

Institute of Technology. J. B. Opfell contributed to the technical aspects of this program and Olga S. Opfell assisted in the preparation of the manuscript, which was reviewed by W. N. Lacey.

## NOMENCLATURE

$A_0, B_0, C_0, a, b, c, \alpha, \gamma$	= coefficients for the Benedict equation of state
$\exp()$	= exponential function
$M$	= molecular weight
$N$	= number of states represented
$\eta$	= mole fraction
$P$	= pressure, pounds per square inch, absolute
$R$	= universal gas constant, (lb./sq. inch)(cu. foot) per (lb.-mole) <sup>o</sup> R.)
$T$	= absolute temperature, <sup>o</sup> R.
$V$	= molal volume, cubic feet per lb.-mole
$Z$	= compressibility factor
$\Delta$	= difference in
$\partial$	= partial differential operator
$\epsilon$	= average relative error
$\Sigma$	= summation operator
Subscripts	
$e$	= value of property predicted using Benedict equation of state
$i$	= refers to component $i$
$j$	= refers to component $j$
$n_i$	= differentiation at constant $n_i$
$P$	= pressure as dependent variable

$T$	= differentiation at constant $T$
$V$	= volume as dependent variable

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# Benedict Equation of State Application to n-Hexane, n-Heptane, n-Nonane, and n-Decane

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The coefficients for n-hexane and n-heptane, n-nonane, and n-decane were established by statistical methods from experimental data. The equation with these coefficients describes the compressibility factor with a standard error of estimate of 1.8% of the maximum value for liquid and gas phases between 80° and 460° F. and up to 10,000 pounds per square inch. The coefficients are not suitable for calculating vapor pressure nor describing the volumetric behavior in the immediate vicinity of the critical state.

The Benedict equation of state may be used to describe the volumetric behavior of the hydrocarbons of relatively high molecular weight, or to predict the behavior of the liquid or gas phases at pressures as high as 10,000 pounds per square inch, but not to describe their phase behavior.

The Benedict equation of state (4, 5) is a useful empirical relation for interpolating the volumetric and phase behavior of the lighter hydrocarbons. The work of Benedict (4, 5) and coworkers was for the most part limited to a maximum pressure of approximately 4000 pounds per square inch.

In an effort to extend the range of pressures to which the equation may be applied, studies of its effectiveness (11, 15) were made at pressures up to 10,000 pounds per

square inch in the temperature interval between -100° and +572° F. for the paraffin hydrocarbons lighter than n-pentane. These studies indicated that the equation could be employed to describe the volumetric behavior of pure hydrocarbons in the liquid and gas phases with reasonable accuracy throughout the greater ranges of pressure and temperature. Sufficient experimental data must be available to permit the equation to be employed as an interpolative rather than an extrapolative device. The error may be large in regions where the relationship of pressure, volume, and temperature established experimentally is not used in the evaluation of the coefficients. Throughout this discussion the term "standard error of estimate" is used as an abbreviation for the phrase "standard error of estimate for the compressibility factor from stated values of the molal volume and temperature."

The coefficients for several of the lighter hydrocarbons as published by Benedict and others (2-6) describe the volumetric behavior of the gas phase and the two-phase pressure of these substances. For mixtures, the thermodynamic properties of the gas phase and the compositions of the co-existing phases in the heterogeneous region were represented with reasonable accuracy (2-6). Conventional least squares techniques (10) with automatic digital computing equipment were employed in

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TABLE I. COEFFICIENTS OF EQUATION FOR VOLUMETRIC PREDICTION<sup>a</sup>

Coefficient	n-Hexane	n-Heptane <sup>b</sup>	n-Nonane	n-Decane
$\gamma = C$				
R	10.73147 <sup>c</sup>	10.73147	10.73147	10.73147
A <sub>0</sub>	-134231.9	6565.56	-496110.0	-1350696.0
B <sub>0</sub>	-12.17264	-0.817193	-37.1787	-99.8270
C <sub>0</sub> × 10 <sup>-8</sup>	37748.5	43706.4	-39148.6	1611.551
a	652083.0	465961.0	3332020.0	7558177.0
b	55.3214	42.3080	219.769	504.735
c × 10 <sup>-8</sup>	57594.0	70536.4	-153015.7	866.937
α	3.56831	9.29192	9.57310	8.81514
γ	0.00000	0.00000	0.00000	0.00000
M	86.172	100.198	128.250	142.276
Standard error of estimate	0.05348	0.02346	0.03700	0.08315
Relative standard error of estimate	0.01696	0.01174	0.00814	0.01670
s <sub>p</sub>	0.0310	0.0287	0.0564	0.1224
s <sub>v</sub>	0.00786	0.00266	0.00242	0.0129
$\gamma = 0.4 V_c^2$				
R	10.73147 <sup>c</sup>	10.73147	10.73147	10.73147
A <sub>0</sub>	86658.0	-168608.8	-156332.3	-73112.4
B <sub>0</sub>	5.42265	-22.2848	-15.45743	-15.16873
C <sub>0</sub> × 10 <sup>-8</sup>	20130.7	24486.9	33616.52	41927.0
a	323927.0	2139579.0	2245931.0	3617130.0
b	24.7450	165.0299	155.2449	253.0891
c × 10 <sup>-8</sup>	152688.7	637120.0	492432.8	1530932.0
α	9.41482	5.68758	13.27955	17.89758
γ	14.0303	18.6603	31.3789	39.2658
M	86.172	100.198	128.250	142.276
Standard error of estimate	0.0479	...	0.0375	0.0778
Relative standard error of estimate	0.01519	...	0.00825	0.0156
s <sub>p</sub>	0.0353	0.0365	0.0540	0.1325
s <sub>v</sub>	0.0118	0.00351	0.00708	0.0164
$\gamma = \infty$				
R	10.73147 <sup>c</sup>	10.73147	10.73147	10.73147
A <sub>0</sub>	2866.37	135635.7	-636944.6	-1350169.0
B <sub>0</sub>	-1.347207	8.43242	-49.0667	-99.7808
C <sub>0</sub> × 10 <sup>-8</sup>	10388.77	12527.19	15905.3	1320.032
a	365322.0	196722.0	3607982.0	7557500.0
b	32.6232	23.4020	248.554	504.632
c × 10 <sup>-8</sup>	...	...	...	...
α	6.41017	22.5751	8.31597	8.81827
γ	∞	∞	∞	∞
M	86.172	100.198	128.250	142.276
Standard error of estimate	0.0552	0.0259	0.0394	0.0832
Relative standard error of estimate	0.01751	0.01296	0.00867	0.01671
s <sub>p</sub>	0.0324	0.0334	0.0586	0.1160
s <sub>v</sub>	0.00980	0.00320	0.00852	0.0127

<sup>a</sup> Recommended only for prediction of behavior in homogeneous regions.

<sup>b</sup> These coefficients should not be employed at pressures above 5000 pounds per square inch.

<sup>c</sup> Values recorded are dimensionally consistent when used in the equation of state with pressure expressed in pounds per square inch, temperature in degrees Rankine, and volume in cubic feet per pound mole. The absolute temperature at the icepoint was taken as 459.69° R.

this investigation in order to establish the coefficients presented for n-hexane, n-heptane, n-nonane, and n-decane. These coefficients, except for n-heptane, may be used to describe the volumetric behavior of the liquid and gas phases at pressures up to 10,000 pounds per square inch in the temperature interval between 80° and 460° F. Values for n-heptane are not reliable for pressures greater than 5000 pounds per square inch. These coefficients are not recommended for calculating vapor pres-

ures from the equality of the fugacities, pressures, and temperatures along two of the branches of the equation of state.

The Benedict equation was employed in the following forms:

$$Z_0 = 1 + \left( B_0 - \frac{A_0}{RT} - \frac{C_0}{RT^3} \right) \gamma V^{-1} + \left( b - \frac{a}{RT} \right) V^{-2} + \frac{a\alpha}{RT} V^{-5} + \frac{cV^{-2}}{RT^3} (1 + \gamma V^{-2}) e^{-\gamma V^{-2}} \quad (1)$$

$$P_0 = RTV^{-1} + (B_0RT - A_0 - C_0T^{-2})V^{-2} + (bRT - a)V^{-3} + a\alpha V^{-6} + cT^{-2}V^{-3}(1 + \gamma V^{-2})e^{-\gamma V^{-2}} \quad (2)$$

The least squares methods developed by Brough (7) were extended by Selleck, Opfell, and Sage (15) in the investigation of propane. A detailed description of these methods of calculation is available (15, 16) and the extensive calculations required to obtain the information presented are not discussed here.

In this program the coefficients were established from experimental information concerning only the volumetric behavior of each compound. No effort was made to impose requirements, that the equation of state describe the vapor pressure-temperature relationship for these compounds. Some deviation from experiment exists in most cases near the critical state of each of the compounds. In each case the calculations were made for three different values of the exponential coefficient, γ. In this respect the current calculations differ slightly from those presented for the compounds methane through n-pentane (11). For the latter materials the coefficients were reported for the value of γ yielding nearly the minimum standard error of estimate.

#### n-HEXANE

The volumetric behavior of n-hexane was investigated by Kelso and Felsing (9) at pressures up to 4600 pounds per

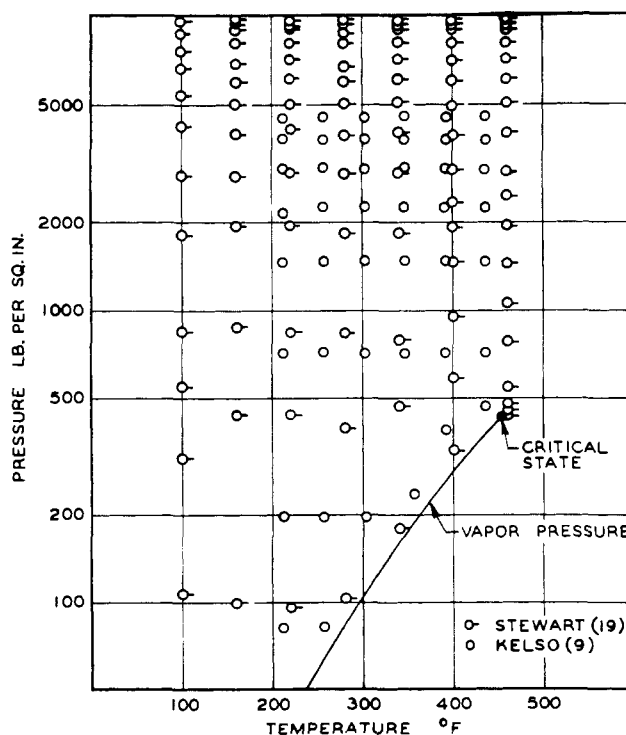


Figure 1. Experimental data used in evaluating coefficients for n-hexane

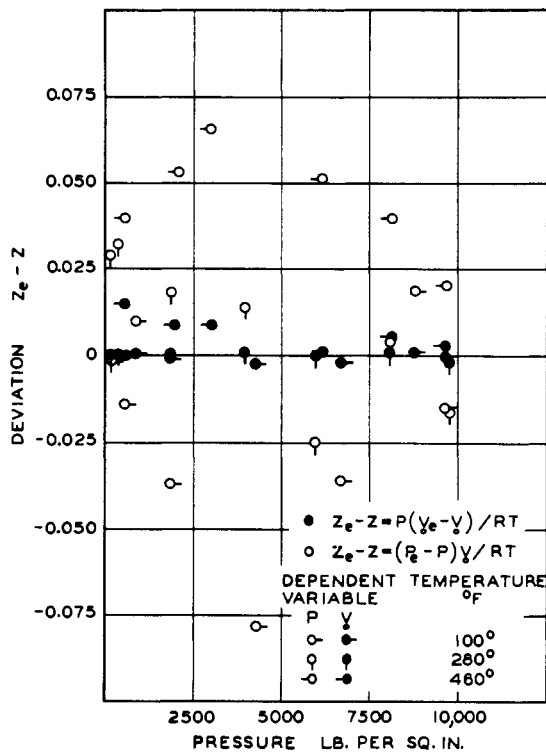


Figure 2. Deviations of predicted compressibility factors for n-hexane from experimental values with molal volume and pressure as dependent variables

square inch in the temperature interval between 212° and 437° F. In addition measurements at somewhat higher pressures were made by Stewart, Sage and Lacey (19). These measurements serve as the background of experimental work used to evaluate the coefficients and covered the range of pressures up to 10,000 pounds per square inch in the temperature interval between 100° and 460° F.

Figure 1 depicts the experimental data employed and indicates the density of information as a function of position in the pressure-temperature plane. It is apparent that all these data lie in the region of liquid states. The coefficients which were derived from them probably can be employed with fair accuracy in establishing the volumetric properties of the gas phase throughout the indicated temperature interval until detailed experimental data for the gas phase are available. The Benedict equation of state predicts the correct behavior of the gas at low pressures, but large uncertainties may exist in the predictions for the gas phase near the two-phase boundary. The coefficients for each of the three values of  $\gamma$  are recorded in a part of Table I along with the standard error of estimate and the fraction which the standard error of estimate represents of the maximum compressibility factor involved. The standard error of estimate is approximately 0.05. The standard error of estimate from temperature and pressure is less than 0.012 for all three values of  $\gamma$ .

Figure 2 shows the deviations of the predicted volumetric data with a value of  $(\gamma V_C^{-2}) = 0.4$  from the more recent experimental measurements (19) for temperatures of 100°, 280°, and 460° F. It is apparent that the molal volume of the liquid phase at a particular pressure and temperature has a much smaller deviation than when the pressures are computed for the same volume and temperature. There was little effect of  $\gamma$  on the degree of agreement of the predicted and experimental data, as may be seen in Table I. With an infinite value of this exponential coefficient, the last term in equations 1 and 2 assumes a value of zero.

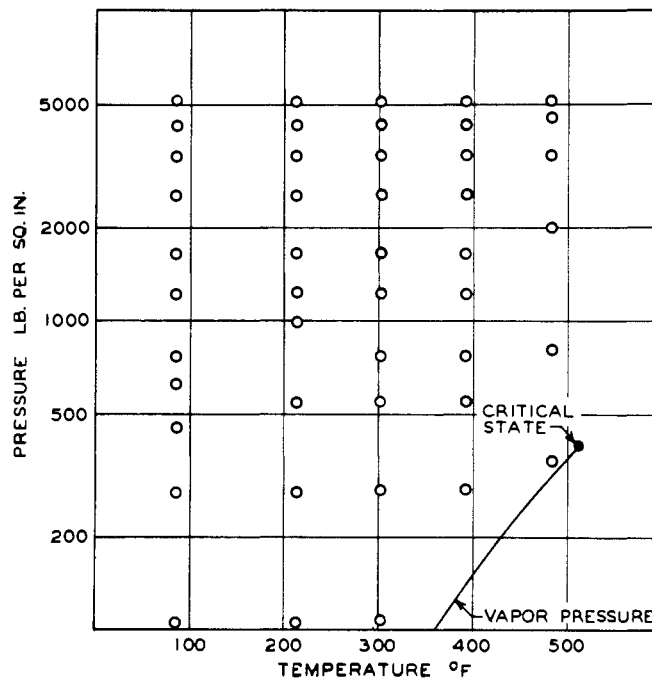


Figure 3. Experimental data used in evaluating coefficients for n-heptane

### n-HEPTANE

In the case of n-heptane the measurements of Beattie and others (1, 18) were used. These data extended from 86° to 482° F. and up to pressures slightly above 5000 pounds per square inch. The distribution of the measurements employed is shown in Figure 3. These data pertain to states in the liquid phase and in the critical region.

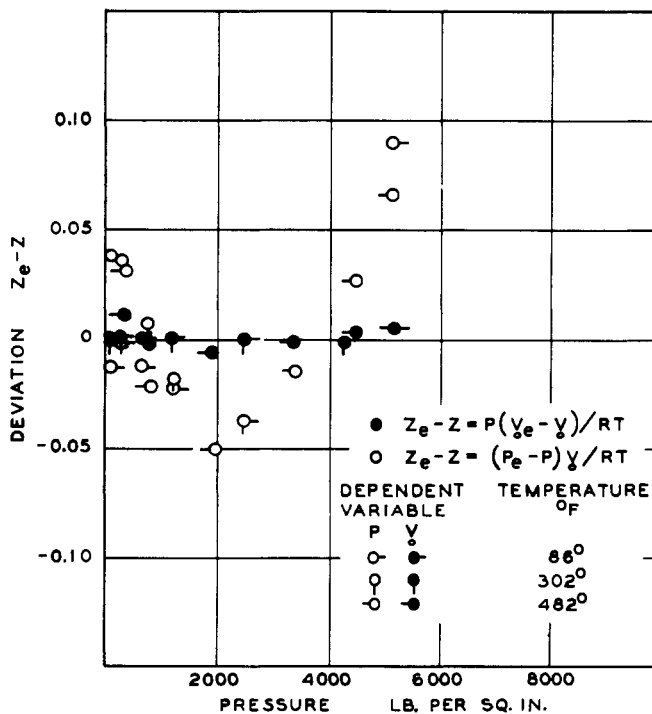


Figure 4. Deviations of predicted compressibility factors for n-heptane from experimental values with molal volume and pressure as dependent variables

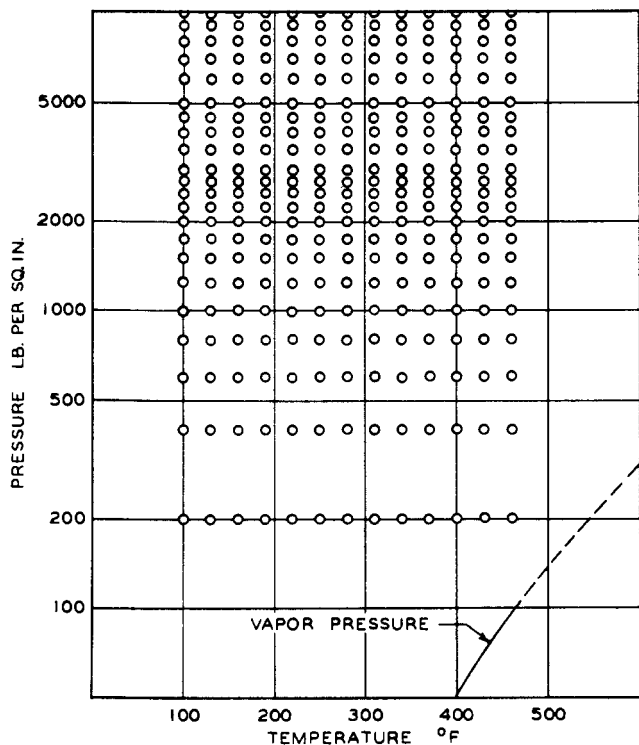


Figure 5. Experimental data used in evaluating coefficients for n-nonane

Coefficients established from these data for the Benedict equation are recorded in a part of Table I. They were established for values of  $(\gamma V_c^{-2})$  of 0, 0.4, and infinity, as was done for n-hexane. Inasmuch as the data extended only to a maximum pressure of 5000 pounds per square inch, the standard errors of estimate

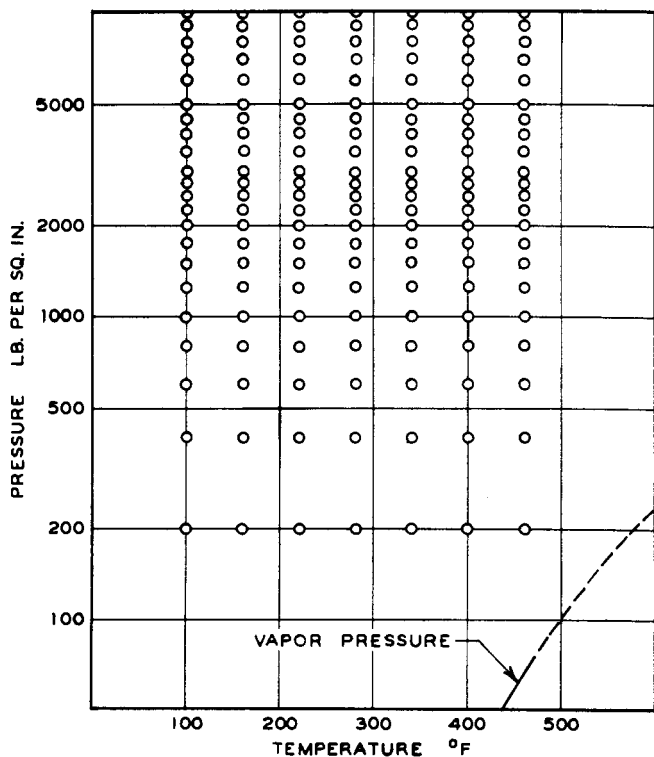


Figure 7. Experimental data used in evaluating coefficients for n-decane

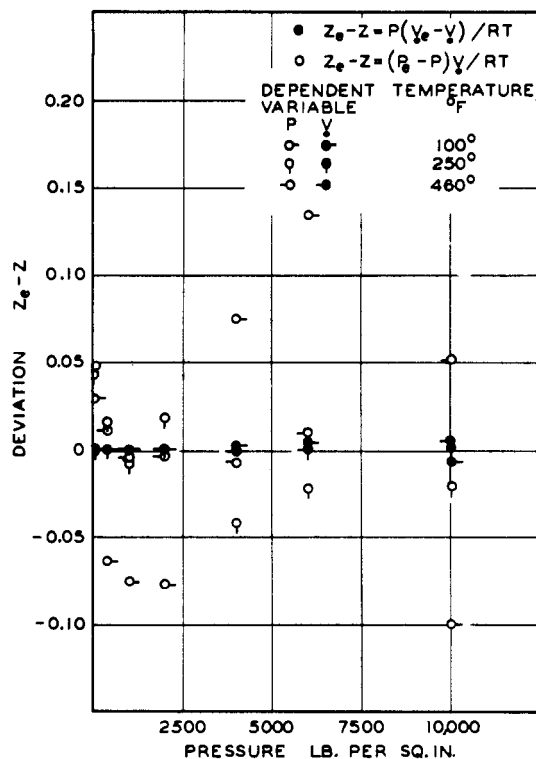


Figure 6. Deviations of predicted compressibility factors for n-nonane from experimental values with molal volume and pressure as dependent variables

for n-heptane were much less than were found for n-hexane. This arises from the fact that the equation describes the volumetric behavior up to 5000 pounds per square inch with greater accuracy than when it is extended to higher pressures. Figure 4 shows a sample of the deviations of the predicted compressibility factors from the experimental values as function of state. For the points with the smaller dispersion the molal volume is the dependent variable, whereas pressure is the dependent variable in the other case. The coefficients recorded in Table I for n-heptane should not be used at pressures above 5000 pounds per square inch.

#### n-NONANE

Only a single set of data (8) was available for evaluating the coefficients of n-nonane. However, these measurements extended throughout most of the region of liquid phase states at pressures up to 10,000 pounds per square inch in the temperature interval between 100° and 460° F. The coefficients for the Benedict equation obtained for values of  $(\gamma V_c^{-2})$  of 0, 0.4, and infinity are recorded in a part of Table I. Distribution of the experimental data used in evaluating them is depicted in Figure 5. All of the experimental data were taken at relatively small specific volumes and pertained exclusively to the liquid phase. The deviations of the predicted from the actual compressibility factors are given in Figure 6. Again, there is a marked difference between the magnitude of the deviations with pressure and with volume as the dependent variable. The standard error of estimate, with molal volume as the dependent variable, is only three times the experimental uncertainty.

#### n-DECANE

The measurements of the volumetric behavior of n-decane were based upon a recent critical review of the

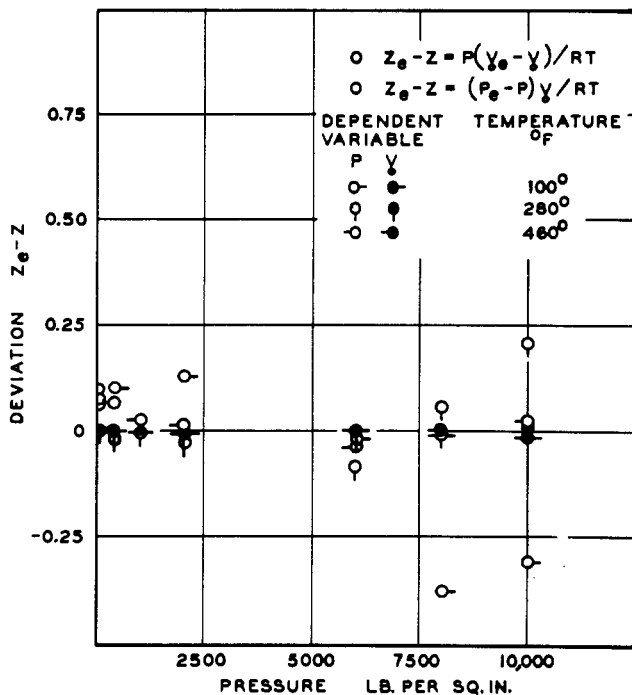


Figure 8. Deviations of predicted compressibility factors for n-decane from experimental values with molal volume and pressure as dependent variables

volumetric behavior of the lighter hydrocarbons (13). This review did not include any measurements in the gas phase and was based upon the studies at high pressure by Shepard (17), Reamer (12), and an investigation by one of the authors (14). The range and density of the experimental data for n-decane are shown in Figure 7, and the coefficients are recorded in part of Table I. In this instance the standard error of estimate was much larger than was the case for the other hydrocarbons. However, when molal volume was the predicted quantity, in place of pressure, used in computing the compressibility factor, rather satisfactory agreement was shown. The deviation of the predicted from the actual compressibility factor using both molal volume and pressure as dependent variables is shown in Figure 8. The maximum value of the compressibility factor was 4.977 for n-decane as contrasted with 2.000 for n-heptane, thus accounting in part for the rather large absolute deviations found at high pressures with volume as the independent variable. These deviations, when compared with the value of the compressibility factor, are of the same order as those found at lower pressures. In addition, the small change in molal volume with pressure found at most of the states investigated tends to make the deviations unusually large with pressure as the dependent variable. Again the magnitude of the standard error of estimate was not markedly influenced by the particular value of the coefficient employed.

The coefficients presented in Table I may be used within the range of pressures and temperatures discussed here. However, attempts to extend either the pressure or temperature range may lead to much larger uncertainties in predicting the volumetric behavior than would be expected from a simple extrapolation of the information presented here. Furthermore, inclusion of many data on liquid phase states in the evaluation of the coefficients of Table I does not permit them to describe the vapor pressure of these hydrocarbons with the accuracy realized by Benedict. They are not recommended at this time for use with existing interaction coefficients (3, 6) in order to predict the phase behavior of mixtures. No adjustment

of the coefficients of Table I has been made to increase their accuracy of prediction of phase behavior.

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## NOMENCLATURE

- $A_0, B_0, C_0, a, b, c, \alpha, \gamma$  = coefficients for the Benedict equation of state  
 $\epsilon$  - base of natural logarithm  
 $M$  - molecular weight  
 $P$  - pressure, pounds per square inch absolute  
 $R$  - universal gas constant, (lb./sq. inch) (cu. foot) per (lb. mole) ( $^{\circ}$  R.)  
 $s_p$  - root-mean-square deviation of experimental compressibility factor from the predicted isotherm when the compressibility factor is computed from the molal volume and temperature  
 $s_v$  - root-mean-square deviation of experimental compressibility factor from the predicted isotherm when the compressibility factor is computed from the pressure and temperature  
 $T$  - absolute temperature,  $^{\circ}$  R.  
 $V$  - molal volume, cubic feet per pound-mole  
 $Z$  - compressibility factor, dimensionless

## Subscripts

- $c$  - critical state  
 $e$  - value of property calculated using the Benedict equation of state

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