

The method gives no information for determining exactly the liquid concentration at which salt saturation occurs. The saturation point for any particular salt concentration can, however, be easily found experimentally.

The prediction cannot be used successfully for systems exhibiting nearly constant relative volatilities. In this case the straight lines in Figure 1 will be very short and the method becomes inaccurate.

#### NOMENCLATURE

- $c, k$  = empirical constants  
 $m$  = molality, g. moles salt/1000 g. solvent  
 $N$  = mole fraction of salt based on total residue composition  
 $T$  = absolute temperature  
 $x$  = mole fraction of the more volatile component in the liquid phase at equilibrium (salt-free basis)  
 $y$  = mole fraction of the more volatile component in the vapor phase at equilibrium  
 $\alpha$  = relative volatility

#### Subscript

- $s$  = system with salt added

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## Equations of State for Propyne

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*P-V-T* data for propyne have been fitted using the Martin-Hou and the Benedict-Webb-Rubin equations of state. The Martin-Hou equation, with its constants calculated from the critical constants and a vapor pressure point for the gas, fits up to 1.1 to 1.5 times the critical density with deviations of less than 1%. The Benedict-Webb-Rubin equation, with its constants calculated by the method of Joffe, resulted in somewhat greater deviations in the low pressure region than did the Martin-Hou equation; however, it also provided a better approximation of the data at high pressures and lower temperatures. The best over-all fit was obtained using the B-W-R equation with its constants determined by a multiple non-linear regression technique, to give a least squares fit to the data themselves.

**E**XTENSIVE *P-V-T* DATA for propyne were recently obtained by Vohra and coworkers (8). These data included over 350 observations, covering the range of 50–200° C. and 6–315 atm. The experimental work has not extended to temperatures above 200° C. because of the polymerization of propyne at these conditions.

The propyne *P-V-T* data were fitted by two equations of state, the Martin-Hou equation (6) and the Benedict-Webb-Rubin equation (3). This paper presents the results of this work.

#### MARTIN-HOU EQUATION

The nine constants in the Martin-Hou equation were calculated from the critical values determined by Vohra (8) and from the normal boiling point (2). The calculations were carried out using an IBM 1620 computer, following the procedure presented in the literature (6, 7). Following the suggestion of Martin and Hou, the constants were

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varied in an attempt to improve the over-all fit, reflecting the uncertainties in the critical volume and several of the derived quantities. However, the best fit was given by the original calculation.

#### Physical Properties of Propyne

Critical Temperature	402.39 ° K.
Critical Pressure	55.54 atm.
Critical Volume	4.0833 cc./gm.
Gas Law Constant	2.0482 cc. atm./mole ° K.
Normal Boiling Point	250.0 ° K.

The derived equation is:

$$P = \frac{2.0482T}{V - 0.8822} + \frac{-6621.6 + 5.4463T - 112,939e^{-0.013667T}}{(V - 0.8822)^2} + \frac{16,844 - 9.2572T + 360,536e^{-0.013667T}}{(V - 0.8822)^3} + \frac{21,935.4}{(V - 0.8822)^4} + \frac{32.872T}{(V - 0.8822)^5}$$

This equation represents the compressibility factor data within 1% for isotherms above the critical at up to 1.1 times the critical density, and up to 1.5 times the critical density on the critical isotherm itself, as shown in Figure 1. All the data below the critical temperature fell within 1%, except on the isotherms from 90–110° C., where the data consists of a relatively few points near the saturation curve. In view of the good fit in other low pressure areas, it is possible that these latter data are somewhat in error, due to the experimental difficulty in obtaining data near the saturation curve.

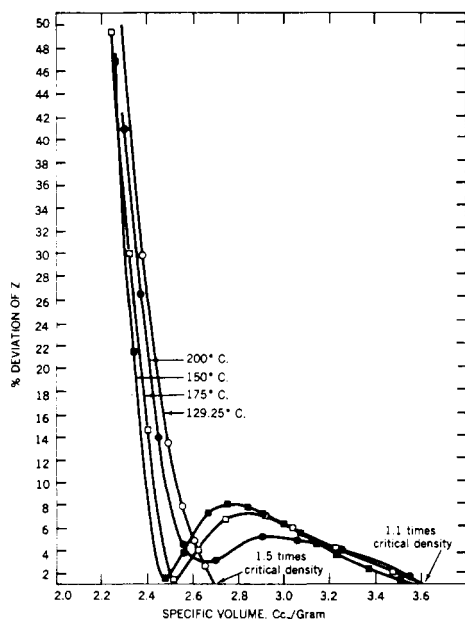


Figure 1. Deviation of Martin-Hou equation at high density

#### BENEDICT-WEBB-RUBIN EQUATION

The ability of the Benedict-Webb-Rubin equation of state to fit wide ranges of  $P$ - $V$ - $T$  data has been well demonstrated (1, 3, 4). In this work, two sets of constants for the equation were calculated and the precision of the fit of the equations to the data was determined.

In the first case, the constants were calculated by the method of Joffe (5). Here, the constants are related to those established for the propane system by the law of corresponding states. Thus, by expressing the B-W-R equation for propane in reduced form,

$$P_r = \frac{T_r}{\phi} + \frac{B_0' T_r - A_0' - C_0/T_r^2}{\phi^2} + \frac{b' T_r - a'}{\phi^3} + \frac{a' \alpha'}{\phi^6} + \left( \frac{c'}{\phi^3 T_r^2} \right) \left( 1 + \frac{\gamma'}{\phi^2} \right) e^{-\gamma'/\phi^2}$$

a set of generalized coefficients can be determined.

This procedure resulted in the B-W-R coefficients shown in Table I. The equation with these coefficients gave a good fit to the data below the critical temperature, with some exceptions.

In the region of the saturation curve, the predictions were generally somewhat high. Furthermore, as was discussed in reference to the Martin-Hou equation, some data near the saturation curve appeared to be low. Accordingly, the deviations for these data are abnormally high, being slightly over 1%.

Table I. Joffe's B-W-R Coefficients.

$B_0$	1.998
$A_0/R$	1870
$C_0/R$	$163.6 \times 10^6$
$b$	9.484
$a/R$	5294
$a\alpha/R$	$0.2782 \times 10^5$
$c/R$	$0.852 \times 10^9$
$\gamma$	9.27

The predictions at pressures well above the critical were relatively poor, especially at the lower temperatures. For example, errors of over 1% occurred at pressures of 55 atm. and higher on the critical isotherm, 140 atm. and above at 150° C., and at 180 atm. and higher at 200° C.

In the second of these cases, the coefficients were determined by a regression of the data themselves. This was done using the Esso Research and Engineering Company's nonlinear multiple regression program for the IBM 7090 computer.

This program approximates the nonlinear functions of the equation with a Taylor expansion. The step-wise regression is carried out on the linearized equation, revising the Taylor expansion each step. The final coefficients obtained are those which provide the minimum sum of the squares of the deviations in the dependent variable.

The dependent variable chosen was the compressibility factor, rather than pressure. In this way, the absolute deviations were minimized for a variable which has a range of less than an order of magnitude. If pressure, which varies over a thirtyfold range, had been used as the dependent variable, the precision of the fit in terms of per cent would have been biased to fit the high pressure data preferentially.

Actually, since the preferable criterion would be the per cent precision over the range of the data, the equation might have been rewritten in terms of the logarithm of the dependent variable. In this way, minimizing the sum of the squares of the absolute deviations of these logarithms would be equivalent to minimizing the per cent deviations of the variable. On the other hand, it was felt that additional error would be introduced by this method because of the greater nonlinearity of the logarithmic form.

The equation resulting from this regression is:

$$P = \frac{2.0482T}{V} + \frac{1.734T - 1554 - 1.949 \times 10^{10}/T^2}{V^2} + \frac{9.241T - 5924}{V^3} + \frac{22,533}{V^6} + \frac{8.342 \times 10^{10}(1 + 7.759/V^2)e^{-7.759/V^2}}{V^3 T^2}$$

The over-all fit of this equation to the data is good, as shown in Figure 2, with an average deviation in the compressibility factor of 0.55%. A few of the deviations from the data at high pressure are 1% or greater, especially at lower temperatures approaching the critical. Ten of the 365 data have prediction errors of 2% or over; most of these are at the high-pressure end of the critical (129.25° C.) and 150° C. isotherms.

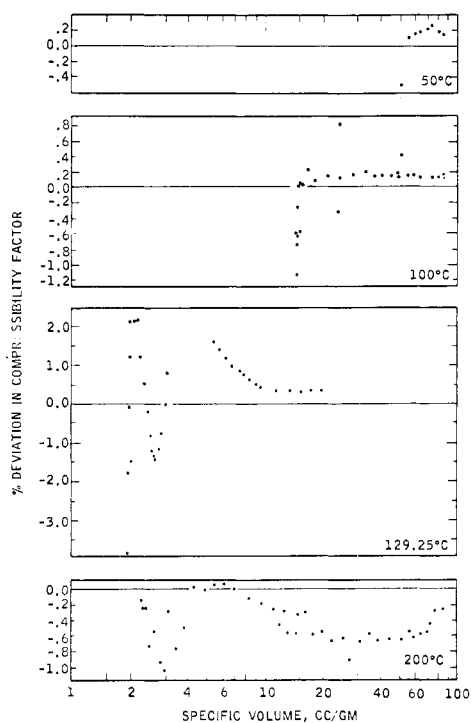


Figure 2. Deviation of Benedict-Webb-Rubin equation

## CONCLUSIONS

From this work, it may be inferred that the Martin-Hou equation is in general superior to the Benedict-Webb-Rubin equation with the Joffe coefficients for predicting the  $P$ - $V$ - $T$  behavior of gases, other than normal paraffins, for which  $P$ - $V$ - $T$  data are unavailable. This is not unexpected, since the constants of the former equation are calculated not only from the critical constants, as are the B-W-R coefficients, but also from an additional piece of information, a vapor pressure point.

However, for the normal paraffin homologous series, upon which the Joffe method is based, it is likely that the B-W-R

equation is at least as applicable as the Martin-Hou equation. This would follow since, for a homologous series, the vapor pressure parameter can be expressed adequately as a function of the critical constants.

Where  $P$ - $V$ - $T$  data are available to calculate the coefficients of an equation of state, this work would indicate that the Benedict-Webb-Rubin equation is superior to the Martin-Hou equation. The equation presented above results in an average deviation in the compressibility factor of 0.55% up to a density of about twice the critical.

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## NOMENCLATURE

$A_0', B_0'$ , etc.	= B-W-R coefficients
$P$	= pressure, atm.
$R$	= gas constant, 2.0482 cc. atm./mole ° K.
$T$	= temperature, ° K.
$V$	= specific volume, cc./gram
$\phi$	= ideal reduced volume, $VP_c/RT_c$
$z$	= compressibility factor

## Subscripts

$c$	= critical property
$r$	= reduced condition

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