36      .5351
 25.00    .7770       .8342   -7.36       .7779    -.12      .5442
   .00    .8035       .8662   -7.80       .8018     .21      .4986
```

```
N-PROPANOL DATA FROM LITERATURE

 TEMP  EXP DEN      RACKETT  ERROR      RIEDEL  ERROR     TEM RED

 80.00   .7520        .7571    -.68      .7564   -.59      .6578
 90.00   .7425        .7450    -.33      .7446   -.28      .6764
100.00   .7325        .7325     .00      .7325    .00      .6951
110.00   .7220        .7197     .32      .7201    .27      .7137
120.00   .7110        .7065     .63      .7073    .52      .7323
130.00   .6995        .6929     .94      .6941    .77      .7510
140.00   .6875        .6789    1.25      .6804   1.03      .7696
150.00   .6740        .6643    1.44      .6663   1.15      .7882
160.00   .6600        .6491    1.65      .6515   1.29      .8068
170.00   .6450        .6332    1.82      .6360   1.39      .8255
180.00   .6285        .6165    1.91      .6197   1.39      .8441
190.00   .6110        .5988    1.99      .6024   1.40      .8627
200.00   .5920        .5799    2.04      .5839   1.37      .8813
210.00   .5715        .5594    2.11      .5638   1.35      .9000
220.00   .5485        .5369    2.11      .5416   1.26      .9186
230.00   .5230        .5115    2.20      .5164   1.27      .9372
240.08   .4920        .4814    2.16      .4862   1.17      .9560
250.00   .4525        .4435    1.99      .4479   1.03      .9745
260.00   .3905        .3810    2.43      .3830   1.92      .9931
263.15   .3450        .3311    4.04      .3296   4.47      .9990
263.50   .3380        .3153    6.71      .3126   7.51      .9996
```

```
ACETIC ACID DATA FROM LITERATURE ***

TEMP   EXP DEN      RACKETT  ERROR      RIEDEL  ERROR     TEM RED

 20.00  1.0491      1.0491     .00      1.0491    .00      .4929
 30.00  1.0392      1.0359     .32      1.0379    .13      .5097
 40.00  1.0284      1.0225     .57      1.0264    .19      .5265
 50.00  1.0175      1.0090     .84      1.0148    .26      .5433
 60.00  1.0060       .9952    1.07      1.0031    .29      .5602
 70.00   .9948       .9813    1.35       .9911    .37      .5770
 80.00   .9835       .9672    1.65       .9789    .47      .5938
 90.00   .9718       .9529    1.94       .9664    .55      .6106
100.00   .9599       .9384    2.24       .9538    .64      .6274
110.00   .9483       .9236    2.61       .9408    .79      .6442
120.00   .9362       .9085    2.95       .9276    .92      .6610
130.00   .9235       .8932    3.28       .9141   1.02      .6778
140.00   .9091       .8776    3.47       .9002    .98      .6947
150.00   .8963       .8616    3.87       .8860   1.15      .7115
160.00   .8829       .8452    4.26       .8713   1.31      .7283
170.00   .8694       .8285    4.71       .8562   1.52      .7451
180.00   .8555       .8113    5.17       .8406   1.74      .7619
190.00   .8413       .7936    5.67       .8245   2.00      .7787
200.00   .8265       .7753    6.20       .8077   2.28      .7955
210.00   .8109       .7564    6.73       .7902   2.56      .8124
220.00   .7941       .7367    7.23       .7718   2.81      .8292
230.00   .7764       .7161    7.76       .7525   3.08      .8460
240.00   .7571       .6946    8.26       .7320   3.31      .8628
250.00   .7364       .6718    8.78       .7101   3.57      .8796
260.00   .7136       .6474    9.28       .6865   3.80      .8964
270.00   .6900       .6211    9.98       .6606   4.26      .9132
280.00   .6629       .5922   10.67       .6317   4.71      .9301
290.00   .6334       .5595   11.67       .5983   5.54      .9469
300.00   .5950       .5209   12.46       .5579   6.23      .9637
310.00   .5423       .4707   13.21       .5035   7.15      .9805
```

```
WATER DATA FROM LITERATURE***

TEMP   EXP DEN      RACKETT   ERROR      RIEDEL   ERROR     TEM RED

   .00    .9986      1.0083     -.98     1.0076     -.90      .4220
 10.01    .9986       .9986      .00      .9986      .00      .4374
 26.68    .9955       .9821     1.34      .9834     1.21      .4632
 37.79    .9919       .9710     2.10      .9731     1.89      .4804
 54.46    .9848       .9541     3.12      .9575     2.78      .5061
 65.57    .9790       .9426     3.72      .9468     3.29      .5233
 82.23    .9691       .9251     4.54      .9306     3.97      .5490
 93.34    .9617       .9132     5.04      .9195     4.38      .5662
111.12    .9488       .8938     5.79      .9015     4.99      .5937
122.23    .9400       .8814     6.23      .8899     5.33      .6108
137.79    .9268       .8637     6.81      .8734     5.76      .6349
148.90    .9169       .8508     7.21      .8613     6.07      .6520
166.68    .8994       .8296     7.77      .8414     6.45      .6795
177.79    .8884       .8159     8.16      .8285     6.74      .6966
193.34    .8715       .7962     8.64      .8100     7.06      .7207
204.46    .8584       .7817     8.93      .7963     7.24      .7378
222.23    .8364       .7577     9.41      .7734     7.53      .7653
233.34    .8218       .7420     9.71      .7585     7.70      .7825
248.90    .8000       .7191    10.11      .7367     7.92      .8065
260.00    .7832       .7020    10.36      .7202     8.04      .8237
277.79    .7536       .6729    10.71      .6921     8.16      .8511
288.90    .7333       .6534    10.89      .6731     8.20      .8683
304.46    .7021       .6239    11.13      .6443     8.23      .8923


***PROGRAM END***
```

APPENDIX

C

COMPUTER RESULTS FOR LIQUID MIXTURES USING THE JOFFE - ZUDKEVITCH METHOD

```
00101                DIMENSION TC(2),RHOC(2),XMW(2),RHOR(2),TREF(2),SL(2)
00103                DIMENSION WD(2),WDR(2),TRR(2),ALPH(2),YM(2),TITLE(20),VO(2)
00104             10 FORMAT(6F10.0)
00105            200 FORMAT(2X,'TEMP',4X,'WGT FRAC',2X,'EXP DEN',2X,'CALC DEN',2X,'ERRO
00105               1R',2X,'CRIT TEMP',2X,'DEN ZERO',2X,'ALPHA',2X,'TR MIX'/)
00106             30 FORMAT(20A4)
00107            150 FORMAT('1'//20A4//)
00110            500 FORMAT(1X,F6.2,4X,F6.4,3X,F6.4,4X,F6.4,2X,F6.3,4X,F6.2,4X,F6.4,2X,
00110               1F8.4,2X,F6.4)
00111            400 FORMAT(//'**PROGRAM END**')
00112                NO=2
00113            300 READ 30,TITLE
00113          C ***READ COMPONENT CONSTANTS***CRIT TDMP,CRIT DENSITY,MOL WGT, REF DENSITY
00113          C REF TEMP, SLOPE OF OMEGA VS TR LINE
00116                READ 10,(TC(N),RHOC(N),XMW(N),RHOR(N),TREF(N),SL(N),N=1,NO)
00116          C **DATA TEST
00131                IF(TC(1))350,350,40
00134             40 SVO=0.0
00135                PRINT 150,TITLE
00140                PRINT 200
```

```
00140      21*      C ***CONSTANTS PREPARATION***
00142      22*            DO 50 J=1,NO
00145      23*            RRR=RHOR(J)/RHOC(J)
00146      24*            TRR(J)=(TREF(J)+273.15)/(TC(J)+273.15)
00147      25*            FAC=1.0-TRR(J)
00150      26*            XNUM=RRR-1.0-0.85*FAC-1.6916*FAC**(1.0/3.0)
00151      27*            XDEN=0.9846*FAC**(1.0/3.0)
00152      28*            WDR(J)=XNUM/XDEN
00153      29*            ALR=5.808+4.923*WDR(J)
00154      30*            RRO=2.38+0.2*ALR
00155      31*            RO=RRO*RHOR(J)/RRR
00155      32*      C ***MOLAR VOLUME AT ABSOLUTE ZERO***
00156      33*         50 VO(J)=XMW(J)/RO
00156      34*      C***READ DATA***DENSITY,WEIGHT FRACTION,TEMPERATURS
00160      35*       1000 READ 10,RHO,XM1,TEMP
00165      36*            IF(RHO)300,300,60
00165      37*      C ***MOLE FRACTION CALCULATION***
00170      38*         60 XM2=1.0-XM1
00171      39*            YM(1)=(XM1/XMW(1))/(XM1/XMW(1)+XM2/XMW(2))
00172      40*            YM(2)=1.0-YM(1)
00173      41*            VOM=YM(1)*VO(1)+YM(2)*VO(2)
00174      42*            XMWM=YM(1)*XMW(1)+YM(2)*XMW(2)
00174      43*      C***MIXTURE DENSITY AT ZERO ABSOLUTE
00175      44*            ROM=XMWM/VOM
00176      45*            TA=TEMP+273.15
00177      46*            TCM=0.0
00200      47*            ALM=0.0
00200      48*      C***MIXTURE ALPHA AND CRIT TEMPERATURE CALCULATION***
00201      49*            DO 100 M=1,NO
00204      50*            TR=TA/(TC(M)+273.15)
00205      51*            IF(0.8-TR)85,90,90
00210      52*         85 TR=0.8
00211      53*         90 WD(M)=WDR(M)+SL(M)*(TR-TRR(M))
00212      54*            ALPH(M)=5.808+4.923*WD(M)
00213      55*            ALM=ALM+ALPH(M)*YM(M)
00214      56*            P=(TC(M)+273.15)*YM(M)
00215      57*        100 TCM=TCM+P
00217      58*            TRP=TA/TCM
00220      59*            FAC=1.0-TRP
00220      60*      C***RIEDEL EQUATION***
00221      61*            RORC=1.0+0.85*FAC+(0.53+0.2*ALM)*FAC**(1.0/3.0)
00222      62*            RORM=2.38+0.2*ALM
00223      63*            ROC=RORC*ROM/RORM
00223      64*      C ***PERCENT ERROR CALCULATION***
00224      65*            PDIF=(ROC-RHO)/RHO*100.0
00224      66*      C ***RESULTS PRINT OUT***
00225      67*            PRINT 500,TEMP,XM1,RHO,ROC,PDIF,TCM,ROM,ALM,TRP
00240      68*            GO TO 1000
00241      69*        350 PRINT 400
00243      70*            STOP
00244      71*            END

     END OF COMPILATION:          NO DIAGNOSTICS.
```

```
ETHANOL-WATER LITERATURE DATA***

 TEMP     WGT FRAC  EXP DEN  CALC DEN  ERROR  CRIT TEMP  DEN ZERO  ALPHA  TR MIX

 10.00      .1000    .9839    .9878     .398   641.84    1.2182    7.1924  .4412
 20.00      .1000    .9819    .9788    -.309   641.84    1.2182    7.2846  .4567
 25.00      .1000    .9804    .9743    -.625   641.84    1.2182    7.3307  .4645
 30.00      .1000    .9787    .9697    -.921   641.84    1.2182    7.3767  .4723
 40.00      .1000    .9747    .9605   -1.459   641.84    1.2182    7.4689  .4879
 10.00      .2500    .9667    .9593    -.764   632.19    1.1877    7.1920  .4479
 20.00      .2500    .9617    .9503   -1.182   632.19    1.1877    7.2816  .4637
 25.00      .2500    .9589    .9458   -1.372   632.19    1.1877    7.3264  .4716
 30.00      .2500    .9561    .9413   -1.550   632.19    1.1877    7.3712  .4795
 40.00      .2500    .9499    .9321   -1.876   632.19    1.1877    7.4608  .4953
 10.00      .5000    .9216    .9121   -1.036   610.46    1.1400    7.1910  .4638
 20.00      .5000    .9138    .9031   -1.179   610.46    1.1400    7.2749  .4802
 25.00      .5000    .9099    .8965   -1.246   610.46    1.1400    7.3168  .4884
 30.00      .5000    .9058    .8939   -1.309   610.46    1.1400    7.3587  .4966
 40.00      .5000    .8975    .8847   -1.425   610.46    1.1400    7.4425  .5130
 10.00      .7500    .8641    .8623    -.202   576.55    1.0961    7.1896  .4911
 20.00      .7500    .8556    .8530    -.312   576.55    1.0961    7.2643  .5085
 25.00      .7500    .8513    .8482    -.365   576.55    1.0961    7.3017  .5171
 30.00      .7500    .8470    .8435    -.415   576.55    1.0961    7.3391  .5258
 40.00      .7500    .8381    .8338    -.508   576.55    1.0961    7.4139  .5431

*PROGRAM END**
```

```
**TEST CASE**ETHYL ETHER-ETHANOL SYSTEM**

 TEMP     WGT FRAC   EXP DEN   CALC DEN   ERROR   CRIT TEMP   DEN ZERO   ALPHA    TR MIX

  50.00     .4858     .7280     .7222     -.802     497.92     1.0263    7.2381    .6490
  80.00     .4858     .6890     .6856     -.488     497.92     1.0263    7.3532    .7092
 100.00     .4858     .6710     .6594    -1.727     497.92     1.0263    7.4298    .7494
 140.00     .4858     .6130     .6003    -2.079     497.92     1.0263    7.5773    .8297
 180.00     .4858     .5340     .5250    -1.682     497.92     1.0263    7.5773    .9101
 200.00     .4858     .4740     .4728     -.254     497.92     1.0263    7.5773    .9502
 210.00     .4858     .4250     .4369     2.806     497.92     1.0263    7.5773    .9703
```

```
DODECANE IN HEXADECANE EXPERIMENTAL DATA***

 TEMP      WGT FRAC  EXP DEN  CALC DEN  ERROR   CRIT TEMP  DEN ZERO  ALPHA   TR MIX

 17.20      .3609     .7661     .7654   -.086    695.08      .9309   7.5671   .4177
 31.20      .3609     .7576     .7565   -.142    695.08      .9309   7.5459   .4379
 49.70      .3609     .7437     .7446    .126    695.08      .9309   7.5178   .4645
 70.00      .3609     .7288     .7313    .348    695.08      .9309   7.4870   .4937
 89.70      .3609     .7156     .7182    .351    695.08      .9309   7.4571   .5220
 17.20      .6513     .7595     .7584   -.151    676.49      .9285   7.5172   .4292
 31.20      .6513     .7493     .7492   -.020    676.49      .9285   7.4981   .4499
 49.70      .6513     .7361     .7369    .111    676.49      .9285   7.4730   .4772
 70.00      .6513     .7214     .7232    .245    676.49      .9285   7.4454   .5072
 89.70      .6513     .7080     .7095    .215    676.49      .9285   7.4187   .5364
```

```
ACETIC ACID IN WATER LITERATURE DATA***

 TEMP     WGT FRAC   EXP DEN   CALC DEN   ERROR   CRIT TEMP   DEN ZERO   ALPHA   TR MIX

   .00      .1000    1.0295    1.0229    -.640     645.60     1.2484    7.0989    .4231
 15.00      .1000    1.0256    1.0093   -1.591     645.60     1.2484    7.2354    .4463
 20.00      .1000    1.0246    1.0047   -1.943     645.60     1.2484    7.2809    .4541
 30.00      .1000    1.0197     .9954   -2.380     645.60     1.2484    7.3719    .4696
   .00      .3000    1.0839    1.0362   -4.399     641.31     1.2667    7.0984    .4259
 15.00      .3000    1.0750    1.0223   -4.906     641.31     1.2667    7.2251    .4493
 20.00      .3000    1.0729    1.0176   -5.158     641.31     1.2667    7.2673    .4571
 30.00      .3000    1.0654    1.0081   -5.380     641.31     1.2667    7.3517    .4727
   .00      .5000    1.1349    1.0491   -7.557     635.17     1.2855    7.0977    .4300
 15.00      .5000    1.1225    1.0348   -7.815     635.17     1.2855    7.2103    .4537
 20.00      .5000    1.1207    1.0299   -8.098     635.17     1.2855    7.2478    .4615
 30.00      .5000    1.1098    1.0202   -8.074     635.17     1.2855    7.3229    .4773
   .00      .7500    1.1953    1.0635   ******     622.41     1.3099    7.0962    .4389
 15.00      .7500    1.1794    1.0485   ******     622.41     1.3099    7.1795    .4630
 20.00      .7500    1.1769    1.0434   ******     622.41     1.3099    7.2073    .4710
 30.00      .7500    1.1636    1.0332   ******     622.41     1.3099    7.2629    .4871
```

```
HEXADECANE IN ISOPROPANOL EXPERIMENTAL DATA***

 TEMP    WGT FRAC  EXP DEN   CALC DEN  ERROR   CRIT TEMP  DEN ZERO   ALPHA   TR MIX

 17.20    .3404    .7810     .7693   -1.494    534.05    1.0116    7.4667   .5437
 31.20    .3404    .7703     .7555   -1.909    534.05    1.0116    7.5308   .5699
 49.70    .3404    .7538     .7369   -2.246    534.05    1.0116    7.6154   .6045
 70.00    .3404    .7352     .7156   -2.664    534.05    1.0116    7.7083   .6425
 17.20    .6160    .7774     .7615   -2.051    572.36     .9776    7.5023   .5073
 31.20    .6160    .7665     .7494   -2.219    572.36     .9776    7.5484   .5317
 49.70    .6160    .7515     .7332   -2.443    572.36     .9776    7.6093   .5641
 70.00    .6160    .7339     .7148   -2.599    572.36     .9776    7.6762   .5995
```

```
ISOPROPANOL IN WATER LITERATURE DATA***

 TEMP     WGT FRAC  EXP DEN   CALC DEN   ERROR   CRIT TEMP  DEN ZERO  ALPHA   TR MIX

   .00     .1000     .9856     .9973    1.187     642.82    1.2184    7.1071    .4249
 20.00     .1000     .9820     .9794    -.263     642.82    1.2184    7.2918    .4560
 30.00     .1000     .9794     .9703    -.926     642.82    1.2184    7.3842    .4716
   .00     .2500     .9727     .9695    -.330     634.66    1.1881    7.1217    .4304
 20.00     .2500     .9615     .9518   -1.014     634.66    1.1881    7.3019    .4619
 30.00     .2500     .9549     .9427   -1.274     634.66    1.1881    7.3920    .4777
   .00     .5000     .9224     .9236     .133     615.21    1.1409    7.1564    .4440
 20.00     .5000     .9069     .9059    -.113     615.21    1.1409    7.3258    .4765
 30.00     .5000     .8990     .8968    -.240     615.21    1.1409    7.4106    .4928
   .00     .5000     .8644     .9236    6.851     615.21    1.1409    7.1564    .4440
 20.00     .5000     .8464     .9059    7.027     615.21    1.1409    7.3258    .4765
 30.00     .5000     .8392     .8968    6.869     615.21    1.1409    7.4106    .4928
```

```
ACETONITRILE IN ISOPROPANOL EXPERIMENTAL DATA ***

 TEMP     WGT FRAC  EXP DEN  CALC DEN  ERROR  CRIT TEMP  DEN ZERO  ALPHA   TR MIX

 17.20     .2932     .7861    .7910    .623    523.15    1.0475   8.5261   .5550
 31.20     .2932     .7734    .7762    .371    523.15    1.0475   8.5514   .5818
 49.70     .2932     .7550    .7561    .143    523.15    1.0475   8.5848   .6171
 70.00     .2932     .7341    .7330   -.150    523.15    1.0475   8.6215   .6559
 17.20     .4927     .7851    .7912    .776    531.46    1.0412   9.1262   .5463
 31.20     .4927     .7716    .7768    .673    531.46    1.0412   9.1228   .5727
 49.70     .4927     .7526    .7572    .612    531.46    1.0412   9.1183   .6075
 70.00     .4927     .7313    .7348    .491    531.46    1.0412   9.1135   .6457
```

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METHANOL IN ACETONITRILE EXPERIMENTAL DATA***

TEMP     WGT FRAC  EXP DEN  CALC DEN  ERROR  CRIT TEMP  DEN ZERO  ALPHA   TR MIX

15.40     .3363     .7910    .7914     .053    534.19    1.0371   9.2356   .5402
25.00     .3363     .7826    .7817    -.118    534.19    1.0371   9.2331   .5581
40.30     .3363     .7688    .7659    -.385    534.19    1.0371   9.2291   .5868
50.10     .3363     .7590    .7555    -.456    534.19    1.0371   9.2265   .6051
15.40     .6502     .7952    .7933    -.239    523.41    1.0481   8.3816   .5513
25.00     .6502     .7851    .7833    -.229    523.41    1.0481   8.4095   .5696
25.00     .6502     .7856    .7833    -.293    523.41    1.0481   8.4095   .5696
40.30     .6502     .7724    .7669    -.710    523.41    1.0481   8.4540   .5989
50.10     .6502     .7615    .7562    -.701    523.41    1.0481   8.4826   .6176
15.40     .8993     .7960    .7954    -.067    515.94    1.0569   7.7895   .5593
25.00     .8993     .7853    .7851    -.025    515.94    1.0569   7.8385   .5779
40.30     .8993     .7749    .7683    -.856    515.94    1.0569   7.9167   .6075
50.10     .8993     .7659    .7572   -1.135    515.94    1.0569   7.9668   .6265
```

```
HEXADECANE IN ISOPROPANOL EXPERIMENTAL DATA****

 TEMP      WGT FRAC  EXP DEN  CALC DEN  ERROR   CRIT TEMP  DEN ZERO   ALPHA   TR MIX

 17.20      .3404     .7810     .7693  -1.494    534.05    1.0116    7.4667   .5437
 31.20      .3404     .7703     .7555  -1.909    534.05    1.0116    7.5308   .5699
 49.70      .3404     .7538     .7369  -2.246    534.05    1.0116    7.6154   .6045
 70.00      .3404     .7352     .7156  -2.664    534.05    1.0116    7.7083   .6425
 17.20      .6160     .7774     .7615  -2.051    572.36     .9776    7.5023   .5073
 31.20      .6160     .7665     .7494  -2.219    572.36     .9776    7.5484   .5317
 49.70      .6160     .7515     .7332  -2.443    572.36     .9776    7.6093   .5641
 70.00      .6160     .7339     .7148  -2.599    572.36     .9776    7.6762   .5995
```

APPENDIX

D

SAMPLE CALCULATION FOR THE JOFFE - ZUDKEVITCH METHOD FOR LIQUID MIXTURES

SAMPLE CALCULATION

Saturated Liquid Density of Acetonitrile in Isopropanol Solution.

Given: Concentration = 29.32 wgt % Acetonitrile

Temperature = 70.0°C

Critical Constants from Literature[5]

	Temp (°C)	Pres (Atm)	Density (g/cc)
Acetonitrile	274.7	47.7	0.231
Isopropanol	235.0	53.0	0.273

Reference Density (g/cc)

Acetonitrile	0.7857	@	20.0°C
Isopropanol	0.7855	@	20.0°C

Calculation Step #1 - Mixture Reduced Temperature

By Kay's Rule:

$$T_{cm} = \sum_{i}^{n} x_i T_{ci}$$

Since x_i is component mole fraction,

$$x_{acet} = 0.2932 \text{ wgt fraction} = 0.3757 \text{ mole fraction}$$

$$x_{iso} = 0.7068 \text{ wgt fraction} = 0.6243 \text{ mole fraction}$$

So: $T_{cm} = (0.3757)(274.7 + 273.15) + (0.6243)(235.0 + 273.15)$

$= 523.06\ ^{o}K = 249.9^{o}C$

and $T_{rm} = \frac{T}{T_{cm}} = \frac{70.0 + 273.15}{523.06}$

$= 0.6560$

Calculation Step #2 - Mixture Density of Absolute Zero.

For Acetonitrile:

$$\rho_{rref} = \frac{\rho_{ref}}{\rho_{c}} = \frac{0.7857}{0.231} = 3.4013$$

$$T_{rref} = \frac{T_{ref}}{T_{c}} = \frac{20.0 + 273.15}{274.7 + 273.15} = 0.5351$$

$$\psi_{ref} = \frac{\rho_{rref}-1.0-0.85(1-T_{rref})-1.6916(1-T_{rref})^{1/3}}{0.9846(1-T_{rref})^{1/3}}$$

$$= 0.9109$$

$$\alpha_{ref} = 5.808 + 4.923\,\psi_{ref} = 10.2924$$

$$\rho_{r}^{o} = 2.38 + 0.2\alpha_{ref} = 4.4385$$

$$\rho^{o} = \rho_{r}^{o}\frac{\rho_{ref}}{\rho_{rref}} = 1.0253 \text{ g/cc}$$

$$V^{o} = W_{mol}/\rho^{o} = 41.05/1.0253 = 40.037 \text{ cc/gmole}$$

For Isopropanol:

$$\rho_{rref} = 2.8773$$

$$T_{rref} = 0.5769$$

$$\psi_{ref} = 0.3336$$

$$\alpha_{ref} = 74503$$

$$\rho^{o}_{r} = 3.8701$$

$$\rho^{o} = 1.0565 \text{ g/cc}$$

$$V^{o} = 56.895 \text{ cc/gmole}$$

For the mixture:

$$V^{o}_{m} = (XV^{o})_{acet} + (XV^{o})_{iso} = 50.5617 \text{ cc/gmole}$$

mixture molecular weight is 52.95

So: $\rho^{o}_{m} = 52.95/50.5617 = 1.0472$ g/cc

Calculation Step #3 - Third Parameter

For Acetonitrile:

ψ = 0.8674 From the Joffe-Zudkevitch Equation for the Temperature of Interest

$\alpha = 5.808 + 4.923\,\psi = 10.086$

This procedure assumes availability of pure component data in the temperature range under investigation. If not available, the subsequent steps would be followed employing the third parameter value calculated at the reference state.

For Isopropanol:

$\psi = 0.3900$

$\alpha = 7.728$

By Kay's Rule, $\alpha_m = 8.614$

Calculation Step #4 - Riedel Equation

$$\rho_{rm} = 1.0 + 0.85(1-T_{rm}) + (0.53 + 0.2\,\alpha_m)(1-T_{rm})^{1/3} = 2.8705$$

$$\overset{o}{\rho}_{rm} = 2.38 + 0.2\,\alpha_m = 4.103$$

$$\rho_m = \rho_{rm}\left(\frac{\rho^o_m}{\rho^o_{rm}}\right) = 2.8705\ \frac{1.0472}{4.103} = 0.7326\ \text{g/cc}$$

Experimental Density = 0.7341 g/cc or 0.20% error

(Data obtained by actual measurement in Part II of the present work.)