III indicates that metaxylene solubility is 46 to 47% at −100° F., independent of the composition of the solution. The 46% metaxylene solubility at −100° F. is just on previously reported theoretical solubility charts as mole percentages of 46 to 48 are given in (*3, 4*).

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Properties of Superheated Liquids

Density and Compressibility of CCl_4

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A capillary tube pycnometer has been developed which enables study of *PVT* behavior of superheated liquids. Experiments were conducted for superheats as high as 42° C., and data for the density and compressibility of CCl_4 are reported for superheats up to 13.1° C. The results are in close agreement with an earlier study by Gibson and Loeffler of CCl_4 under subsaturated conditions.

ALTHOUGH the phenomenon of liquid superheating accompanies a variety of natural as well as industrial processes, the technical literature contains very little information about the behavior of liquids under superheated conditions. The purpose of this paper is to discuss experimental techniques for studying the superheated liquid state and to report the *PVT* behavior of pure CCl_4 at low pressures under modest superheats.

EXPERIMENTAL CONSTRAINTS

According to the nucleation theory of Volmer (*8*), the probability of formation of a critically sized vapor phase embryo in a homogeneous liquid under superheated conditions increases as the volume of the liquid phase increases. Thus, one could, at least in principle, prevent vapor phase nucleation at very high superheats by reducing the effective volume of the liquid phase, as has been observed by several investigators under rather specialized circumstances (*2, 5*). Since, however, there are practical limits to the minimum size of an experimental system, and since nucleation also can occur (and, in practice, usually does occur) at the interface between the liquid and its container, it is necessary to constrain a superheated system in additional ways. In this study, retardation of vapor phase nucleation was effected by eliminating pre-existing vapor phase nuclei at solid-liquid interfaces, promoting interfacial wetting, and reducing thermomechanical fluctuations. The first and second constraints were accomplished by degassing both the experimental apparatus and the test liquid using high vacuum techniques. The effect of thermomechanical shock was arrested by mounting the apparatus on specially designed shock mounts embedded in massive concrete walls.

APPARATUS AND PROCEDURE

A schematic diagram of the over-all apparatus appears in Figure 1. Principal components include a high vacuum system, *HVS*, a liquid degasser, *LD*, a Torricellian barometer, *TB*, a nitrogen reservoir, *NR*, a dust trap, *DT*, and the pycnometer itself, *CP*. Additional details of the pycnometer system appear in Figure 2.

The liquid to be superheated was stored in a spherical quartz bulb, *QB*, which was blown from vitreous silica and connected to the rest of the borosilicate glass pycnometer by means of a graded seal. The total superheated volume (*QB* and adjacent stem) was determined gravimetrically using pure mercury (3.244106 cc. at 24° C.). The effect of pressure and temperature on this volume was calculated from the physical properties of pure SiO_2 using standard equations from the literature (*6, 7*).

Changes in volume of the liquid stored in *QB*, produced by changes in temperature or pressure, were calculated from displacements of the N_2 - CCl_4 interface in the small bore capillary tube, *SBC*, whose mean radius (0.01011 cm.) was determined according to a technique described by Giddings (*4*). The bypass valve, *BPV*, and associated reservoir, *BPR*, were included because the volumetric capacity of *SBC* was too small to accommodate the over-all changes in volume produced during an isobaric run.

The experimental program was begun by assembling the glassware as in Figure 1, using one-shot glass break-out valves (*V1, V3*) to separate *LD* and *NR* from *CP*. The internal surfaces of the apparatus then were degassed by raising their temperature to 350° C. under a high vacuum of 10^{-7} mm. of Hg. (Since the conductance of capillary tubing is small under high vacuum conditions, *QB* was exhausted through a bypass line which was later sealed off at *S1*.) Degassing was continued for about 10 days, during which time the liquid degasser was set in operation. (Spectroscopic grade CCl_4 charged to *LD* was freed from dissolved gases by operating the unit as a fractionating

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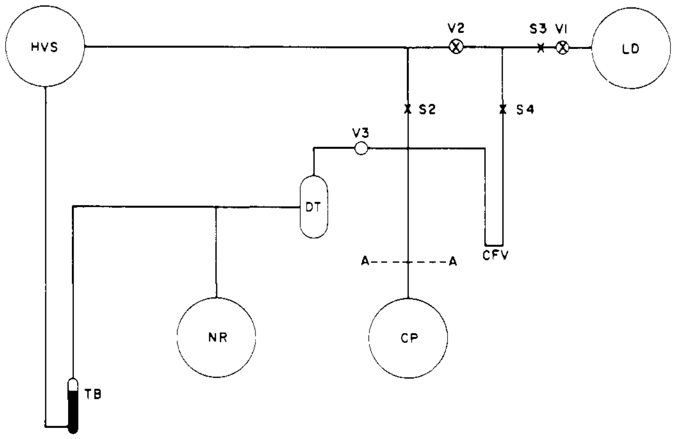

Figure 1. Schematic diagram of apparatus

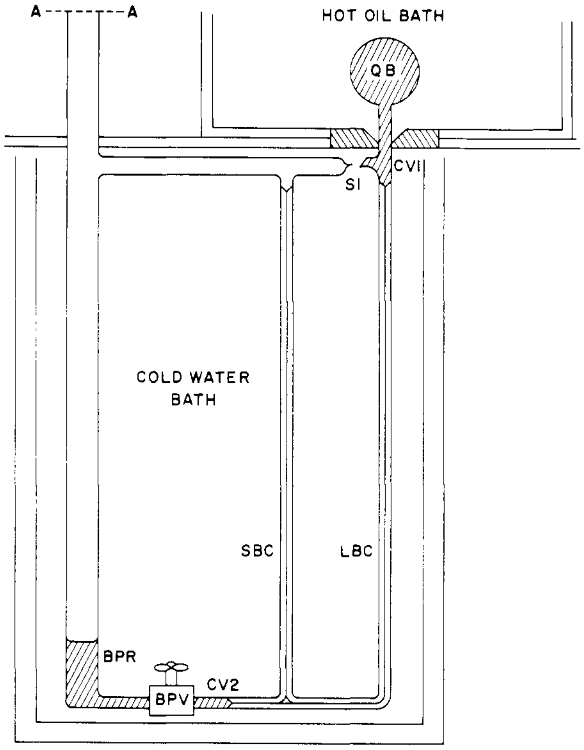

Figure 2. Capillary pycnometer

column under essentially total reflux, withdrawing the more volatile (dissolved) gases, as well as some CCl_4, through a capillary orifice located beyond the overhead condenser.)

With completion of degassing, *HVS* was removed by collapsing the glass line at *S*2 with a hand torch. CCl_4 was then charged to *CP* through *V*1, condensing the vapor in place by cooling *QB* with crushed ice. Vapor flow to *CP* was stopped by surrounding a capillary freeze valve, *CFV*, with liquid nitrogen. *LD* was then removed by sealing the glass line at *S*3; but since this operation resulted in thermal decomposition of some CCl_4, the material contained between *CFV* and *S*3 was exhausted through *V*2 and the glass line resealed at *S*4. Finally, the small amount of [solid] CCl_4 in *CFV* was transferred to *CP*.

Following the charging operation, *CP* was pressurized with N_2 through V_3, and the temperature baths were set in operation. The temperature in the upper (hot oil) bath was controlled with a Hallikainen thermotrol, while that in the lower (cold water) bath was established by equilibrating a large mass of water in a Dewar flask with surrounding room air. Temperatures in these baths were measured with NBS certificated thermometers, using a Beckman in the upper bath. Maximum observed deviations in these temperatures were 0.001° and 0.01° C. in the upper and lower baths, respectively.

The procedure for taking the data was initiated by raising the temperature in *QB* to 69.83° C. at a constant pressure of 1104 mm. of Hg, leaving *BPV* in the open position. At steady state, *BPV* was closed and the relative positions of the menisci in *SBC* and *BPR* were recorded. Data for the 1104-isobar was obtained by raising the temperature of the oil bath in 2° C. steps, recording the elevation of the meniscus in *SBC*, and restoring the meniscus to its rest position (by opening and closing *BPR*) after each step. Data for the isotherms were obtained by dropping the pressure in *QB* at constant temperature, recording interfacial positions in *SBC* after each decrement. Actually, data were taken for both increasing and decreasing temperatures (as well as decreasing and increasing pressures). Within the resolution (0.001 cm.) of the cathetometer used to measure interfacial position, no hysteresis in the results was observed.

CALCULATIONS

Starting with results reported by Gibson and Loeffler (*3*) at 1104 mm. of Hg and 69.83° C., relative values of the density of CCl_4 were obtained by relating changes in position of the meniscus in *SBC* to changes in mass in *QB* as follows:

$$\rho_i = \frac{V_{H1}}{V_{Hi}}\left[\rho_1 - \frac{\pi R^2 \rho_0 (h_i - h_1)}{V_{H1}} + \frac{V_{co}\left(\frac{\partial \rho}{\partial P}\right)_0 (P_1 - P_i)}{V_{H1}}\right]$$

where ρ_1, V_{H1}, h_1, and P_1 are the density, hot volume, interfacial position, and bulb pressure at 1104 mm. of Hg and 69.83° C., and ρ_0, V_{co}, $(\partial\rho/\partial P)_0$ are the density, cold volume, and pressure coefficient of density under conditions of temperature and pressure present in the lower bath. Thus, $\rho_1 V_{h1}$ represents the initial mass of CCl_4 which was present in V_{H1}, $\rho_i V_{Hi}$ the mass contained in V_{Hi}(V_{Hi} is V_{H1} corrected for temperature and pressure) at any subsequent state, $\pi R^2 \cdot \rho_0 \cdot (h_i - h_1)$ the mass appearing (or disappearing) in *SBC*, and $V_{co}(\partial\rho/\partial p)_0(P_1 - P_i)$ the correction for the compressibility of the liquid contained in $V_{co} = CV1 + CV2$. Although the procedure requires *a priori* knowledge of ρ_0 and $(\partial\rho/\partial P)_0$ [in addition to ρ_1 and $(\partial\rho/\partial P)_1$], the results are insensitive to variations in these values of the order reported in previous studies.

In addition to the above procedure, several second-order effects were investigated (and found negligible), including the effects of capillarity on the pressure distribution in *SBC* (obtained experimentally by measuring capillary rise in *SBC* with *BPV* open), evaporation at the $N_2 - CCl_4$ meniscus (obtained experimentally by observing the meniscus over prolonged periods under stationary conditions), variations in pressure and temperature in *QB* on the mass contained in the nonisothermal section of tubing passing through the bottom of the upper bath (calculated from numerical solutions (*1*) to the heat conduction problem in this region), and solubility of N_2 in CCl_4.

RESULTS AND DISCUSSION

The results are summarized in Figure 3, where the data obtained under superheated conditions are indicated by the dashed line portions of the four isotherms reported (the numerical values listed beside these data points are calculated values of liquid superheat in ° C.). Although

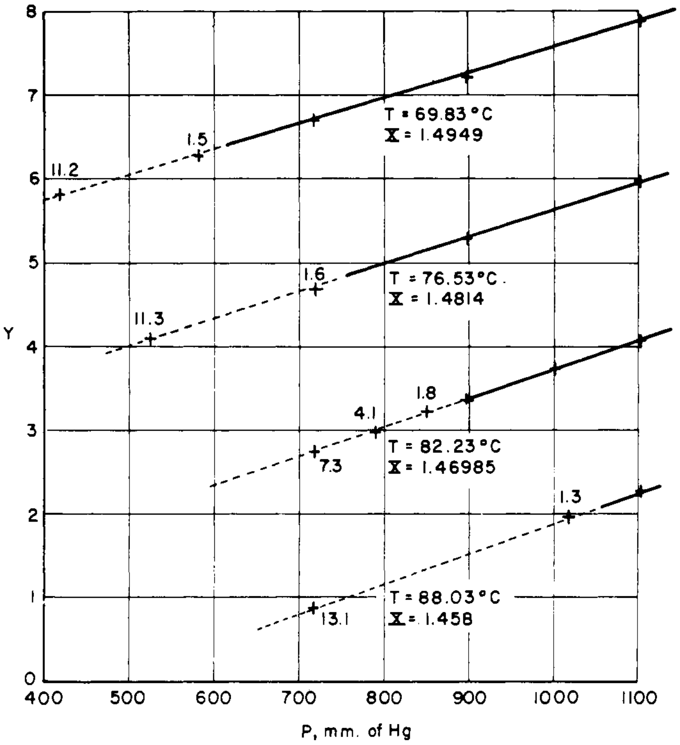

Figure 3. Density of superheated CCl_4
$\rho = X + 10^{-4}Y$, g./cc.

data are reported for a maximum superheat of 13.1° C., experiments were conducted for superheats as high as 42° C. The additional information is not reported because the corrections for evaporative losses from the N_2-CCl_4 interface became excessively large at nitrogen pressures below about 300 mm. of Hg.

The data are evaluated in Table I, where a and b are coefficients in linear least-squares fits to the Y's as a function of P, and $\sigma(b)$ is a confidence limit for the slope b. Atmospheric values of the density (line seven) were obtained by linear interpolation, and are to be compared with values (line eight) calculated from the curve-fit expression for specific volume reported by Gibson and Loeffler (*3*). Calculated values of the coefficient of compressibility κ (line nine) are to be compared with values (line 10) obtained from the Gibson-Loeffler study.

Figure 3 shows that the density of CCl_4 under superheated conditions is in agreement with a linear extrapolation of the data obtained under subsaturated conditions. Thus, there is no anomalous behavior of the liquid state, at least for nonpolar spherical molecules such as CCl_4, on entering the superheated region. Furthermore, from the excellent agreement between the data reported here and those obtained by Gibson and Loeffler, it is clear that the G-L equation of state

$$v = 0.647091 + 8.282 \times 10^{-4}(t - 45) + 14.776 \times 10^{-7}(t - 45)^2 + 4.5 \times 10^{-9}(t - 45)^3, \ \rho = 1/v$$

Table I. Properties of CCl_4 under Superheated Conditions at 760 Mm. of Hg[a]

t, ° C.	69.83	76.53	82.23	88.03
X, g./cc.	1.49490	1.48140	1.46985	1.45800
Y, g./cc.	6.82	4.82	2.85	0.94
a	4.42	2.27	0.14	−1.89
$b \times 10^3$	3.16	3.35	3.57	3.72
$\sigma(b) \times 10^3$	0.04	0.03	0.02	0.01
ρ	1.495582	1.481882	1.470135	1.458094
$\rho_{G\text{-}L}$	1.495584	1.481889	1.470144	1.458102
$\kappa \times 10^7$, (mm. Hg)$^{-1}$	2.11	2.26	2.42	2.55
$\kappa_{G\text{-}L} \times 10^7$	2.11	2.27	...	...

[a] $\rho = X + 10^{-4}Y = a + bP$, $\sigma(b) = [S_e^2(Y_i)/\Sigma(P_i - P)^2]^{1/2}$, $\kappa = (\partial\rho/\partial P)_T/\rho = 10^{-4}b/\rho$.

in conjunction with the reported compressibilities is an excellent representation of the superheated liquid state over the range of temperature and pressure studied. Clearly, however, this conclusion is favored by the very narrow range of thermodynamic coordinates employed, and if the superheated region could be penetrated more deeply and/or the saturated state were to approach the critical, one would expect the superheated state to require more sophisticated treatment. Of course, the attendant experimental difficulties would be amplified, but the effort would seem to be justified in terms of the utility of the results in developing a satisfactory theory for the liquid state.

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