DENSITIES OF POLAR AND NON-POLAR

COMPOUNDS AND THEIR MIXTURES

BY

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A THESIS

PRESENTED IN PARTIAL FULFILLMENT OF

THE REQUIREMENTS FOR THE DEGREE

OF

MASTER OF SCIENCE IN CHEMICAL ENGINEERING

AT

NEWARK COLLEGE OF ENGINEERING

Newark, New Jersey
1974

APPROVAL OF THESIS

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APPROVED:

NEWARK, NEW JERSEY

May, 1974

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

TABLE OF CONTENTS

INDEX OF TABLES

TABLE OF FIGURES

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:

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

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

V_o 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:

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

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:

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

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:

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

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

$$D = 0.93 - B$$

These authors reported an accuracy of $\pm$ 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:

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

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:

$$\frac{V}{V_{sc}} = V_r^0 (1.0 - \omega V_r^1) \tag{10}$$

where V_r^0 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:

$$V_{sc} = \frac{V_{0.6}}{0.3862 - 0.0866} \tag{10b}$$

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:

$$T_{cm} = \sum_{i}^{n} X_i T_{ci} \qquad (11)$$

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,

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

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

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

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) CONVENTIONAL RIEDEL EQUATION

(2) CURVE FITTED RIEDEL EQUATION

(3) CURVE FITTED PSEUDO-PARABOLIC
EQUATION

○   DATA POINT

FIGURE II

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

(1) CONVENTIONAL RIEDEL EQUATION

(2) CURVE FITTED RIEDEL EQUATION

(3) CURVE FITTED PSEUDO-PARABOLIC
    EQUATION

O   DATA POINT

FIGURE III

REDUCED SATURATED LIQUID
DENSITY OF ETHANOL
vs.
REDUCED TEMPERATURE

(1) CONVENTIONAL RIEDEL EQUATION

(2) CURVE FITTED RIEDEL EQUATION

(3) CURVE FITTED PSEUDO-PARABOLIC
    EQUATION

o   DATA POINT

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°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:

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

P_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($^{\circ}$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 determin-
ations 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 evapor-
ation 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 $10^{\circ}C$ below the boiling point of the more volatile component. Practical minimum for this study was about $15^{\circ}C$ 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.

Group 1. 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 °C	gm/cc	
	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

Temperature °C	gm/cc Percent Dodecane in Hexadecane	
	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	gm/cc Percent Acetonitrile	
°C	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	gm/cc Percent Hexadecane	
°C	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

PERCENT

DODECANE

0.00

36.09

65.13

100.00

○ DATA POINTS

● LITERATURE POINTS

DENSITY, GM/CC

TEMPERATURE, C

0.780

0.770

0.760

0.750

0.740

0.730

0.720

0.710

0.700

0.690

0   10   20   30   40   50   60   70   80   90   100

FIGURE V

DENSITY OF METHANOL –
ACETONITRILE SOLUTIONS
VS.
TEMPERATURE

FIGURE VI

DENSITY OF DIMETHOXYETHANE – WATER SOLUTIONS

VS.

TEMPERATURE

FIGURE VII

DENSITY OF ACETONITRILE -

ISOPROPANOL SOLUTIONS

VS.

TEMPERATURE

PERCENT

ACETONITRILE

29.32

49.27

48.

FIGURE VIII

DENSITY OF HEXADECANE -
ISOPROPANOL SOLUTIONS
VS.
TEMPERATURE

ERROR ANALYSIS

Sources of Uncertainties

1. Temperature - The mercury-in-glass thermometer employed could be read to an uncertainty of about $\pm$ 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. Sample Mass Uncertainty - 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).

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.

55.

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A P P E N D I X

A

EXPERIMENTAL EQUIPMENT

FIGURE IX
EQUIPMENT DIAGRAM
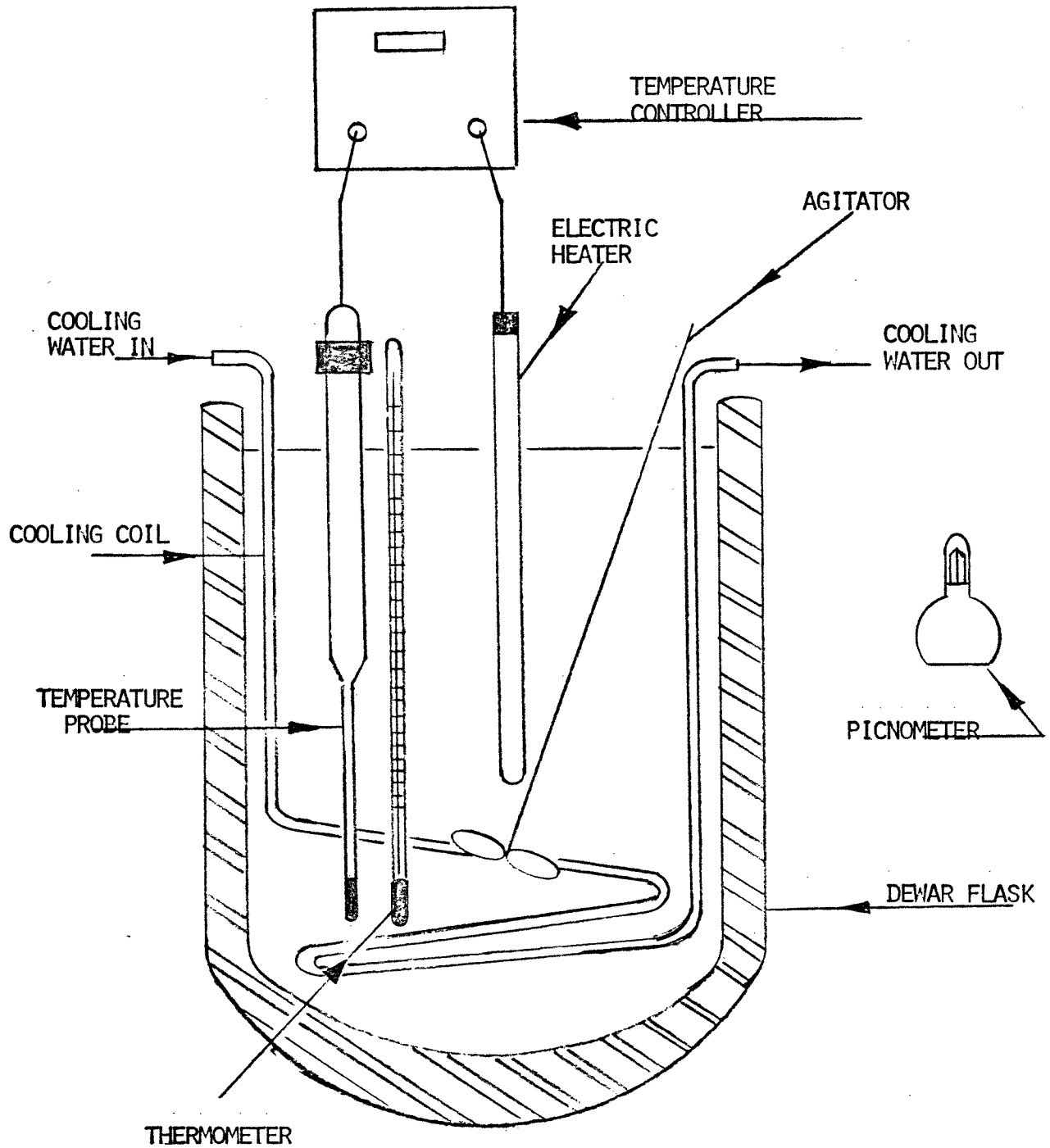
APPARATUS SPECIFICATIONS

"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

A P P E N D I X

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-7.3078
00141   22*            CONST=0.53+0.2*ALPH
00143   23*            FAC=1.0-TRR
```

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64.

```
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=TEMAB/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	.3857	-.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

71.

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

A P P E N D I X

C

COMPUTER RESULTS FOR LIQUID MIXTURES USING THE

JOFFE - ZUDKEVITCH METHOD

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00101     1*        DIMENSION TC(2),RHOC(2),XMW(2),RHOR(2),TREF(2),SL(2)
00103     2*        DIMENSION NO(2),NOR(2),TRR(2),ALPH(2),YM(2),TITLE(20),VO(2)
00104     3*     10 FORMAT(6F10.0)
00105     4*    200 FORMAT(2X,'TEMP',4X,'WGT FRAC',2X,'EXP DEN',2X,'CALC DEN',2X,'ERRO
00105     5*       1R',2X,'CRIT TEMP',2X,'DEN ZERO',2X,'ALPHA',2X,'TR MIX'/)
00106     6*     30 FORMAT(20A4)
00107     7*    150 FORMAT('1'//20A4//)
00110     8*    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     9*       1F8.4,2X,F6.4)
00111    10*    400 FORMAT(//'**PROGRAM END**')
00112    11*        NO=2
00113    12*    300 READ 30,TITLE
00113    13*  C ***READ COMPONENT CONSTANTS***CRIT TEMP,CRIT DENSITY,MOL WGT, REF DENSITY
00113    14*  C REF TEMP, SLOPE OF OMEGA VS TR LINE
00116    15*        READ 10,(TC(N),RHOC(N),XMW(N),RHOR(N),TREF(N),SL(N),N=1,NO)
00116    16*  C **DATA TEST
00131    17*        IF(TC(1))350,350,40
00134    18*     40 SVO=0.0
00135    19*        PRINT 150,TITLE
00140    20*        PRINT 200
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```
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	.8985	-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 CASEETHYL 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	.5599
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

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	.7026	.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	8.4093	.5696
25.00	.6502	.7856	.7833	-.293	523.41	1.0481	8.4093	.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	.7310	.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

A P P E N D I X

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

$$= 523.06 \text{ °K} = 249.9°C$$

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

$$= 0.6560$$

<u>Calculation Step #2</u> – Mixture Density of Absolute Zero.

For Acetonitrile:

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

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

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

$$= 0.9109$$

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

$$\rho_r{}^0 = 2.38 + 0.2 \, \alpha_{ref} = 4.4385$$

$$\rho^0 = \rho_r{}^0 \frac{\rho_{ref}}{\rho_{rref}} = 1.0253 \text{ g/cc}$$

$$V^0 = W_{mol}/\rho^0 = 41.05/1.0253 = 40.037 \text{ cc/gmole}$$

For Isopropanol:

$$\rho_{rref} = 2.8773$$

$$T_{rref} = 0.5769$$

$$\psi_{ref} = 0.3336$$

$$\alpha_{ref} = 74503$$

$$\rho^0{}_r = 3.8701$$

$$\rho^0 = 1.0565 \text{ g/cc}$$

$$V^0 = 56.895 \text{ cc/gmole}$$

For the mixture:

$$V^0{}_m = (XV^0)_{acet} + (XV^0)_{iso} = 50.5617 \text{ cc/gmole}$$

mixture molecular weight is 52.95

So: $\rho^0{}_m = 52.95/50.5617 = 1.0472$ g/cc

Calculation Step #3 - Third Parameter

For Acetonitrile:

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

α = 5.808 + 4.923 ψ = 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:

ψ = 0.3900

α = 7.728

By Kay's Rule, α_m = 8.614

Calculation Step #4 - Riedel Equation

ρ_{rm} = 1.0 + 0.85(1-T_{rm}) + (0.53 + 0.2α_m)(1-T_{rm})$^{1/3}$ = 2.8705

ρ^o_{rm} = 2.38 + 0.2α_m = 4.103

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

Experimental Density = 0.7341 g/cc or 0.20% error

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