INTERFACIAL TENSION IN A BINARY LIQUID SYSTEM

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ABSTRACT

The interfacial tension ($\gamma$) and the density difference ($\Delta\rho$) between the mutually saturated phases carbon tetrachloride-perfluoromethylcyclohexane have been determined as a function of temperature. Interfacial tensions were measured by the drop-volume technique and the densities by the hydrostatic method. The data are reported for 35 temperatures which range from $\Delta T = T_c - T = 0.058$ to $20.65^\circ C$, where $T_c = 26.625 \pm 0.005^\circ C$ is the critical solution temperature of the mixture.

The data may be fit to the power law forms

$$\gamma = \gamma_0 (1 - T/T_c)^\sigma$$

and

$$\Delta\rho = A (1 - T/T_c)^\phi$$

with $\gamma_0 = 29.1 \pm 2.1$ dyne/cm, $\sigma = 1.27 \pm 0.02$, $A = 0.333 \pm 0.003$ gm/cm$^3$ and $\phi = 0.342 \pm 0.003$. These results are shown to be in agreement with certain of the scaling law predictions.
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CHAPTER I

INTRODUCTION

Some General Considerations

The thermodynamic description of a binary liquid system may be expressed by a coexistence curve, which at constant pressure gives the equilibrium composition of the two liquid phases as a function of temperature. The (upper) critical solution temperature is the temperature above which the two liquids are miscible, forming one phase regardless of composition. The temperature dependence of liquid properties in the neighborhood of such a critical point is not well understood theoretically, nor is there a broad range of experimental agreement, since the experiments are difficult to perform and interpret.

The critical solution temperature is closely analogous to the liquid-vapor critical temperature in a one-component system. Most of what will be said is applicable to both types of critical point; however, there are subtle but important differences between them.

The approach to either type of critical point is manifested in the limiting values of certain equilibrium properties. Those of interest in the present context are the density difference between the phases $\Delta \rho$; the isothermal compressibility $k_T$; a length parameter $L$, proportional to
the interfacial width and identified as the Ornstein-Zernike\(^{(42)}\) correlation length; and the interfacial tension \(\gamma\).

From the physical consequences of the limiting values of the thermodynamic properties as \(T \to T_c\), e.g. the divergence of the compressibility, it is rather natural to assume

\[
\begin{align*}
\Delta \rho &= \text{const } (\Delta T)^{\phi}, \\
\kappa_T &= \text{const } (\Delta T)^{f}, \\
L &= \text{const } (\Delta T)^{\nu}, \\
\gamma &= \text{const } (\Delta T)^{\sigma},
\end{align*}
\]

(\text{I-1})\quad (\text{I-2})\quad (\text{I-3})\quad (\text{I-4})

with \(\Delta T = T_c - T\).

The constant coefficients lie outside the scope of classical thermodynamics since they depend on the spacial distribution of molecules and the intermolecular potential. A direct route to the evaluation of the coefficients is available through light scattering measurements. In particular, the liquid-vapor surface tension coefficients for argon and nitrogen have been computed recently by Widom and Fisk\(^{(59)}\). Usually it is necessary to correlate or "best fit" the experimental data to determine the coefficients and the exponents.

We are concerned here mainly with the exponents \(\phi\) and \(\sigma\), but we must concern ourselves with \(f\) and \(\nu\) also, for it is impossible, with the exception of Onsager's
\( \sigma = 1 \) \(^{(41)}\) and Yang's \( \beta = 1/8 \) \(^{(61)}\) for the two-dimensional Ising gas, to compute any pair of exponents without fixing the value of any other pair. This results from the scaling laws, two of which were deduced from the square-gradient theory by Widom\(^{(58)}\): 

\[
\nu = f/2, \tag{I-5}
\]

\[
\sigma = f/2 + 2\beta. \tag{I-6}
\]

Stillinger\(^{(50)}\) obtained the same results from physical cluster theory.

Dictated by a large amount of experimental data for one-component systems\(^{(22)}\), \( \beta \) is usually set at or equal to 1/3. The data for two-component systems is sparse, but the "1/3 law" is close to the physical situation. The values for \( \sigma, f \) and \( \nu \) are much more uncertain.

Objectives

The objectives of this work are threefold. The first is to experimentally determine \( \beta \) and \( \sigma \) in a binary system over several decades in \( \Delta T \). The system perfluoro-(methylcyclohexane)-carbon tetrachloride, suggested for a study of interfacial tension by Hildebrand\(^{(28)}\), has several advantages and was selected for this work. Both components are non-polar and are available in a high degree of purity. \( T_c = 28.626^\circ C \), as determined very accurately by Thompson and Rice\(^{(52)}\), is close to room temperature and makes for
experimental convenience. For this system, Thompson and Rice also determined $\beta = 0.33 \pm 0.02$ for the range $0.0001 \leq \Delta T \leq 0.008$, and Zimm\textsuperscript{(62)} estimated $f \approx 1.2$

(actually for the osmotic compressibility).

A high degree of precision and accuracy are required for the data of this type. For this reason, interfacial tension is measured by the drop-volume technique. Since determination of interfacial tension in the critical region by this method has not been previously attempted, a second objective is to determine how close to $T_c$ the measurements can be made.

Thirdly, it is proposed to determine if any theoretical or empirical methods can be used to predict data of this type. A review of the theory is given in the following chapter.
CHAPTER II

THEORY

Classical thermodynamics, in the form of the dividing surface concept, is shown to yield a relation between the exponents $\beta$ and $\sigma$. From statistical thermodynamics, the distribution function method is examined. Critical properties are considered from the phenomenological viewpoint.

Classical Thermodynamics

The classical theory is due primarily to Gibbs$^{(18)}$, who introduced the concept of a dividing surface and thereby gave precise meaning to the excess properties of the interface.

The work of Buff$^{(4,5)}$ has clarified the dividing surface concept, and has emphasized that the interfacial tension is not dependent on the location of this surface. Buff's formalism is more general than Gibbs' in that it includes the effects of curvature. A review of Buff's work and its connection with Gibbs' convention is given by Melrose$^{(39)}$.

van der Waals$^{(54)}$ was the first to consider the variation of properties through a surface zone of finite thickness. This alternative thermodynamic description has been reviewed and extended by Bakker$^{(2)}$, Verschaffelt$^{(55)}$, Guggenheim$^{(23)}$ and Eriksson$^{(11,12)}$. 
The dividing surface is a mathematical surface of zero thickness which may be used as a reference state. The surface excess of an extensive variable $\mathcal{\Phi}$ is given by

$$\mathcal{\Phi}^S = \mathcal{\Phi} - \mathcal{\Phi}' - \mathcal{\Phi}''$$

where ' and " denote the bulk phases and $\mathcal{\Phi}$ is the value for the whole system. The relevant properties for a planar surface are the total energy $U^S$, the entropy $S^S$ and the excess density of mass $\Gamma_i^S = N_i^S/A$, with $i$ the number of components and $A$ the interfacial area. The free energy is accordingly $F^S = U^S - TS^S$. The classical definition of interfacial tension

$$\gamma = \left( \frac{\partial F^S}{\partial A} \right)_{T,V,N_i} = \left( \frac{\partial F}{\partial A} \right)_{T,V,N_i}$$

is not very intuitively appealing. An alternative definition based on hydrostatic arguments has been given by Kirkwood and Buff (32).

Eq. (II-1), with the dividing surface placed such that $\Gamma_i^S = 0$, gives the absorption equation for a binary system (10)

$$S^SdT + d\gamma + \Gamma_2^S d\mu_2 = 0,$$  \hspace{1cm} (II-2)

where $\mu$ is the chemical potential. For immiscible or partially miscible liquid pairs, Eq. (II-2) is nearly impossible to verify experimentally.

Lovett (38) has offered an interesting critical exponent inequality by utilizing the dividing surface concept.
For a one-component system, with $\lambda_s$ the distance from the $\Gamma^s=0$ surface to the $S^s=0$ surface, Lovett writes with the aid of Eq. (II-2)

$$\lambda_s \Delta \rho = \Gamma^* = - \frac{d\gamma}{d\mu} = - \left( \frac{d\gamma}{dT} \left( \frac{d\mu}{dT} \right)^{-1} \right),$$

where $\Gamma^*$ is the excess density of mass at the $S^s=0$ surface. $\lambda_s$, as computed from thermodynamic data for water and argon, diverges near $T_c$. If in general, $\lambda_s \rightarrow \infty$ and $d\mu/dT \rightarrow 0$ as $T \rightarrow T_c$, and since $\Delta \rho \sim (\Delta T)^\theta$ and $\gamma \sim (\Delta T)^\sigma$, the prescription

$$\sigma < \beta + 1 \quad (\text{II-3})$$

is required. This result is directly amendable to experimental verification.

Before returning to more rigorous exponent laws, we will briefly review the theory for the direct calculation of interfacial tension from the pair correlation function.

**Statistical Thermodynamics**

The interfacial tension may be expressed in terms of the pair correlation function $g(r)$ by the Kirkwood-Buff-Fowler equation

$$(17,32)$$

$$\gamma_2 = \frac{\pi}{3} \int_0^{\infty} r^4 \left[ \rho_1^2 u_{11}(r) g_{11}(r) - 2 \rho_1 \rho_2 u_{12}(r) g_{12}(r) + \rho_2^2 u_{22}(r) g_{22}(r) \right] dr. \quad (\text{II-4})$$
The number densities $\rho_i$ appear since the true density distribution in the transition zone is unknown (step model). The $u(r)$ are intermolecular pair potentials with $u'(r)=du/dr$. Eq. (II-4) is useful for the following cases: i) 1 is a liquid and 2 its dilute vapor, i.e. $\rho_1 >> \rho_2 \quad (T<<T_c)$ and $g_{11}$ is just $g$ in the liquid. Numerical calculations for this case have been carried out for simple liquids by Kirkwood and Buff\(^{(32)}\) and Shoemaker, et. al.\(^{(49)}\). The latter authors found better agreement with experimental surface tensions if constants $\epsilon$ and $\bar{r}$ for $u(r) = -4\epsilon\left[\left(\frac{\bar{r}}{r}\right)^6 - \left(\frac{\bar{r}}{r}\right)^{12}\right]$ are chosen to satisfy simultaneously the pressure and internal energy equations of state\(^{(13)}\) rather than by using gas viscosities and second virial coefficients. Shoemaker, et. al. also found in general that $\gamma$(step) > $\gamma$(experimental), in agreement with the fluctuation theory of interfaces\(^{(7)}\).

ii) 1 is a liquid and 2 its vapor of appreciable density. For this case Fowler\(^{(17)}\) wrote for the $g$'s $(T_c-T_c)$

$$g(r) = g_c(r) + x(r) \frac{(T_c-T)}{T_c},$$

where $g_c$ is a constant and $x(r)$ is some function of $r$. This assumption is in error in view of the Ornstein-Zernike prediction that $G(r) = g(r) - 1$ decays with an exponential envelope. Fowler's most serious assumption was that of selecting the index $\sigma = \frac{1}{2}$, from which he retrieved $\sigma = 1.67$. In view of the x-ray scattering data near $T_c$
for argon as determined recently by Mikloaj and Pings (40),
calculation of surface tension for case ii) by the method of Shoemaker, et. al. might prove practical if values for
the configurational energy were available. Mikloaj and
Pings determined potential function constants by expanding
g(r) in a power series in density with coefficients deter-
mined from Mayer functions. iii) Phases 1 and 2 are
partially miscible liquids. The only practical solution
here is to assume g(r) = 0, r < a_o; g(r) = 1, r > a_o, where
a_o is the hard-sphere radius. Girifalco and Good (20) also
assumed the combining rules ε_{i2} = (ε_{11} * ε_{22})^{1/2} and
\bar{g}_{i2} = (\bar{g}_{12} + \bar{g}_{22})/2, and wrote Eq. (II-4) as

\[ \gamma_{i2} = \gamma_i + \gamma_2 - \phi(\gamma_i \gamma_2)^{1/2} \]  

(II-5)

with \( \gamma_i \) the surface tension of pure i and \( \phi \sim 1 \). For
systems of high mutual solubility (\( T \sim T_c \)), Good (21) has
modified Eq. (II-5) to read

\[ \gamma_{i2} = \gamma_i + \gamma_2 + (x_i - x_i') \Delta \gamma - 2\phi[(\gamma_i - \Delta \gamma)((x_i') \Delta \gamma + x_i \Delta \gamma)]^{1/2} \]

(II-6)

with \( \Delta \gamma = \gamma_i - \gamma_2 > 0 \) and \( x_i' \) the mole fraction species i in
phase j.

Paul and deChazal (44) developed an empirical
equation for systems of high reciprocal solubility
\[
\gamma_a = \left[ (0.0041 \pi \rho \rho_2) / 12 \right] A_{12} \left[ -\frac{ln S(x)}{1 - S(x)} \right]^{2.41} \tag{II-7}
\]

where \( S(X) = X_1^2 - X_2^1 \) and \( A_{12} \) is the London (non-polar) attractive constant. Neither Eq. (II-6) nor Eq. (II-7) have been tested to any extent near \( T_C \).

It is possible to circumvent the assumptions necessary in the distribution function method by using arguments based on the dimensions of the physical quantities involved. This idea is the principle of corresponding states, from which van der Waals(54) recognized that

\[
\gamma = V_c^{-\frac{3}{2}} T_C \cdot f(T/T_C) \tag{II-8}
\]

for the surface tension of simple liquids. \( V_c \) is the critical molar volume and \( f(T/T_C) \) is a universal function shown by Guggenheim(22) to be \( 4.4 (1 - T/T_C)^{11/9} \text{erg}/^{\circ}\text{K mole}^{2/3} \), i.e. \( \sigma = 1.22 \). van der Waals also suggested the empirical equation

\[
\gamma = \gamma_0 (1 - T/T_C)^\sigma \tag{II-9}
\]

where \( \gamma_0 \) is a constant. If \( \sigma = 1.25-1.29 \), this equation fits surface tensions of liquid argon, xenon and nitrogen with great accuracy over a wide temperature range(6).
The extension of Eq. (II-9) to binary mixtures was derived from the van der Waals (classical) theory of the critical point by Cahn and Hilliard\(^8\).

**Classical Theory of the Critical Point**

Recall the defining equations for the critical indices

\[
\begin{align*}
\Delta \rho & \sim (\Delta T)^\beta \\
\kappa_T & \sim (\Delta T)^{-f} \\
\lambda & \sim (\Delta T)^{-y} \\
\gamma & \sim (\Delta T)^{\sigma}.
\end{align*}
\]

The classical theory is centered about the assumption that the pressure and free energy may be expanded in a Taylor series in powers of \(\rho - \rho_c\) at \(T_c\). From the pressure expansion the result is the van der Waals equation and the corresponding exponents \(\beta = \frac{1}{2}\) and \(f = 1\). The free energy expansion leads to the Cahn-Hilliard result

\[
\gamma = B \int_{-\infty}^{\infty} \left[ \frac{\partial \rho(z)}{\partial z} \right]^2 dz,
\]

the interfacial tension is proportional to the square of the density gradient through the interface. \(z\) is the distance perpendicular to the interface and \(B\) is a constant presumed independent of temperature. Lovett\(^{38}\) relaxed the assumption of continuity of states (that the critical
point is an analytic point) and obtained from Eq. (II-10) the classical result

$$\gamma = (B/K_r)^{\frac{1}{2}} \Delta \rho^2/b \rho_c$$  \hspace{2cm} (II-11)$$

which gives $\sigma = f/2 + 2\beta$, as was shown earlier by Widom (cf. Eq. (I-6)). To be consistent with $\beta = \frac{1}{2}$ and $f = 1$, $\sigma = 1\frac{1}{2}$ for the classical theory.

The classical value of $\psi$ for pure fluids was arrived at by Ornstein and Zernike (42) in connection with their study of critical opalescence. From a Taylor series expansion of the Fourier transform of the direct correlation function $C(r)$, the net correlation function $G(r) = g(r) - 1$ was found to decay as

$$G(r) \approx (4\pi R^2 \rho)^{-1} \exp\left(-\frac{r}{\Lambda}\right), \quad r \to \infty$$  \hspace{2cm} (II-12)$$

where $\Lambda$ is the correlation range (length) and $R^2$ is the second moment of $C(r)$, $R^2 = \rho \frac{1}{2} \rho \int r^2 C(r) dr$. With this result and the fluctuation theorem for the isothermal compressibility

*Widom and Fisk (59) reached Eq. (II-11) by solving for $\rho(\xi)$. Lovett avoided this by choosing a model for the chemical potential in the 'loop' region. Lovett's results were essentially insensitive to the form of the model.*
\[ kT \rho K_T = 1 + \rho \int G(r) dr \]  

(II-13)

\( \Lambda \) and \( K_T \) may be related by \( \Lambda^2 = R^2 kT \rho K_T \). Then the divergence of \( K_T \) as \( T \to T_c \) implies the divergence of \( \Lambda \), and \( G_c(r) \) decays as \( r^{-1} \). If \( \Lambda \) can be identified with the interface thickness \( L \) (or something proportional to \( L \)), it follows that \( \sigma = \rho/2 = \frac{1}{2} \) for the classical theory**, provided \( R^2 kT \rho \) is independent of temperature.

We conclude by noting that Lebowitz and Percus, \((36)\) construction of the chemical potential in the context of the density gradient theory identifies the interfacial tension coefficient as

\[ \sigma = \frac{\Lambda^2}{6\rho^2 K_T} \]  

(II-14)

As Widom and Fisk point out, Fisher's modification (cf. preceding footnote) gives a slight temperature dependence \( \sigma \propto (\Delta T)^{-\delta} \).

In order to ascertain the validity of the classical exponents, we will examine the relevant experimental data.

** Fisher\((14)\) has pointed out that Eq. (II-12) is probably incorrect at \( T_c \). This seems to be confirmed by experiment\((3,9)\), although the results are not clear cut. Fisher proposes \( G_c(r) \) decay as \( r \) to the power \(-(1+\eta)\) (in three dimensions); whence \( \sigma = (2-\eta)\rho \) with \( \eta \approx 0.1 \).
Experimental Data

In a truly elegant experiment, Thomson and Rice\(^{(52)}\) determined the top of the coexistence curve for the system perfluoromethylcyclohexane (PFMCH) - carbon tetrachloride (the system chosen for study in this work). The temperature was controlled to within \(\pm 5\times 10^{-5}\)°C and the solutions were extremely pure. The data are fitted by Heller\(^{(27)}\) in terms of the difference between the volume fraction of CCl\(_4\) in the upper phase and that in the lower phase vs. \(\Delta T\), for which \(\beta = 0.335\pm 0.02\). Thus we find a cube-root law.

For the index \(f\) in a binary mixture, the relevant parameter is the osmotic compressibility, \(K_1^0\), defined by\(^{(27)}\)

\[
\frac{C_1}{C_2} = \rho_2 k T \frac{\partial m_{a_1}}{\partial m_{a_2}},
\]

where in the present nomenclature \(c\) is the concentration in molecules/cm\(^3\), \(a\) is the activity and \(\rho\) the macroscopic density. Zimm\(^{(62)}\) measured the light scattering near \(T_c\) for PFMCH-CCl\(_4\) as a function of temperature and composition. From the slope of the zero-angle reciprocal intensity, \(K_1^0\) (and thus \(f\)) may be determined. However, Zimm also determined the slope of the volume-fraction vs. activity curves, from which Heller\(^{(27)}\) finds \(f \approx 1.2\). Zimm's sample was not particularly pure since it was exposed to air and the observed \(T_c = 28.31\)°C was \(\sim 0.3\)°C below that of Thomson and Rice. Other work by Chu\(^{(9)}\) on \(\beta-\beta'\)-dichloroethyl...
ether-n-dodecane yields $f \sim 1.0-1.25$. The measurements are exceedingly difficult, and for pure fluids Fisher's (15) assessment of the experimental situation gives $f \geq 1.2$. For binary mixtures, $f$ seems from all indications to be $\sim 1.1$ although this value is by no means certain.*

The only experimental measurement of the interfacial thickness parameter is that of Gilmer, et. al. (19) for cyclohexane-methanol. They found $\nu = 0.76 \pm 0.1$, which is quite good, considering that this measurement is perhaps the most difficult of any to make near $T_c$. These data has been scrutinized carefully by Lovett (38) and Buff, et. al. (7) in terms of capillary wave theory. To be consistant with the interfacial tension data of Atack and Rice (1), the latter theory predicts $\nu = 0.63 \pm 0.03$.

The interfacial tension data for cyclohexane-aniline taken by Atack and Rice are the only published data near $T_c$ that have been given serious attention**. The data were taken by capillary rise, and as fit originally by Atack and Rice, $\sigma = 1.38$. Cahn and Hilliard felt the data were consistant with $\sigma = 1.5$, thus satisfying the classical theory. When Lovett (38) made a gravitational correction to

*That $f$ (pure) = $f$ (mixture) has never been seriously doubted, but it has never been proven either.

**Webb (56) reports unpublished data for cyclohexane-methanol with $\sigma = 1.23$ as determined by an optical technique. Webb felt a previous value $\sigma = 1.09$ by capillary rise was questionable. The author thanks Prof. Buff for pointing out this data.
to the original data, he found $\sigma = 1.29$, in agreement with Eq. (II-3) ($\beta = 1/3$ for this system). However, Buff and Lovett\textsuperscript{6} later report $\sigma = 1.29-1.31$ for only $0.995 < T/T_C < 0.999$. The inference here is that $\sigma$ may rise with temperature, at least for a binary mixture.

Considering the pure liquids fit by Eq. (II-9) and the corrected data of Attack and Rice, Buff and Lovett imply a universal coefficient $\sigma = 1.27 \pm 0.02$. This implication is supported by Widom and Fisk\textsuperscript{59}, although the experimental situation seems far too uncertain to make such a conclusion.

Obviously, more experimental data is needed to confirm the existence of a universal interfacial tension index. The present discussion should suffice to illustrate that the capillary rise, although an absolute method, may not be a particularly good one for binary mixtures near the critical solution temperature.

Scaling Laws

It is obvious that the classical theory fails to predict the experimental data. This discrepancy may be explained in terms of the singular nature of the critical point\textsuperscript{(14,59)}. Regardless of the difficulties surrounding the analytic behavior of the critical isochore, the Cahn-Hilliard (square-gradient) theory, Eq. (II-10), is fundamentally correct. If Cahn and Hilliard had used,
say, \( \varphi = 1/3 \) and \( f = 1.25 \), they would have retrieved from Eq. (I-5) and (I-6) \( \sigma = 1.29 \), which agrees with the data of Atack and Rice as fit by Lovett, but is somewhat higher than the corresponding states index 1.22 (cf. Eq. (II-8)). This result, as Lovett\(^{38} \) states, shows the square-gradient theory may be quite good, provided the correct temperature dependence of the parameters is used in the theory.

However, Widom\(^{58} \) revealed that Eqs. (I-5) and (I-6) fail to predict the two-dimensional Ising exponents for which exact values are known. To resolve this discrepancy, Widom used arguments based on the dimensionality of the system, and gave the modified scaling laws

\[
\nu = \frac{(f + 2\varphi)}{d} \tag{II-16}
\]

\[
\sigma = \frac{(f + 2\varphi)(d-1)}{d} \tag{II-17}
\]

where \( d \) is the dimensionality. Eqs. (II-16) and (II-17) give the two dimensional exponents exactly, and using the three-dimensional continuum fluid values\(^{33,60} \) \( \varphi = 10/29 \) and \( f = 1.10 \), Widom computes \( \sigma = 1.20 \) and \( \nu = 0.598 \), both within reason, but lower than the values claimed by Buff and his school. However, both sets of scaling laws yield
\[ \sigma + \gamma = f + 2\beta \] 

which may be taken as fundamentally correct. The scaling laws only give the temperature dependence of interfacial tension relative to the temperature dependence of other properties, and to this extent, the theory is verified.

The central question may now be stated as: is there a universal interfacial tension index for binary mixtures as there appears to be (corresponding states says there will be) for pure liquids, and if so, does \( \sigma \text{(mixture)} = \sigma \text{(pure liquid)} \)? Intuition tells us that the processes at a binary liquid interface may be of a fundamentally different character than those in a pure system. In fact, there is no a priori reason to believe that \( T_c \) and \( p_c \) for a binary system are single valued functions of composition. Hopefully, the results of the experiment described in the next chapter will shed some light on these questions.
Interfacial Tension

For the measurement of interfacial tension between two liquids, both the drop-volume and capillary rise methods have been developed to the necessary degree of sophistication to yield high precision and accuracy. Both methods suffer from the drawback that the densities of the two phases in equilibrium must be determined. The density measurements are of considerable difficulty in themselves, especially near $T_c$.

The capillary rise is an absolute method provided the contact angle is accurately known. However, near the critical solution temperature, the value of the contact angle is difficult to determine and may be different from zero. This was pointed out by Hildebrand in reference to the capillary rise measurements of Attack and Rice discussed previously.

The drop-volume is not an absolute method in the sense that it requires calibration with liquids of known interfacial tension. However, the drop-volume method is independent of the contact angle, and this is particularly advantageous for low interfacial tensions in the critical region. The drop-volume method also insures complete
equilibrium prior to and during the measurements. The lowest value reported for interfacial tension by Atack and Rice was 0.0054 dyne/cm for \( \Delta T = T_c - T = 0.349^\circ C \). In order to determine if a lower \( \Delta T \) might be possible with the drop-volume method, an extensive series of preliminary experiments were undertaken. With the smallest dropping tip used, it was found that discrete drops would form for \( \Delta T \) as low as 0.05-0.06\(^\circ\)C. Since this appeared to be a significant improvement over the capillary rise, the drop-volume was the method selected.

The interfacial tension in terms of the volume of a single drop, \( V \), is

\[
V \Delta \rho g = 2\pi r \gamma \cdot f(r/V^{1/3}).
\]  

(III-1)

\( \Delta \rho \) is the density difference between the phases (in this work we consider the case of drops of heavy phase falling into light phase), \( g \) is the gravitational constant, \( r \) is the radius of the dropping tip, and \( f(r/V^{1/3}) \) is a correction factor. Harkins and Brown (25), in a series of classic experiments, determined \( f(r/V^{1/3}) \) for a wide range of \( r/V^{1/3} \), and thereby standardized the drop-volume method.

The curve of \( f(r/V^{1/3}) \) vs. \( r/V^{1/3} \) closely resembles a cubic equation, but was apparently never fit as such by Harkins. A fit of the curve is useful since in actual
practice it is often necessary to interpolate between tabulated values. Rewriting Eq. (III-1) as

$$\gamma = V \Delta \rho \frac{F}{r}$$  \hspace{1cm} \text{(III-2)}

where \(F = 1/(2\pi f)\), Lando and Oakley\(^{(34)}\) fit the correction curve for the original data points in the region \(0.3 \leq r/V^{\frac{1}{2}} \leq 1.2\) by multiple regression. Their work has been improved upon by Strenge\(^{(51)}\) who gave a cubic equation

$$F = 0.16696 + 0.19301(r/V^{1/3})$$
$$- 0.04886(r/V^{1/3})^2 - 0.04963(r/V^{1/3})^3,$$

with a mean error for the individual data points of \(F \pm 0.00057 \pm 0.0036\) on \(f\).

The procedure for determining the interfacial tension is as follows: i) experimentally measure \(V, \Delta \rho\) and \(r\). ii) compute \(r/V^{\frac{1}{2}}\) (\(r/V^{\frac{1}{2}}\) should be such that \(0.3 \leq r/V^{\frac{1}{2}} \leq 1.2\)). iii) compute \(F\) from Eq. (III-3). iv) compute the interfacial tension from Eq. (III-2).

A. Measurement of drop volume. The drop volume was measured by a micrometer syringe, 0.25 cm\(^3\) capacity, manufactured by Roger Gilmont Instruments, Inc. It consists of a micrometer attached by a swivel joint to a precision ground borosicilate glass piston. The piston is ground to an accuracy of \(5 \times 10^{-5}\) in. so as to fit the precision bore
glass cylinder with a clearance of 5 microns. Extreme care must be used to avoid particles of dust or dirt from entering the cylinder. This occurred once during preliminary experiments, resulting in a scratched piston which had to be replaced.

Two teflon 0-rings seal the piston-cylinder arrangement against outside contamination. One 0-ring seals against the rear of the flanged cylinder. The second 0-ring was mounted on the piston with a special tool at the factory*. The cylinder is equipped with a standard male Luer joint, and the seal between this joint and the stainless steel Luer hub of the dropping tip was secured with teflon tape. Thus the liquid came into contact with only glass, stainless steel and teflon.

The syringe was sealed in the glass interfacial tension apparatus by way of a female standard taper \((29/42\) ground glass joint. A male \(29/42\) solid teflon stopper was drilled out to a diameter slightly larger than the aluminum adapter of the syringe. Two 0-ring grooves were machined in the syringe adapter, viton-A 0-rings fit into the grooves, and the teflon part force fit on the adapter. This provided the inside seal. The seal between

*Thanks are due to Dr. Roger Gilmont for providing this service.
the outside of the teflon part and the glass joint was aided by a 0.001" $\frac{29}{42}$ teflon sleeve. The syringe was lowered into the apparatus and the $\frac{29}{42}$ fittings seated carefully and firmly by hand. This formed a leak tight seal which, because of the teflon sleeve, was easily broken. The efficiency of the seals was confirmed by measuring the critical solution temperature of the mixture in the apparatus several times during the measurements. This temperature, an extremely sensitive indicator of contamination, did not change over a period of six weeks.

The micrometer was driven by a 1/4" flexible shaft. The shaft was connected to a knob on the panel board through a series of rigidly mounted right-angle and planetary gears, resulting in a geardown of 50:1. Each division of the micrometer head corresponds to $1 \times 10^{-4}$ cm. These divisions may be split quite easily by eye, thus giving a readability to $\pm 5 \times 10^{-5}$ cm. There are 500 divisions per turn of the micrometer head, therefore one turn of the knob corresponds to a 0.001 cm displacement of the piston.

The cross-sectional area of the piston is given by the manufacturer as approximately $0.1 \text{ cm}^3$. The area was checked by measuring the diameter of the piston at eight positions with a cathetometer telescope. The mean diameter so obtained was 0.3567 cm, thus the cross-sectional area is $\pi (0.3567)^2/4 = 0.09996 \text{ cm}^2$, which is within the
tolerance given by the manufacturer. This value is relative
to a temperature of 24.4°C. However, the area of the piston
was not corrected for the coefficient of expansion of
borosilicate glass (3.25x10^{-6}/°C) since this correction is
negligible over the 25°C range of the experiments. The
volume dispersed is then \((0.09996) \cdot \Delta L \text{ cm}^3\), where \(\Delta L\) is
the displacement of the piston in cm.

B. Dropping tips. Preliminary experiments revealed
that for the temperature range to be studied, dropping tips
in the range \(0.004 \text{ cm} \leq r \leq 0.05 \text{ cm}\) were required to
insure \(0.3 \leq \d f(r/V_h^b) \leq 1.2\). Examination of the drop
formation process with a 65X telescope showed that for the
case of drops of the heavy (PFMCH) phase falling into the
light (CCl\(_4\)) phase, the drops formed on the inside
circumference of the tip (i.e., CCl\(_4\) preferentially wets
the face of the tip) and therefore this was the circumfer-
ence to be used in the calculation of the interfacial
tension.

The tips were made either from 304 stainless steel
hypodermic needles or short pieces of 304 tubing which had
been welded onto Luer hubs. The following procedure,
which enabled the production of several tips with a single
set of operations, is similar to that of Lang and Wilke\(^{(35)}\).
One face of a 2½" diameter x 1-1/4" thick cylindrical brass block was made smooth and at 90° to the side on the lathe. Nine 1/8" holes were drilled through the block perpendicular to the faces. The last 1/4" of the holes were made composite by inserting 1/8" brass rods which had another extremely small hole slightly larger than a tip drilled through them. A 1.6 mm deep circular area slightly smaller in diameter than the cylindrical block was milled in a smaller brass block. The circular area was lined with aluminum foil and the block containing the holes was placed on top of the circular area. The blocks were placed on a hot plate maintained at 150°F and molten Wood's metal, which melts below the boiling point of water, was placed in to the holes of the large block with an eyedropper. The tips are inserted into the holes, and Wood's metal drawn up into the ends of the tips with a syringe so that the tips were filled with and surrounded by Wood's metal. After the metal had solidified, the smaller block was removed, leaving a thin circular disk of Wood's metal attached to the larger block. This disk contained the ends of the dropping tips. The aluminum foil was necessary to insure the Wood's metal would stick to the larger block. The disk was ground away using successively #320, 400 and 600 grit carborundum paper on a power grinder. The final polishing was done by hand, using crocus cloth.
The block was placed in boiling water and the tips removed. The Wood's metal was removed from the inside of the larger tips with boiling water and compressed air. Considerable difficulty was encountered in unplugging the smaller tips. The Wood's metal was finally removed by placing the tips in boiling water in an ultrasonic cleaner for several days.

Five tips that spanned the range of $r/V^{1/2}$ were selected. The inside diameters of these tips were then examined with a Zeitz metallograph. The three larger tips had been previously reamed by the High Pressure Equipment Co. and were extremely round and sharp on the inside circumference. The two smaller tips were considerably rougher, and were made round by lapping with a wire coated with 1 micron diamond paste. Photographs of the ends of the tips were taken under high magnification with the metallurgical microscope, and three such photographs are shown in Figure 1.

With the microscope optics unchanged, a scale was also photographed corresponding to each photograph of a tip. The distance between the center of the marks on the scale is 0.001". From the distance between the marks on the photographs, as determined with a cathetometer telescope, the magnification of the respective photographs of the tips was determined. The diameters of the tips were measured at eight positions on the photographs, and the actual mean diameters computed from the magnification previously obtained.
DROPPING TIPS

FIGURE 1
The mean inside radii so obtained for the five tips were, in cm: 0.00658, 0.00831, 0.01475, 0.02721, and 0.05203. The two smaller tips were out of round by less than 0.0004 cm and the three larger tips by less than 0.0002 cm.

C. Apparatus. The interfacial tension apparatus was constructed entirely of pyrex glass, and was designed to facilitate easy handling and cleaning. The instrument was mounted from a sturdy 1/4" angle iron frame, so that it fit inside the temperature bath without touching any part of the bath. The angle iron frame was bolted to the wall and the floor of the laboratory in order to minimize the effect of vibrations.

A schematic diagram of the interfacial tension apparatus is given in Figure 2. The center chamber A, in which the sample and the end of the dropping tip rested, was equipped with a teflon-coated magnetic stirring bar. The chamber has optically flat glass walls in front and rear so as to render the drops visible without distortion. The chambers B and C may be used for mixing or holding one or both of the phases. The liquids were moved among the chamber by argon pressure through the manifold D. The argon was prefilled to remove any water vapor and its pressure could be reduced by the two regulators E to the
INTERFACIAL TENSION APPARATUS

FIGURE 2
equivalent of about one inch of water pressure. A needle valve F made for fine control of the liquid flow and the two-way teflon valves G were used to bleed the system to the atmosphere. The three-way teflon valve H, which must be above the level of the liquid in the bath, connects any two of the chambers A, B and C. This valve was employed when it became necessary to shift the interface from the filling position, above the tip, to the measuring position, below the tip. Figure 3 shows the interface in the latter position. Viton-A 0-rings were used with the joints I. With these joints, the three arms J between the apparatus and the manifold could be easily disconnected.

Density

For the determination of the densities of two partially miscible liquid phases in equilibrium, the hydrostatic or suspended sinker method is preferable to the pycknometric method. The principal advantage of the former method is that the measurements may be taken in situ, this condition being mandatory near the critical solution temperature. The present procedure follows closely that of Forziati, et. al. (16).

An analytical balance may be adapted to in situ density measurements by removing the pan and attaching to the balance arm a long, fine wire at the end of which is
fastened a glass sinker or plummet. The combined plummet and wire are weighed first in air, balanced by \( W'_A \) grams of weights, then in the liquid, balanced by \( W'_L \) grams of weights. The apparent loss in true weight, \( W_A - W_L \), is equal to the mass of the liquid displaced, thus

\[
\rho_L = \frac{(W_A - W_L)}{V(T)}, \tag{III-4}
\]

where \( \rho_L \) is the liquid density in \( \text{gm/cm}^3 \), and \( V(T) \) is the volume of the plummet in \( \text{cm}^3 \) at a temperature \( T \). The \( W \) are the weights corrected for the buoyancy of air\(^{57} \)

\[
W_A = W'_A + D_a (V(T)-V_w), \tag{III-5}
\]

\[
W_L = W'_L - \frac{D_v}{V_w}, \tag{III-6}
\]

where \( D_a \) is the density of air at the weighing conditions, and \( V_w = W'/D_w \) is the volume occupied by the \( W' \) weights consisting of a material having a density \( D_w \). \( W'_A \) needs to be determined only once for a given plummet, since Eq. (III-5) gives the weight of the plummet \textit{in vacuo}. For 5th decimal accuracy, it is necessary to apply the buoyancy corrections to each weighing. The downward force
on the wire due to the surface tension of the liquid must be subtracted from $W_L$.

A. **Apparatus.** A Sartorius Model 2403 single-pan analytical balance was used for the weighings. The balance is accurate to $\pm 5 \times 10^{-4}$ gm in the optical range. This balance was not equipped for weighing below, so a 1/4" hole was drilled in the base. The only position for this hole was between two weight control levers on the underside of the balance. Fortunately, this position enabled a wire to hang vertically from the bridle hook to the underside of the balance without touching any part of the circumference of the hole.

The balance and the plywood platform upon which it sat were placed in a glove box. The latter acts as a shield against drafts and dust, and was positioned over the temperature bath, being supported there by the angle iron rack. Two inch diameter holes were drilled through the platform and the floor of the glove box in line with the hole in the base of the balance. A photograph of the entire experimental apparatus, showing the balance in position in the glove box, is given in Figure 3. In order for the balance to maintain this position in the box, it was necessary to remove the top cover of the balance.
EXPERIMENTAL EQUIPMENT

FIGURE 3
The front of the glove box was replaced with a 1/4" thick plexiglas sheet, in which was cut a 6" diameter hole so as to enable the manipulation of the balance controls. The glass window of the glove box was covered with heavy wrapping paper to shut out light from the room. A 3X magnifying glass was placed inside the glove box in line with the balance scale, so that readings could be made conveniently through the plexiglas at some distance away.

A 25 mm pyrex glass tube, equipped with a teflon-coated magnetic stirring bar, was used to hold the liquids. This size tube was necessary to eliminate wall effects and prevent the wires from entangling with each other. The tube was clamped securely from below the angle iron frame, and the open end of the tube was secured in the glove box by a rubber stopper.

All wires, plummets and balance parts were handled with nylon gloves. After cleaning the switching weights, the balance pan (but not the bridle or tare ring) was removed, and two 25 gm weights threaded onto the weight carriage to compensate for the weight of the pan.

On the underside of the plywood platform, two hooks were attached, which in turn held the plummets, via two 0.003" tantalum wires. The plummets are of borosicilicate glass, weighted with mercury, and were obtained from the Sargent-Welch Co. The lengths of the wires and the glass
tube were selected so as to allow each plummet to rest in its respective phase with about two cm of that phase above and below the plummet, and to insure the entire sample would be at least four inches below the top of the bath liquid. Preliminary experiments showed that a critical mixture of 49.1 ml PFMCH and 60.9 ml of CCl₄ satisfied these requirements.

The tantalum wires were connected to the bridle hook of the balance by a 0.005" karma wire, which passed through the hole in the balance, extended about two inches below the hole, and terminated with a counterweight. When taking a measurement, one of the tantalum wires was hooked to the counterweight, while the other wire remained attached to its hook on the platform. This order was reversed when weighing in the other phase. When measurements were not being taken, a cork, which had been wrapped in aluminum foil, was tightly fitted in the open end of the tube, the wires being forced between the cork and the tube wall. The cork was removed for about one minute during each measurement. The evaporation loss from the liquid in the tube was so small, however, that no detectable change in the critical solution temperature of the mixture could be observed during the experiment.
B. **Calibration of plummets.** The plummets were calibrated with degassed distilled water, and Eq. (III-4). The details of the calibration are given in Appendix A.

The volumes so obtained were

\[ V(T) = 2.01031\{1 + 9.75 \times 10^{-6} (T-25.30)\} \text{ cm}^3 \]

for the heavy phase plummet, and

\[ V(T) = 2.01061\{1 + 9.75 \times 10^{-6} (T-25.30)\} \text{ cm}^3 \]

for the light phase plummet.

**Temperature Control and Measurement**

The temperature of the sample was controlled by a Neslab Model TV70 constant temperature bath. The bath has a capacity of 70 liters and double-walled safety glass windows on two opposite sides. The heating element is a wire coil sealed inside a quartz spiral, and control is effected by mercury contact thermometer. Since the top one-third of the contact thermometer is exposed to the room, the performance of the bath is largely dependent on ambient conditions.

The bath was covered with 1" thick fiberglas insulation, with holes cut in the insulation for the bath controls and for viewing the sample. The laboratory temperature could be controlled at 24.40±0.05°C with the house air conditioning and an on-off contact thermometer. The heat
load to the contact thermometer was supplied by light bulbs. A YSI Model 72 proportional controller in conjunction with another set of light bulbs was also employed. Unfortunately, the air conditioner was not reliable, and this caused not only delay in the work but personal discomfort as well. If the air conditioner was working, or if the bath temperature was slightly above the ambient temperature, the bath control was always ±0.005°C or better. The heat sink for this case (tap water) could be regulated with a flowrater. Some problems were encountered as a result of the temperature fluctuations of the tap water. An alternative procedure of circulating water at a constant temperature from an auxiliary bath was tried. The main bath control was sporadic under these conditions, inasmuch as a series of control loops will tend to overcorrect for temperature fluctuations.

For measurements below room temperature, cooling was provided by a Neslab Model PBC-2 bath cooler, which is equipped with a special coil designed to match the temperature bath. The cooler has no method of regulation other than a maximum-minimum rate device, and the heat sink it provides is therefore regulated entirely by the contact thermometer of the temperature bath. The bath control was at least ±0.01°C for these conditions.
It is important to emphasize that the optimum control of \( \pm 0.005^\circ C \) was obtained at and close to the critical solution temperature, since the difference between this temperature and the ambient temperature was always less than about \( 4^\circ C \).

The temperatures were measured by a set of \( 1/100^\circ C \) calorimeter thermometers made by the Brooklyn Thermometer Co. The thermometers were calibrated with a platinum resistance thermometer, which had been calibrated by the National Bureau of Standards, and a G-2 Mueller bridge. The results of the calibrations were

<table>
<thead>
<tr>
<th>Thermometer</th>
<th>Correction</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-11°C</td>
<td>+0.031</td>
</tr>
<tr>
<td>9-21°C</td>
<td>+0.036</td>
</tr>
<tr>
<td>19-31°C</td>
<td>+0.007</td>
</tr>
</tbody>
</table>

Since the optimum control was \( \pm 0.005^\circ C \) and the thermometers read only to the nearest \( 0.01^\circ C \), more than two significant figures after the decimal point on the reported temperatures is not justified. However, for relative differences, the third place could be estimated by averaging over the bandwidth of the temperature fluctuations. This was aided by a 3X thermometer magnifier. The temperatures are so reported with the last figure set below, as in \( T_c = 28.625^\circ C \).
Chemicals

The perfluoromethylcyclohexane was synthesized by the Imperial Smelting Co. and was purchased through the Pierce Chemical Co.* The specifications for this material as furnished by the manufacturer are:

boiling point \(76^\circ\text{C}\)
melting point \(-36^\circ\text{C}\)
index of refraction \(1.2600\) (\(20^\circ\text{C}\))
purity \(> 99\) mol % by GLC, with remaining 1% non-surface active fluorocarbon isomers

The carbon tetrachloride was manufactured by E. Merck (Darmstadt) and was obtained through the Brinkmann Instrument Co. The specifications are:

boiling point 75-76°C
index of refraction 1.4605 (\(20^\circ\text{C}\))
density 1.561 gm/cm\(^3\) (\(20^\circ\text{C}\))
purity \(> 99.5\) mol %

A sensitive indicator of contamination (usually water) in either of these materials is the critical solution temperature of their mixture. Indeed, the work of Rice\(^{(47)}\)

*The author is indebted to Prof T. M. Reed of the University of Florida for help in locating the PFMCH.
has shown that a concentration of $2 \times 10^{-6}$ mole of water per ml of solution raised $T_c$ in a cyclohexane-aniline mixture by $0.2^\circ C$. It is therefore essential that the sample not be exposed to air.

The coexistence curve of PFMCH-CCl$_4$ was determined in the beautiful experiments of Thompson and Rice\(^{(52)}\). The materials were subjected to an elaborate purification procedure, and $T_c$ was determined as $28.626^\circ C$, with a critical composition of 0.551 total volume fraction CCl$_4$.

For the materials used in this work, the critical solution temperature was found to be $28.625 \pm 0.005^\circ C$, with a volume fraction CCl$_4$ of $0.552 \pm 0.003$. The details of this determination are given in the following section. The closeness of this result of $T_c$ as determined by Thomson and Rice was quite surprising, especially for commercially available materials. These chemicals were therefore used without further purification.

The argon used as an inert atmosphere in the experiment was Matheson research grade, 99.9995 min vol %, with a dew point of $-110^\circ F$. The argon was filtered over a molecular sieve dessicant prior to introduction into the apparatus.
Procedure

A. Preliminary. The glass and teflon parts of the micrometer syringe, charging syringes, stirring bars, dropping tips, density tube and interfacial tension apparatus were immersed in a chromic acid cleaning solution held at 250°C. After one hour, all parts were removed from the acid, flushed with tap water and distilled water, and dried over a hot plate. The smaller parts were flushed with CCl₄ and stored under a glass bell jar. The interfacial tension apparatus and the density tube, after having dried for several days, were capped and mounted from the angle iron rack so that they sat deep in the temperature bath but did not touch any part of the bath. To remove residual water from the capillary connecting tubes of the apparatus, dry argon was bled through the tubes for several hours.

The unopened sample bottles and the charging syringes were placed in the glove box, which was then sealed and purged with argon. The liquids were subsequently handled by way of rubber gloves through the ports in the box. The liquids were quickly transferred to the apparatus via the syringes in the amounts corresponding to the critical mixture. These were 49.1 ml PFMCH and 60.9 ml CCl₄ for the density tube and 26.8 ml PFMCH and 33.2 ml CCl₄ for the interfacial tension apparatus. The glass plummets were
lowered into the density tube and the wires attached to the hooks on the plywood platform. The temperature bath was filled with 14 gallons of distilled water, 3 gallons of ethylene glycol and 5 drops of microbiocide, and brought to about 2°C above the critical solution temperature.

B. Determination of Critical Solution Temperature.

The mixture was stirred in the center chamber for about one hour. The critical solution temperature was then determined by observing the onset of critical opalescence from above T_C. The bath was shut off so as to allow slow cooling of the sample, which could be observed with the aid of a parallel light source from behind the bath.

The phenomenon of critical opalescence is quite dramatic, as is shown in the sequence of photographs in Figure 4. In frame A, the mixture is about 1°C above T_C and is a transparent, pale yellow. On further cooling, the solution remains transparent, but deepens in color, passing from yellow to brilliant orange to red, finally taking on a wine or blood red cast.

The solution separates at the bottom of the chamber due to the gravitational field, as was pointed out by Thompson and Rice. They actually determined
\[ \frac{dT_C}{dp} = 39 \text{ mdegC/atm}, \]
with p the pressure and the increase in pressure at a distance h from the top of the sample
Dropping tip is in center of chamber
dark object at lower right is magnetic stirring bar,
opalescence is visible in Frame C.

CRITICAL OPALESCENCE

FIGURE 4
being \( \rho gh \). Since \( dT_c/dp \) is positive, Thompson and Rice concluded that there are planes of constant (increasing) \( T_c \) as one travels down the tube, and that separation will take place in the lower regions regardless of composition. For the chamber used in this work, \( h \sim 4 \text{ cm} \), thus \( T_c \) (bottom) - \( T_c \) (top) \( \sim 0.3 \text{ mdegC} = 0.0003^\circ \text{C} \), which was well beyond the resolution of the thermometer. The first separation is occurring in Figure 4, frame B, but is difficult to see since the picture is in black and white. To observe the appearance of the white fog, the 65X telescope was focused on the bottom of the curved surface of the chamber. Frame C shows phase separation has definitely taken place, and a halo of droplets or clusters has formed around the circumference of the chamber. There is now an enormous amount of light scattering, since the fluctuations in the sample extend over regions of large, almost visible size. The solution is white by reflected light. The remaining frames in Figure 4 show that the solution darkens as the two liquids further separate, and finally turns a deep, nearly black, brown color which is opaque to direct light. The last frame shows light phase material moving rapidly or flowing in jets up the walls of the chamber as a result of the large concentration gradients.
The temperature of first appearance of the white moon-shaped cloud was measured several times and the results were:

<table>
<thead>
<tr>
<th>Thermometer Reading</th>
<th>+0.007°C Correction = $T_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>28.62°C</td>
<td>28.62°C</td>
</tr>
<tr>
<td>28.619</td>
<td>28.626</td>
</tr>
<tr>
<td>28.616</td>
<td>28.622</td>
</tr>
<tr>
<td>28.617</td>
<td>28.623</td>
</tr>
<tr>
<td>28.619</td>
<td>28.626</td>
</tr>
<tr>
<td>28.620</td>
<td>28.627</td>
</tr>
</tbody>
</table>

$T_c$ ave = 28.625 ± 0.005°C

Unfortunately, the temperature control was insufficient to check this result from below $T_c$. Although the cloud point did not deviate from the average over a period of six weeks, this does not eliminate the possibility of a constant (high) error in the determination of $T_c$ (see Chap. IV).

C. **Drop volume and density measurement.** A run was conducted as follows. A tip was selected, mounted on the micrometer syringe, and the syringe seated in the apparatus. The sample was heated to a temperature above $T_c$ and stirred for about one hour. The sample in the density tube was subjected to the same procedure.
The syringe was filled with the one-phase mixture, quickly removed from the apparatus, expelled of gas, and replaced. The bath temperature was brought below $T_c$ to a previously set temperature with cooling water, and the water rate adjusted until the bath reached optimum control. From one to 24 hours were required for the sample to reach equilibrium (two clear phases) depending on $\Delta T$. By filling the syringe with a one phase mixture, equilibrium between the phases that formed in the syringe and the remainder of the sample was assured.

A flexible shaft was connected to the syringe drive, and the syringe flushed to expel any residual light phase in the tip. Drops were dispersed at a rate of one per minute, which is the minimum time allowable without introducing dynamic effects. Since the drops were so small, it was necessary to view them with a 65X telescope. After counting a certain number of drops and recording the micrometer displacement, the plummets were weighed in their respective phases. This sequence was repeated three times. The mean dry and wet bulb temperatures of the room were determined by averaging thermometer readings taken during the course of the run. The barometric pressure was recorded from a barometer in the laboratory.
The bath was heated above $T_c$, the syringe emptied into the chamber and the sample mixed for one hour. The syringe was refilled, the temperature reset, and the whole procedure repeated again. Five series of runs were made, for 35 temperatures in the range $0.058 \leq \Delta T \leq 20.65^\circ C$. The raw data are reported in Appendix B.

D. Visual data. Figure 5 shows a dropping sequence. $\Delta T$ is about $1^\circ C$ and the tip is 0.01475 cm on the inside radius. These photographs clearly show the drop wets the inside circumference of the tip. The last photograph shows a secondary drop trailing in the wake of the larger drop. At least one secondary drop was always obtained. The volume of the large drop in Figure 5 is about $3 \times 10^{-5}$ cm$^3$, and the diameter of the secondary drop is about $1/100$ that of the large drop. Thus the volume of the secondary drop is about $3 \times 10^{-11}$ cm$^3$, which is negligible in the measurement of the drop-volume.

If $\Delta T$ became too low for a particular tip, the drops would form spontaneously, making it impossible to determine their volume. At first, this phenomenon was thought to be due to leaking O-rings in the syringe, but a check at a temperature well below $T_c$ revealed that this was not the case. The following conclusions were reached after an extensive study of the problem of drop formation and
Inside radius of the tip is 0.01475 cm,
$T_c - T \sim 1^\circ C$, drop volume $\sim 3 \times 10^{-5}$ cm$^3$,
magnification $\sim 22X$. 

DROPPING SEQUENCE

FIGURE 5
wettability. Apparently, if the inside diameter of the tip is larger than the equilibrium diameter of the drop that forms, the interfacial tension is so low that the drop will neck off inside the tip. Since the drop has nothing to adhere to, it will fall under the influence of gravity, thereby displacing continuous phase which is sucked into the tip, apparently by the reduced pressure caused when the drop moves out of the tip. Once the process is started, it will continue indefinitely until either the temperature is lowered or there is no longer any heavy phase in the syringe. The spontaneous formation of drops limited \( \Delta T \) to 0.05 \(^\circ\)C, since the smallest tip available was 0.00658 cm in radius. Even at these conditions, the measurement was difficult, since drops sometimes formed by themselves. With smaller tips, perhaps readings closer to \( T_c \) could have been made, although this is by no means certain.

The formation on the inside circumference also prevented the function \( f(r/V^{1/5}) \) from ever reaching the minimum on the Harkins correction curve. For outside circumference wetting, the minimum may have been obtained, but dispersion of light phase upward into heavy phase was never tried in these experiments.

An error analysis of the data taken by the above procedure is given in Appendix C. The relative errors in
interfacial tension and density difference are found to be about 7% and 1%, respectively. The lowest interfacial tensions may therefore be reported to \( \pm 0.0001 \) dyne/cm, although for absolute values, the fourth place is somewhat uncertain and is set below, i.e., 0.024\(_4\) dyne/cm. The absolute densities are reported to \( \pm 0.0002 \) gm/cm\(^3\), with the fifth place in \( \Delta \rho \) being set below.
CHAPTER IV

RESULTS AND DISCUSSION

Experimental Data

The experimental data for 35 temperatures are presented in Table I. The original data from which these values were calculated are given in Appendix B.

If the power law dependence holds, Eqs. (I-1) and (I-4) will give linear plots on logarithmic coordinates. The data are so plotted in Figure 6 and Figure 7. The curves show increasing scatter as the critical point is approached, and that the linear relationship appears to hold, surprisingly so for interfacial tension, over the entire range of temperature. The uncertainty in $\Delta \rho$ is considerably less than in $\gamma$, which is to be expected since $\gamma$ is perturbed by the error in both drop volume and $\Delta \rho$.

Specifying the functional form of the curves as

$$\Delta \rho = A(1 - T/T_c)^\beta,$$
$$\gamma = \gamma_0(1 - T/T_c)^\sigma,$$

(IV-1)  (IV-2)
### TABLE I

**EXPERIMENTAL DATA**

\[ T_c = 28.62^\circ C = 301.78^\circ K \]

<table>
<thead>
<tr>
<th>Run Series No.</th>
<th>( T, ^\circ C )</th>
<th>( T, ^\circ K )</th>
<th>( \Delta T )</th>
<th>( \Delta p, \text{gm/cm}^3 )</th>
<th>( \gamma, \text{dyne/cm} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>28.56 (_2)</td>
<td>301.72 (_2)</td>
<td>0.05 (_8)</td>
<td>0.0217 (_3)</td>
<td>0.0013</td>
</tr>
<tr>
<td>1</td>
<td>28.52 (_7)</td>
<td>301.68 (_7)</td>
<td>0.09 (_8)</td>
<td>0.0228 (_7)</td>
<td>0.0017</td>
</tr>
<tr>
<td>2</td>
<td>28.51 (_5)</td>
<td>301.67 (_5)</td>
<td>0.11 (_0)</td>
<td>0.0226 (_8)</td>
<td>0.0020</td>
</tr>
<tr>
<td>3</td>
<td>28.51 (_4)</td>
<td>301.67 (_4)</td>
<td>0.11 (_1)</td>
<td>0.0234 (_8)</td>
<td>0.0024</td>
</tr>
<tr>
<td>2</td>
<td>28.48 (_5)</td>
<td>301.64 (_5)</td>
<td>0.14 (_0)</td>
<td>0.0240 (_3)</td>
<td>0.0026</td>
</tr>
<tr>
<td>1</td>
<td>28.47 (_2)</td>
<td>301.63 (_2)</td>
<td>0.15 (_3)</td>
<td>0.0269 (_1)</td>
<td>0.0033</td>
</tr>
<tr>
<td>3</td>
<td>28.45 (_8)</td>
<td>301.61 (_8)</td>
<td>0.16 (_7)</td>
<td>0.0269 (_6)</td>
<td>0.0023</td>
</tr>
<tr>
<td>1</td>
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<td>301.58 (_7)</td>
<td>0.19 (_8)</td>
<td>0.0282 (_0)</td>
<td>0.0048</td>
</tr>
<tr>
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<td>301.57 (_5)</td>
<td>0.21 (_0)</td>
<td>0.0286 (_9)</td>
<td>0.0042</td>
</tr>
<tr>
<td>2</td>
<td>28.37 (_3)</td>
<td>301.53 (_3)</td>
<td>0.25 (_2)</td>
<td>0.0296 (_4)</td>
<td>0.0053</td>
</tr>
<tr>
<td>3</td>
<td>28.34 (_5)</td>
<td>301.50 (_5)</td>
<td>0.28 (_2)</td>
<td>0.0307 (_8)</td>
<td>0.0060</td>
</tr>
<tr>
<td>1</td>
<td>28.31 (_9)</td>
<td>301.47 (_9)</td>
<td>0.30 (_6)</td>
<td>0.0319 (_3)</td>
<td>0.0067</td>
</tr>
<tr>
<td>2</td>
<td>28.29 (_4)</td>
<td>301.45 (_4)</td>
<td>0.33 (_1)</td>
<td>0.0330 (_3)</td>
<td>0.0070</td>
</tr>
<tr>
<td>3</td>
<td>28.24 (_3)</td>
<td>301.40 (_3)</td>
<td>0.38 (_2)</td>
<td>0.0340 (_7)</td>
<td>0.0067</td>
</tr>
<tr>
<td>1</td>
<td>28.22 (_8)</td>
<td>301.38 (_8)</td>
<td>0.39 (_7)</td>
<td>0.0341 (_1)</td>
<td>0.0090</td>
</tr>
<tr>
<td>2</td>
<td>28.19 (_2)</td>
<td>301.35 (_2)</td>
<td>0.43 (_3)</td>
<td>0.0358 (_6)</td>
<td>0.0102</td>
</tr>
<tr>
<td>3</td>
<td>28.15 (_3)</td>
<td>301.31 (_3)</td>
<td>0.47 (_2)</td>
<td>0.0365 (_6)</td>
<td>0.0094</td>
</tr>
</tbody>
</table>
\( T_c = 28.625^\circ C = 301.785^\circ K \)

<table>
<thead>
<tr>
<th>Run Series No.</th>
<th>( T,^\circ C )</th>
<th>( T,^\circ K )</th>
<th>( \Delta T )</th>
<th>( \Delta \rho, \text{gm/cm}^3 )</th>
<th>( \gamma, \text{dyne/cm} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>28.13</td>
<td>301.29</td>
<td>0.48</td>
<td>0.0378</td>
<td>0.0122</td>
</tr>
<tr>
<td>3</td>
<td>28.01</td>
<td>301.17</td>
<td>0.61</td>
<td>0.0398</td>
<td>0.0119</td>
</tr>
<tr>
<td>1</td>
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<td>301.04</td>
<td>0.74</td>
<td>0.0434</td>
<td>0.0187</td>
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<tr>
<td>1</td>
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<td>300.77</td>
<td>1.01</td>
<td>0.0470</td>
<td>0.0244</td>
</tr>
<tr>
<td>2</td>
<td>27.56</td>
<td>300.72</td>
<td>1.05</td>
<td>0.0472</td>
<td>0.0253</td>
</tr>
<tr>
<td>1</td>
<td>27.15</td>
<td>300.31</td>
<td>1.46</td>
<td>0.0534</td>
<td>0.0389</td>
</tr>
<tr>
<td>1</td>
<td>26.65</td>
<td>299.81</td>
<td>1.96</td>
<td>0.0588</td>
<td>0.0578</td>
</tr>
<tr>
<td>4</td>
<td>25.86</td>
<td>299.02</td>
<td>2.75</td>
<td>0.0653</td>
<td>0.0824</td>
</tr>
<tr>
<td>4</td>
<td>24.95</td>
<td>298.11</td>
<td>3.66</td>
<td>0.0723</td>
<td>0.1206</td>
</tr>
<tr>
<td>4</td>
<td>23.55</td>
<td>296.71</td>
<td>5.08</td>
<td>0.0803</td>
<td>0.1742</td>
</tr>
<tr>
<td>4</td>
<td>21.77</td>
<td>294.93</td>
<td>6.85</td>
<td>0.0893</td>
<td>0.2403</td>
</tr>
<tr>
<td>4</td>
<td>19.97</td>
<td>293.13</td>
<td>8.66</td>
<td>0.0979</td>
<td>0.3157</td>
</tr>
<tr>
<td>4</td>
<td>18.58</td>
<td>291.74</td>
<td>10.05</td>
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<td>0.3886</td>
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<tr>
<td>4</td>
<td>16.06</td>
<td>289.22</td>
<td>12.56</td>
<td>0.1128</td>
<td>0.5228</td>
</tr>
<tr>
<td>5</td>
<td>14.27</td>
<td>287.43</td>
<td>14.36</td>
<td>0.1174</td>
<td>0.5415</td>
</tr>
<tr>
<td>5</td>
<td>12.32</td>
<td>285.48</td>
<td>16.30</td>
<td>0.1245</td>
<td>0.6760</td>
</tr>
<tr>
<td>5</td>
<td>10.01</td>
<td>283.17</td>
<td>18.62</td>
<td>0.1304</td>
<td>0.8450</td>
</tr>
<tr>
<td>5</td>
<td>7.98</td>
<td>281.14</td>
<td>20.65</td>
<td>0.1363</td>
<td>0.9890</td>
</tr>
</tbody>
</table>
with \( T \) in \( ^oK \), \( T_c = 301.78^oK \), the parameters were determined using a non-linear least squares program*, from which

\[
A = 0.333 \pm 0.003 \text{ gm/cm}^3 \\
\beta = 0.342 \pm 0.003 \\
\gamma_0 = 29.1 \pm 2.1 \text{ dyne/cm} \\
\sigma = 1.27 \pm 0.02
\]

where the tolerances are asymptotic standard deviations. The relative error in the coefficients, \( R_A \sim 0.003/0.03 = 1\% \) and \( R_{\gamma_0} \sim 2/29 = 7\% \), are close to those predicted by the error analysis for \( \Delta \rho \) and \( \gamma \), respectively.

However, Eq. (IV-2) yields, upon substitution of \( \gamma_0 \) and \( \sigma \), estimates of \( \gamma \) which are consistently low. The suspicion here is that the experimental \( T_c \) may have been underestimated. To investigate this possibility, the program was allowed to search for the optimum \( T_c \) consistent with the best \( \gamma_0 \) and \( \sigma \) for functions of the power law form. For \( \gamma \), the data are too uncertain near \( \Delta T = 0 \) to obtain a reasonable value of \( T_c \). The \( \Delta \rho \) data are considerably better, however, and this procedure gave

\[
A = 0.352 \pm 0.003 \text{ gm/cm} \\
\beta = 0.358 \pm 0.003 \\
T_c = 301.845 \pm 0.009^oK.
\]

*Paul Sampson, Health Sciences Computing Facility, UCLA, Biomedical Package #85, Nov. 1964 (rev. 1968).
Now with the new value of $T_c$ fixed in Eq. (IV-2), $\gamma$ and $\sigma$ were determined as before with the results

$\gamma = 29.8 \pm 2.1$ dyne/cm

$\sigma = 1.28 \pm 0.02$.

The new values of $\gamma$ and $\sigma$ improve considerably the ability of Eq. (IV-2) to predict the data. The value of $\sigma$ as determined with the higher $T_c$ is essentially unchanged, although the value of $\beta$ seems entirely too high.

It is difficult for the author to believe the critical solution temperature may have been underestimated by as much as 0.06°C, as the above procedure indicates. That this occurred is not beyond the realm of possibility, however, since when cooling the bath, even at an extremely slow rate, the liquid sample may have been slightly warmer than indicated by the thermometer. Although this discussion raises some interesting questions as to how the data should be interpreted, we can only report for $T_c$ what was observed, 28.625 ± 0.005°C. This temperature was measured repeatedly, and although there was some scatter about the mean, no value was anywhere close to 301.845°C (28.685°C).

To determine the accuracy of the $\Delta \beta$ data, the density of the one phase mixture at two temperatures above $T_c$ was measured, and the results compared with those of Thompson and Rice, as obtained by the quartz-spiral method:
<table>
<thead>
<tr>
<th>$T, ^\circ C$</th>
<th>$\rho$ (mixture), gm/cm$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>This Work</td>
<td></td>
</tr>
<tr>
<td>28.71</td>
<td>1.6336</td>
</tr>
<tr>
<td>28.010</td>
<td>1.6330</td>
</tr>
<tr>
<td>Thompson and Rice</td>
<td></td>
</tr>
<tr>
<td>28.707</td>
<td>1.6338</td>
</tr>
<tr>
<td>28.008</td>
<td>1.6330</td>
</tr>
</tbody>
</table>

These results show the sample was at or extremely close to the critical composition and that the technique for $\Delta \rho$ is quite valid.

For the interfacial tension data, only a qualitative assessment of the accuracy is possible. Close examination of Figure 7 reveals that for run #3, with the 0.00831 cm tip, the $\gamma$ values appear low. If this is a discrepancy, it probably resulted from a wetted circumference less than the inside circumference of the tip. This particular tip never gave consistent results, even in preliminary experiments. On the other hand, if the points for run #3 are of a different population, the drop-volume method (correction factor) may not be applicable near $T_c$, and it would be naive to assume this could not be true. If we relax the assumption that $f(r/V^{1/3})$ is universal for all liquids, but retain its temperature independence, the present procedure should at least give the correct $\sigma$. To resolve this question, the data should be redetermined by an independent method. Unfortunately, any such method would require an
equal, if not greater, effort than the present procedure, and in particular, would likely be unable to attain

\[ \Delta T \approx 0.06. \]  

In fact, the present measurements when compared with those of Thompson and Rice, are really in the "sub-critical" region, and the interfacial tension is already so low that measurements with \( \Delta T \approx 0.001 \) are difficult to imagine.

The data do reveal, within the limits of scatter, that there are no breaks as such in the interfacial tension curve over the range of temperature investigated. If such a break does occur, it is probably at a temperature below the freezing point of CCl₄.

Scaling Laws

For the data taken here, \( 1.27 = \sigma < \beta + 1 = 1.34 \), thus confirming Lovett's inequality.

Using Zimm's value of \( f = 1.2 \), and \( \beta = 0.342 \) as determined in this work, Eq. (I-6) yields \( \sigma = 1.28 \). Similarly, Thompson and Rice's \( \beta = 0.335 \) from volume fractions gives \( \sigma = 1.27 \). With the modified scaling law, Eq. (II-17), the results are \( \sigma = 1.26 \) and 1.25 for \( \beta = 0.342 \) and 0.335, respectively. Thus, for the PFMCH-CCl₄ mixture, three independent sets of data are consistent with \( \beta = 0.33 \pm 0.02 \), \( \sigma = 1.27 \pm 0.02 \) and \( f = 1.2 \), all of which fall within the theoretical limits.
One would therefore expect \( \nu \approx 1.2/2 = 0.6 \) for the interfacial thickness parameter to be nearly correct.

With respect to the existence of a universal \( \sigma \), let us examine the experimental data which are available over a temperature range suitable for the reliable determination of \( \beta \), \( \gamma \) and \( \sigma \). The parameters in Table II, with the exception of cyclohexane-methanol\(^{56}\) and PFMCH-CCl\(_4\), as obtained in this work, have been calculated by Buff and Lovett\(^{6}\) and Lovett\(^{38}\).

Table II reveals the trend \( \sigma \) (polar) < \( \sigma \) (non-polar) for both pure liquids and mixtures. The positions of nitrogen and cyclohexane-aniline seem to be reversed in this respect, but the uncertainty in the data for the latter system has already been pointed out. This inequality is not unexpected in view of Harkins'\(^{26}\) postulate that the interfacial tension is inversely proportional to the discreteness of the interfacial region.

A reasonable explanation of the data in Table II might be as follows. Consider the square-gradient theory valid for all liquids and liquid mixtures, but allow

\[
\gamma = C(1 - T/T_c)^{-n}, \quad \text{(IV-3)}
\]

where the index \( n \) is related to Fisher's \( \sqrt{\gamma} \) in some manner. Then by corresponding states,

\[
\gamma = C(1 - T/T_c)^{\sigma^{-n}},
\]
<table>
<thead>
<tr>
<th>System</th>
<th>$T/T_c$ max</th>
<th>$\sigma$</th>
<th>$\beta$</th>
<th>$\gamma$, dyne/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Argon</td>
<td>0.96</td>
<td>1.281</td>
<td>0.341</td>
<td>38.07</td>
</tr>
<tr>
<td>Xenon</td>
<td>0.98</td>
<td>1.287</td>
<td>0.345</td>
<td>54.6</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.98</td>
<td>1.247</td>
<td>0.317</td>
<td>29.09</td>
</tr>
<tr>
<td>PFMCH-CCl$_4$</td>
<td>0.9999</td>
<td>1.273</td>
<td>0.341</td>
<td>29.1</td>
</tr>
<tr>
<td>Cyclohexane-methanol</td>
<td>0.9997</td>
<td>1.23</td>
<td>0.34</td>
<td>100</td>
</tr>
<tr>
<td>Cyclohexane-aniline</td>
<td>0.9989</td>
<td>1.288</td>
<td>$\sim 1/3$</td>
<td>37.8</td>
</tr>
<tr>
<td>Water</td>
<td>0.97</td>
<td>1.19</td>
<td>$\sim 1/3$</td>
<td></td>
</tr>
</tbody>
</table>
where \( n = 0 \) for non-polar systems. Assuming, say, \( \sigma = 1.27 \) for all liquids and mixtures, we get \( n = 0.08 \) for water, etc. A relation between \( n \) and surface entropy would seem logical.

The task of the theory is to explain, if only qualitatively, the existence of the index \( n \). Indeed, if the polar molecules follow a potential of the Keesom(31) type, a non-zero temperature dependence of \( \lambda \) is not surprising. We have implicitly assumed \( \sigma \) and \( n \) are independent of concentration, which for temperature dependence alone, seems reasonable. However, the C's are concentration dependent, and how they should be scaled, other than by empirical mixing rules, is not clear in the context of corresponding states.

**Proposed Work**

An examination of the systems fluorocarbon-heptane, heptane-water and fluorocarbon-water or aniline-hexane, hexane-water and aniline-water would reveal the effect of polarity. In fact, the data for several polar-polar systems(26) \( (T<T_c) \) shows \( \gamma \) passing through a maximum, i.e., \( \sigma = 0 \). The theoretical interpretation of this peculiar behavior is exceedingly difficult, but any general theory will have to explain it. In general, work should proceed to improve the theoretical situation away from the critical point and the experimental situation close to it.
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Ref. (1).


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(54) van der Waals, J. D., J. Physik. Chem., 13, 657(1894).


APPENDIX A
APPENDIX A

CALIBRATION OF PLUMMETS

The plummets were calibrated, using Eq. (III-4), with degassed distilled water.

The density of the air may be calculated (57) by measuring the room temperature, \( T \)°C, the barometric pressure, \( p \) mm Hg, the percent relative humidity, \( H \), and the equation

\[
D_a = (0.001293)(p-k)/(1+0.00367T)760.
\]  

(A-1)

\( k \) is a correction term which depends on the amount of moisture in the air

\[
k = (0.0038)H_{p^o},
\]  

(A-2)

where \( p^o \) is the vapor pressure of water at \( T \)°C.

The surface tension correction, in terms of the mass \( m \) to be subtracted from \( W_L' \), is

\[
m = 2\pi rl/g,
\]  

(A-3)

where \( r \) is the radius of the wire which passes through the surface of the liquid*.

*Eq. (A-3) is correct only if the contact angle between the wire and the liquid is zero. That \( \cos \theta \sim 1 \) for both water and \( \text{CCl}_4 \) was confirmed by examination with a 65X telescope.
The plummets and their respective wires were weighed in air and in water with the temperature bath controlling at 25.30°C. At the time of calibration, \( T(\text{dry bulb}) = 24.5^\circ\text{C}, \)
\( T(\text{wet bulb}) = 12.2^\circ\text{C}, \)
therefore \( H = 20.6\% \) \(^{(24)}\). The other constants were: \( p = 737.62 \text{ mm Hg}, \) \( p^0(24.5^\circ\text{C}) = 23.13 \text{ mm Hg} \)
\( (30), \) \( \gamma(25^\circ\text{C}) = 72 \text{ dyne/cm} \) \(^{(26)}\), \( g = 979.99 \text{ cm/sec}^2 \) \(^{(53)}\)
and \( r = 0.0038 \text{ cm}. \) From Eqs. (A-1), (A-2) and (A-3), 
\( k = 1.849, \) \( D = 0.001148 \text{ gm/cm}^3 \) and \( m = 0.0017 \text{ gm}. \)

The mean weights of the plummets were (\( h \) refers to the heavy phase plummet and \( l \) to the light phase plummet):

\[
\begin{align*}
W_h' &\quad \text{gm} \\
W_l' &\quad \text{gm} \\
h &\quad 14.9985 \\
l &\quad 14.9984
\end{align*}
\]

Here, the \( W_l' \) have been corrected for the surface tension of water. The absolute density of water \(@ 25.30^\circ\text{C} \) is 0.996967 \text{ gm/cm}^3 \(^{(24)}\) and the density of the stainless steel weights is 7.88 \text{ gm/cm}^3 \(^{(48)}\). Combining Eqs. (III-4), (III-5) and (III-6),

\[
V(T) = (W_h' - W_l') \left[1 - \frac{D_a}{D_w} \right] / (\rho_L - \rho_a),
\]

whence

\[
V_h(25.30^\circ\text{C}) = 2.01031 \text{ cm}^3,
\]
\[
V_l(25.30^\circ\text{C}) = 2.01061 \text{ cm}^3.
\]

For the volumes at any temperature,
\[ V(T) = V_o \left[ 1 + 3 \alpha(T - T_o) \right] \]

where \( V_o = V(25.30^\circ C), \ T_o = 25.30^\circ C, \ \alpha_{\text{glass}} = 3.25 \times 10^{-6}/^\circ C \).

Therefore

\[ V_h(T) = 2.01031 \left[ 1 + 9.75 \times 10^{-6}(T - 25.30) \right] \text{ cm}^3, \]

\[ V_1(T) = 2.01061 \left[ 1 + 9.75 \times 10^{-6}(T - 25.30) \right] \text{ cm}^3. \]

The density of each phase may now be determined at any temperature using Eq. (III-4) and the buoyancy corrections. However, the appropriate surface tension is now that for the top phase \(^*\), \text{CCl}_4 (saturated with PFMCH), taken as (constant) 25 dyne/cm\(^2\)\(^**\). The correction is therefore \((25/72)(0.0017) = 0.0006 \text{ gm.} \)

The surface tension correction is quite large, and if not accounted for, will affect the absolute densities in the 3rd decimal place. However, the correction will cancel in calculation of the density difference \( \Delta \rho \).

---

\(^*\) For the sake of completeness, the interfacial tension between the two liquid phases also results in a correction for the long wire (heavy phase) plummet. This correction, which is neglected, is of the order of 0.000002 gm.

\(^**\) This is justified since \( dV/dT(\text{CCl}_4) \approx 0.1 \) over the temperature range relevant to this work.
APPENDIX B

EXPERIMENTAL DATA

Explanation of Table III

T : The corrected temperature of the bath, °C
r : The inside radius of the dropping tip, x10^2 cm
ΔL: The mean displacement of the micrometer/# drops,
    x10^4 cm
V : The volume of one drop, x10^5 cm^3
F : The Harkins correction factor (Eq. (III-3))
γ : The interfacial tension, dyne/cm (Eq. (III-2))
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Explanation of Table IV

$T$ : The corrected temperature of the bath, °C

$T_w$ : The wet bulb temperature of the laboratory, °C

$T_d$ : The dry bulb temperature of the laboratory, °C

$p$ : The barometric pressure, mm Hg

$H$ : The percent relative humidity

$W_L(h)$: The uncorrected mean weight of the heavy phase

\[
W_L(h) = 14.9985 \text{ gm}, \text{ constant for all determinations}
\]

$W_L(l)$: The uncorrected mean weight of the light phase

\[
W_L(l) = 14.9984 \text{ gm}, \text{ constant for all determinations}
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Explanation of Table V

T : The corrected temperature of the bath, °C

\( W_L(h) \): The weight of the heavy phase plummet in the heavy phase, corrected for the surface tension and the buoyancy of air, gm

\( W_L(l) \): The weight of the light phase plummet in the light phase, corrected for the surface tension and the buoyancy of air, gm

\( \rho_h \): The density of the heavy phase, gm/cm³

\( \rho_l \): The density of the light phase, gm/cm³

\( \Delta \rho \): The density difference \( \rho_h - \rho_l \), gm/cm³
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APPENDIX C

ERROR ANALYSIS

If a derived or computed measurement, \( u \), is a function of the directly measured parameters \( x, y, \ldots \),

\[
 u = u(x, y, \ldots) ,
\]

then the derivation \( \delta u_i = u_i - \bar{u} \), where \( \bar{u} \) is the mean of \( n \) measurements, is

\[
 \delta u_i = \frac{\partial u}{\partial x_i} \delta x_i + \frac{\partial u}{\partial y_i} \delta y_i + \ldots
\]

By definition, the standard deviation is

\[
 S_u = \left[ \frac{\sum_{i=1}^{n} (\delta u_i)^2}{n} \right]^{\frac{1}{2}}
\]

Alternatively, we may consider the relative error, \( R_u = \delta u/u \), which for linear functions of the form (C-1) is

\[
 R_u = R_x + R_y + \ldots
\]

Eq. (C-4) enables one to easily identify the largest contribution to the total error, and thereby take steps to reduce the particular \( R_x, \ldots \).
Density

From Eqs. (III-4), (III-5) and (III-6),

$$\rho_L = \left\{ W_A' + D_A [V - (W_A'/D_w)] - [W_L' - D_A (W_L'/D_w)] \right\} / V, \quad (C-5)$$

and

$$\delta \rho_L = \frac{\partial \rho_L}{\partial W_A} \delta W_A' + \frac{\partial \rho_L}{\partial W_L} \delta W_L' + \frac{\partial \rho_L}{\partial D_A} \delta D_A$$

$$+ \frac{\partial \rho_L}{\partial V} \delta V + \frac{\partial \rho_L}{\partial D_w} \delta D_w. \quad (C-6)$$

Taking the appropriate partial derivatives in Eq. (C-6) and using the values $\delta W_A' = 5 \times 10^{-5}$ gm,

$\delta W_L' = 5 \times 10^{-5}$ gm, $\delta D_A = 1 \times 10^{-6}$ gm/cm$^3$, $\delta V = 1 \times 10^{-5}$ cm$^3$, and $\delta D_w \approx 0$,

$$\delta \rho_L = (0.248 + 0.248 + 0.873 + 0.200) \times 10^{-4}$$

$$= 1.57 \times 10^{-4} \text{ gm/cm}^3.$$

Although the deviation in $\Delta \rho$ is considerably smaller than this, we will also take $\delta \Delta \rho = 2 \times 10^{-4}$ gm/cm$^3$. For the worst possible case (nearest $T_c$) $\Delta \rho = 0.02173$ gm/cm$^3$, and

$$R_{\Delta \rho} \approx (2 \times 10^{-4} / 2 \times 10^{-2}) (100) = 1\%.$$ This is an extremely conservative estimate of the error in $\Delta \rho$. 
Interfacial Tension

From Eq. (III-2),

$$\delta \gamma / \gamma = \delta V / V + \delta \rho / \rho + \delta r / r + \delta F / F.$$  (C-7)

a) $V = A \Delta L$, where $A$ is the area of the piston and $\Delta L$ is the micrometer travel, therefore

$$\delta V = A(\delta \Delta L) + \Delta L(\delta A)$$

(neglecting $\delta V$ due to the coefficient of expansion of the glass). $A \approx 10^{-1}$ cm$^2$, $\Delta L = 20 \times 10^{-4}$ cm (100 drops). The deviation in $A$ is $2 \pi r \Delta r$, where $r$ (piston) = 0.1784 cm,

$$\delta r = 1 \times 10^{-4}$$

cm (cathetometer). Thus $\delta A = 1.12 \times 10^{-4}$ cm$^2$.

$\delta \Delta L = 1 \times 10^{-4}$ cm (micrometer), therefore

$$\delta V = 1 \times 10^{-5} \text{ cm}^3$$

and $(\delta V / V)(100) = 5.1\%$.

b) From the above estimate for density difference,

$$\delta \rho = 1\%.$$

c) $r$ (tip) = $0.658 \times 10^{-2}$ cm, $\delta r = 1 \times 10^{-5}$ cm (from magnification of photographs), therefore $(\delta r / r)(100) = 0.15\%$.

d) $F = 0.2524$, $\delta F = 5.7 \times 10^{-4}$ (Eq. (III-3)), thus

$$(\delta F / F)(100) = 0.23\%.$$

From Eq. (C-7),

$$R_y = \delta \gamma / \gamma = 5.1 + 1.0 + 0.15 + 0.23$$

$$= 6.4\%,$$

and the error in $V$ amounts to about 80% of the error in $\gamma$.

Therefore, the precision of the interfacial tension
measurements depends primarily on the number of drops counted in the determination of \( V \).

For the lowest value of interfacial tension \( (\Delta T = 0.05^\circ \text{C}) \) \( \gamma = 0.0013 \text{ dyne/cm} \), \( \delta \gamma = (1.3 \times 10^{-3})(6.4 \times 10^{-2}) \approx 1 \times 10^{-4} \). The last figure in the reported \( \gamma \) is somewhat more uncertain than this since \( V \) may be determined by only three significant figures. The \( \gamma \) values are therefore reported with the 4th place set below, i.e., \( 0.0013 \) dyne/cm with a deviation of 0.0001.
VITA

George W. Paul was born on August 25, 1940, in Mexico, Missouri. He received the Bachelor of Science and Master of Science degrees from the University of Missouri at Columbia. The author was awarded an American Chemical Society Petroleum Research Fund Fellowship in 1968. He is a member of Sigma Xi.
The undersigned, appointed by the Dean of the Graduate Faculty, have examined a thesis entitled

INTERFACIAL TENSION IN

A BINARY LIQUID SYSTEM

presented by George W. Paul

a candidate for the degree of Doctor of Philosophy

and hereby certify that in their opinion it is worthy of acceptance.

L. E. Marc de Chazal

Truman S. Storvick

Paul W. Schmidt
Local identifier  Paul 1969

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