Correlation of the Constants of the Benedict-Webb-Rubin-Friend Equation of State for 2-Methyl Paraffins

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Canjar, Smith, Volianitis, Galluzzo, and Cabarcos (*1*) developed a correlation of the constants of the Benedict-Webb-Rubin-Friend equation of state for normal paraffinic hydrocarbons:

$$P = d\,RT - d^2 \{[Ao + ad\,(1 - \alpha\,d^3)] - (Bo - bd)\,RT + \frac{1}{T^2}[Co - cd(1 + \gamma\,d^2)\,\exp - \gamma\,d^2]\}$$

Each of the constants was correlated separately by the use of critical temperature and structural properties as parameters.

This empirical correlation was based on *n*-butane, *n*-pentane, and *n*-heptane. Pressures calculated from the correlated constants deviated on the average by 0.57% from experimental values (*1*). Critical pressures were also precisely reproduced.

Data for *n*-hexane were not used in the correlation. However pressures calculated from the interpolated constants deviated less than 1% from the limited experimental data of Kelso and Felsing (*3*).

More recently the strength of the correlation was reinforced by the agreement of calculated pressures for *n*-hexane with the more extensive data of Griskey and Canjar (*4*). Plots of pressure residual curves (*rp* = pressure calculated − pressure observed) are shown in Figure 1.

It was also found that the critical pressure for *n*-octane could be calculated precisely with extrapolated constants.

The agreement obtained with the correlation led to the idea that it could possibly also represent isomeric paraffins. However calculations proved this hypothesis to be incorrect.

Then a similar correlation for the 2-methyl paraffins correlation was developed. It is similar in many respects to the earlier correlation for the normal paraffins. One difference is that the ratio of carbon atoms in the straight chain to the total carbon atoms in the molecule is also used as a parameter. There are also some differences in specific constant correlation.

Correlation equations are given below:

$$(A_o)^{1/3}\frac{N_s}{N_t} = 2.9163 - (0.21528)\,(10^6)\left(\frac{1}{Tc^2}\right) \quad (2)$$

$$B_o = (0.00039286)\,(Tc) - (0.022714) \quad (3)$$

$$\log[(C_o - C'_o)\,10^{-5}] = (2.440)\,\log\left[\left(\frac{Tc - Tc'}{10}\right)\frac{N_t}{N_s}\right] - (1.2038) \quad (4)$$

$$a = (2.6222)\,(Tc)^{1/2} - 51.108 \quad (5)$$

$$(b \times 100)^{1/3} = (0.0075000)\,(Tc) - 1.4350 \quad (6)$$

$$\frac{1}{Nt}\,(C \times 10^{-5}) = (0.17857)\,(Tc) - (65.678) \quad (7)$$

$$\log\,(\alpha \times 10^3) = (0.0038570)\,(Tc) - 1.5467 \quad (8)$$

$$\log\,(\gamma \times 10^2) = (0.0030122)\,(Tc) - 0.70738 \quad (9)$$

2-methyl propane (isobutane), 2-methyl butane (isopentane), and 2-methyl pentane (isohexane) were used as base compounds for the correlation.

Benedict, Webb, and Rubin (2) reported constants for 2-methyl propane and 2-methyl butane, but none for 2-methyl pentane. In checking the reported constants the authors found that the 2-methyl butane values yielded calculated pressures which greatly deviated from the experimental values of Isaacs, Li, and Canjar (*5*).

The failure of the constants to represent these data for 2-methyl butane is not surprising, since Benedict obtained them using the earlier limited data of Young (*6*). (The data of Isaacs, Li, and Canjar was unavailable at that time.)

It was therefore necessary to determine a set of constants for 2-methyl butane as well as 2-methyl pentane with experimental data (*3*, *5*). This was done, but it did not solve the problem of correlation. Attempts to correlate these constants proved unsuccessful, and it was not until several sets of constants were calculated and tested that a suitable correlation was developed. The constants for the base compounds, as well as extrapolated constants for 2-methyl hexane and 2-methyl heptane, are given in Table 1.

The constants from the correlation reproduced the compressibility data with an average deviation of less than 1%. Average deviations and appropriate density and temperature ranges for individual compounds were − 0.90% (0.5 to 7.0 g. mole/liter; 104.4° to 237.8°C.) for 2-methyl propane, 0.94% (1.5 to 5.5 g. mole/liter; 200°

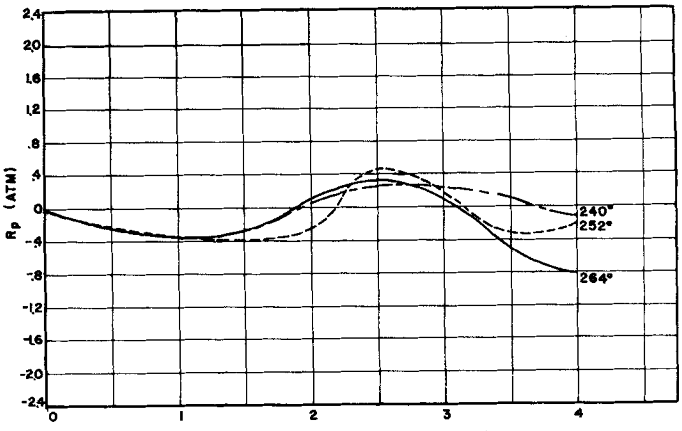

Fig. 1. R_D pressure residual vs. density.

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TABLE 1. CORRELATION CONSTANTS

	2-methyl propane	2-methyl butane	2-methyl pentane	2-methyl hexane*	2-methyl heptane*
A_o	10.233	13.470	14.930	15.799	16.603
B_o	0.1375	0.1584	0.1729	0.1856	0.1977
C_o	0.8499×10^6	1.4833×10^6	2.8500×10^6	4.9530×10^6	7.6430×10^6
a	1.9376	5.1429	7.4286	9.2778	11.001
b	0.04243	0.08333	0.1215	0.1643	0.2131
c	0.2860×10^6	0.8333×10^6	1.400×10^6	2.0314×10^6	2.7600×10^6
α	0.001074	0.001700	0.00235	0.00314	0.00413
γ	0.0340	0.0480	0.0620	0.0776	0.0960

* Extrapolated with correlation.

to 300°C.) for 2-methyl butane, and 0.16% (1.5 to 5.5 g. mole/liter; 250° to 275°C.) for 2-methyl pentane. Additionally calculated critical pressures differed by 0.220, 1.68, and 0.300 atm. from observed values for these compounds.

Extrapolated constants for 2-methyl hexane and 2-methyl heptane were used to calculate critical pressures for these compounds. These calculated pressures differed by 0.377 and 0.295 atm. respectively from the literature values for 2-methyl hexane (*7*) and 2-methyl heptane (*8*).

Only the constants for 2-methyl propane (isobutane) were fitted to the two-phase region. The remaining constants were fitted only to the superheated vapor region. It is not recommended that they be used in the estimation of properties for the vapor-liquid dome.

It is difficult to evaluate correlations of this type because they afford methods of estimating compressibility data which cannot be measured easily or at all. However it is apparent that the correlation does reproduce the compressibility data and critical points of the base compounds with good precision. Furthermore good agreement is obtained with extrapolated correlation constants for the critical points of 2-methyl hexane and 2-methyl heptane.

On the basis of this analysis it is recommended that the correlation be used to estimate higher molecular weight 2-methyl paraffins compressibility data. The procedure recommended in the paper of Canjar, Smith, Volianitis, Galluzzo, and Cabarcos (*1*) should be used for compounds higher in molecular weight than 2-methyl heptane (no literature critical temperatures are given for such compounds). This procedure is as follows:

1. Estimate roughly the critical temperature of the compound.
2. Calculate the Benedict-Webb-Rubin-Friend equation constants from the correlation equations.
3. Calculate pressure as a function of density at the assumed critical point.
4. If the slope is zero at the isotherm's inflection point, then the assumed critical temperature is correct. If it is not, another temperature should be assumed, and steps 1 to 4 should be repeated.

NOTATION

A_o, B_o, C_o, a, b, c, α, γ = constants of the Benedict-Webb-Rubin-Friend equation of state
Tc = critical temperature
Tc' = critical temperature of 2-methyl propane
$C'o$ = co-constant for 2-methyl propane
N_s = number of carbon atoms in the straight chain
N_t = total number of carbon atoms

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Effect of Natural Convection Instabilities on Rates of Heat Transfer at Low Reynolds Numbers

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Variation of the density and viscosity of a fluid in a pipe due to temperature variation can affect the heat transfer coefficient *h* because of changes in the velocity profile and because of transition to an unsteady flow if the distortion of the velocity profile is sufficiently large. For water these effects will primarily be due to density variations. This paper presents experimental data on the effect of unsteady flow on the heat transfer coefficient for flow of water in a vertical pipe. Two types of heat transfer experiments are conveniently conducted, one with a constant heat flux at the wall and the other with a constant temperature wall. When heating or cooling with a constant temperature wall the difference between the wall temperature and the bulk fluid temperature ΔT is changing throughout the heat transfer section, and therefore the effect of the heat transfer upon the flow field is changing as well. When heating with a constant flux, if the changes in temperature are affecting only the density appearing in the gravity term

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