Determination of Constants for the Benedict-Webb-Rubin-Friend Equation of State from Limited Data

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Benedict, Webb, and Rubin (*1*) have outlined the method for determining constants for the equation of state that they developed. A minimum of three experimental isotherms are required to fit the constants for the superheated vapor region. Actually, five or six isotherms should be used to insure a precise fit.

Unfortunately, many cases exist where only limited data are available. A technique for determining Benedict constants from such data would be a useful tool for the process engineer. The present investigation outlines two such methods.

The first technique adjusted a proposed set of constants to fit precisely experimental data. This method permitted the simultaneous adjustment of seven of the eight Benedict constants by fitting a residual pressure ($P_{obs} - P_{calc}$) curve (vs. density) with the Benedict-Webb-Rubin-Friend equation in incremental form.

The Benedict-Webb-Rubin-Friend equation is

$$P_{calc} = B_oRTd^2 + bRTd^3 - A_od^2 - ad^3 + \alpha\, ad^6 - \frac{C_od^2}{T^2} + \frac{cd^3}{T^2}(1 + \gamma d^2)\, e^{-\gamma d^2} + RTd \qquad (1)$$

Now if we rewrite for P_{obs}

$$P_{obs} = P_{calc} + P_{res} = RTd^2 (B_o + \Delta B_o) + RTd^3 (b + \Delta b) - d^2 (A_o + \Delta A_o) - d^3 (a + \Delta a) + (\alpha + \Delta\alpha)(a + \Delta a) d^6 - \frac{(C_o + \Delta C_o) d^2}{T^2} + \frac{(c + \Delta c) d^3}{T^2}(1 + \gamma d^2)\, e^{-\gamma d^2} + RTd \qquad (2)$$

Note that γ is excluded from the incremental treatment. This was done to reduce the complexity of the equation.

Solving for P_{res} yields

$$P_{res} = \left(RT\Delta B_o - \Delta A_o - \frac{\Delta C_o}{T^2} \right) d^2 + (RT\Delta b - \Delta a) d^3 + (\alpha\Delta a + a\Delta\alpha + \Delta\alpha\Delta a) d^6 + \left(\frac{\Delta C}{T^2}\right) [(1 + \gamma d^2)\, d^3 e^{-\gamma d^2}] \qquad (3)$$

and

$$P_{res} = a_1 (T)\, d^2 + a_2 (T)\, d^3 + a_3\, d^6 + a_4 (T)\, [(1 + \gamma d^2)\, d^3 e^{-\gamma d^2}] \qquad (4)$$

where a_1, a_2, and a_4 are functions of temperature.

If Equation (4) is fitted to a residual curve, a_1, a_2, a_3, a_4 can be determined. Then the Benedict constants can be adjusted to fit precisely the existing experimental data.

The following method was used to fit Equation (4):

1. Residual pressures obtained using any rough set of Benedict constants were plotted vs. density for each isotherm. A recommended method of estimating a rough set of constants is to use the correlation of Griskey and Canjar (*2*).

2. Equation (4) was fitted to the residual data of the highest temperature isotherm, and values of a_1, a_2, a_3, and a_4 were obtained.

3. Since a_3 was not a function of temperature, it was held constant at another temperature and the value of $a_4(T_2)$ fixed by the expression

$$\left[\frac{a_4(T_2)}{a_4(T_1)}\right] = \left[\frac{C_o/T_2^2}{C_o/T_1^1}\right] = \left[\frac{T_1^2}{T_2^2}\right] \qquad (5)$$

Then the equation

$$P_{res} - a_3d^6 - \frac{a_4(T_2)\ [d^3(1 + \gamma d^2)]}{d^2} = a_1(T_2) d^2 + a_2(T_2) d^3 \qquad (6)$$

was used to find a_1 and a_2.

4. Constants can then be adjusted using the values of a_1, a_2, a_3 and a_4. First the two simultaneous equations

$$a_2(T_2) = RT_2\Delta b - \Delta a \qquad (7)$$

$$a_2(T_1) = RT_1\Delta b - \Delta a \qquad (8)$$

were solved to yield Δa and Δb.

Then $\Delta\alpha$ was calculated from the equation

$$a_3 = a\Delta\alpha + \Delta\alpha\Delta a + \alpha\Delta a \qquad (9)$$

knowing Δa made it possible to calculate Δc from the relation

$$\Delta c = a_4 (T_1) \times T_1^2 \qquad (10)$$

This left ΔB_o, ΔA_o, and ΔC_o to be determined from the equations

$$RT_1\, \Delta B_o - \Delta C_o/T_1^2 = a_1 (T_1) - \Delta A_o \qquad (11)$$

$$RT_2\, \Delta B_o - \Delta C_o/T_2^2 = a_1 (T_2) - \Delta A_o \qquad (12)$$

They were determined by assuming a value for ΔA_o and solving the above equations.

5. Then, the Benedict constants were determined by adding the Δ's to the original constants assumed.

6. The foregoing technique will work for cases where at least two isotherms are available.

7. A one-isotherm situation can be handled by modifying the technique with the following equations:

$$a_1 (T_1) = RT_1\, \Delta b - \Delta a \qquad (13)$$

$$a_2 (T_1) = RT_1\, \Delta B_o - \Delta A_o - \frac{\Delta C_o}{T_1^2} \qquad (14)$$

$$a_3 = a\Delta\alpha + \Delta\alpha\Delta a + \Delta a\alpha \qquad (15)$$

$$a_4 (T_1) = \frac{\Delta c}{T_1^2} \qquad (16)$$

$$(P_{res})_c = (RT_c\, \Delta B_o - \Delta A_o - \Delta C_o/T_c^2) d_c^2$$
$$(RT_c\, \Delta b - \Delta a) d_c^3 + (\alpha\Delta a + a\Delta\alpha + \Delta\alpha\Delta a) d_c^6$$

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TABLE 1. BENEDICT EQUATION CONSTANTS

Constant	Technique 1 3-methyl-pentane	Technique 1 2, 3-dimethyl-butane	Technique 1 2, 2, 4-trimethyl-pentane	Technique 2 3-methyl-pentane	Technique 2 2, 3-dimethyl-butane	Technique 2 2, 2-dimethyl-butane
A_o	17.973	13.828	—221.47	12.203	16.430	11.842
B_o	0.17900	0.09209	0.2060	0.08151	0.19000	0.19214
$C_o \times 10^{-6}$	1.8861	1.8670	72.400	2.2125	2.5534	3.3595
a	4.3546	5.5238	12.529	5.9716	4.6956	10.108
b	0.08637	0.10994	0.21153	0.11224	0.079000	0.14000
$c \times 10^{-5}$	8.9829	8.5505	5.5768	9.5556	11.346	17.483
$\alpha \times 10^3$	3.0450	2.2759	3.7987	2.2500	3.5948	2.1890
$\gamma \times 10^2$	7.2131	6.5044	10.459	6.2500	7.5000	5.6500

$$+\left(\frac{\Delta c\, d_c^2}{T_c^2}\right)\frac{(1+\gamma d_c^2)}{e^{-\gamma d_c^2}} \quad (17)$$

The only other pieces of data needed are the critical temperature and density.

This technique has been programmed in Fortran language. The program has been deposited with the American Documentation Institute.

The foregoing technique was applied to experimental data for 3-methyl pentane [(3), two experimental isotherms], 2,3-dimethylbutane [(4), two experimental isotherms] and 2,2,4-trimethylpentane [(5), one isotherm].

The constants determined by this technique are given in Table 1. Average deviations of less than 1% were found for calculated pressures, and good agreement for the critical points were obtained. Deviations and density and temperature ranges were 0.11% (3.2 to 6.0 g. mole/liter; 250° to 275°C.) for 3-methylpentane, 0.31% (1.5 to 5.0 g. mole/liter; 250° to 275°C.) for 3-dimethylbutane, and 0.49% 3.2 to 5.0 g. mole/liter; 275°C.) for 2,2,4-trimethylpentane. In addition, calculated critical pressures differed by 0.75, 0.30, and 0.03 atm. from the observed values for these compounds.

Another technique was developed that could be used for situations in which either two to three isotherms were available.

The technique was as follows:

1. Residual pressure curves were calculated for the existing data with any rough set of Benedict constants. Again the correlation of Griskey and Canjar (*2*) could be used to estimate a rough set of constants.
2. Residual curves were then interpolated at two temperatures intermediate to existing data when three isotherms were available (that is, if data at 523°, 548°, and 573°K. were available then curves were interpolated at 535.5° and 560.5°K.).

Likewise, if two isotherms were available then one interpolation and two extrapolations were made (experimental data at 523° and 548°K. then interpolate at 535.5°K., extrapolate at 510.5° and 560.5°K.).

3. Next, values of pressure were calculated and corrected by the pressure residual value from the interpolated and extrapolated curves. This procedure yielded five isotherms of data (either three experimental and two derived, or two experimental and three derived).
4. Constants were then determined as outlined by Benedict, Webb, and Rubin (*1*).

The constants so determined are listed in Table 1. They were used to calculate data for 2,2-dimethylbutane [(6), three isotherms] as well as 2,3-dimethylbutane and 3-methylpentane.

Average deviation of calculated pressures and density and temperature ranges for the above compounds were 0.08% (3.2 to 6.0 g. mole/liter, 250° to 275°C.) for 3-methylpentane, 1.01% (1.5 to 5.0 g. mole/liter, 250° to 275°C.) for 2,3-dimethylbutane, and 0.6% (1.8 to 5.0 g. mole/liter, 225° to 275°C.) for 2,2-dimetylbutane. Calculated critical pressures deviated from observed values by 0.44, 0.34 and 0.11 atmosphere respectively.

Pressures calculated with a reduced form of the Benedict Equation (7) generally were found to have deviations of at least an order of magnitude greater than those calculated with the constants determined by both techniques in this investigation.

In addition, the constants of this work were found to hold only for the critical and superheated vapor regions and not for the two-phase region. It is not recommended that these constants be used in estimating properties for the vapor-liquid dome.

CONCLUSIONS

1. Two techniques were developed that determined Benedict-equation constants from limited data.
2. These techniques were used to determine Benedict constants for 3-methylpentane, 2,2-dimethylbutane, 2,3-dimethylbutane and 2,2,4-trimethylpentane. Calculated compressibilities deviated by less than 1% from experimental values.

NOTATION

$A_o, B_o, C_o, a, b, c, \alpha, \gamma$ = constants of the Benedict-Webb-Rubin-Friend Equation
P_{calc} = pressure calculated from Benedict equation, atm.
P_{obs} = experimentally determined pressure, atm.
P_{res} = residual pressure ($P_{obs} - P_{calc}$) atm.
R = gas constant
T = temperature, °K.
$a_1(T), a_3(T), a_4(T)$ = constants, functions of temperature
a_2 = constant
d = density, g. mole/liter
d_c = critical density, g. mole/liter
$\Delta A_o, \Delta B_o, \Delta C_o, \Delta a, \Delta b, \Delta c, \Delta\alpha$ = incremental change in Benedict constants

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