The PVT Properties Calculation of Water by BWR Equation

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Abstract: A series of thermodynamic functions are applied to generalize the Benedict-Webb-Rubin equation. The method has been successfully applied to this equation, which reduced the constants of BWR equation from eight to one. The calculation of PVT behavior of water over the entire thermodynamic surface is successful with satisfactory deviation.

Keywords: Benedict-Webb-Rubin Equation of state, thermodynamic properties, water.

The classical theory of the equation of state first formulated by van der Waals[1] has shown that a universal relation among pressure, volume, and temperature exists. In spite of the large number of equations of state that have appeared during the last century, very few people seems to have developed an equation with a reasonable number of empirical constants, and few constants have a clear physical significance. The successful empirical development is the virial type equation of state. It is the only one that can be justified on the basis of statistical thermodynamics. But virial type equation was not widely used because its coefficients are hard to find. The best output of the virial equation is surely the eight-parameter equation of Benedict-Webb-Rubin[2] (BWR equation), the drawback is that it has eight empirical parameters which have no physical foundation. The BWR equation has the following form[2]

$$P = \frac{RT}{V} + \frac{B_0 RT - A_0 - C_0/T^5}{V^2} + \frac{bRT - a}{V^3} + \frac{a\boldsymbol{a}}{V^6} + \frac{c/T^5}{V^3}\left(1 + \frac{\boldsymbol{g}}{V^2}\right)e^{-\boldsymbol{g}/V^2} \tag{1}$$

Where P is the pressure, T is the absolute temperature, V is the molar volume, and R is the gas constant which equals 8.3145J/mol K, B_0, C_0, A_0, b, a, c, $\boldsymbol{a}$, $\boldsymbol{g}$, are constants which can be obtained from Martin-Hou's[3] conditions except $\boldsymbol{g}$.
If we give the following definitions

$$f_1(T) = B_0 RT - A_0 - C_0/T^5 \tag{2}$$

$$f_2(T) = bRT - a \tag{3}$$

$$f_3(T) = a\boldsymbol{a} \tag{4}$$

$$f_4(T) = c/T^5 \tag{5}$$

Then the equation can be changed to the following form

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$$P = \frac{RT}{V} + \frac{f_1(T)}{V^2} + \frac{f_2(T)}{V^3} + \frac{f_3(T)}{V^6} + \frac{f_4(T)}{V^3}\left(1 + \frac{g}{V^2}\right)e^{-g/V^2} \tag{6}$$

Martin-Hou[3] (1955) studied the pressure-volume diagram and compressibility chart thoroughly. They found out that all substances should satisfy the following conditions.

$$P_c = \frac{RT_c}{V_c} + \frac{f_1(T_c)}{V_c^2} + \frac{f_2(T_c)}{V_c^3} + \frac{f_3(T_c)}{V_c^6} + \frac{f_4(T_c)}{V_c^3}\left(1 + \frac{g}{V_c^2}\right)e^{-g/V_c^2} \tag{7}$$

$$\left(\frac{dP}{dV}\right)_{T_c} = 0 \qquad\qquad at \qquad critical\ point \tag{8}$$

$$\left(\frac{d^2P}{dV^2}\right)_{T_c} = 0 \qquad\qquad at \qquad critical\ point \tag{9}$$

$$\left(\frac{d^3P}{dV^3}\right)_{T_c} = 0 \qquad\qquad at \qquad critical\ point \tag{10}$$

$$\left(\frac{d^4P}{dV^4}\right)_{T_c} = 0 \qquad\qquad at \qquad critical\ point \tag{11}$$

$$\left[\left(\frac{dZ}{dP_r}\right)_{T_r}\right]_{P_r=0} = 0 \qquad\qquad at \qquad T = T_B \tag{12}$$

$$\left[\left(\frac{dZ}{dP_r}\right)_{T_r}\right]_{P_r=0} = -(1 - Z_c) \qquad\qquad at \qquad T' \cong 0.8T_c \tag{13}$$

$$\left(\frac{dP}{dT}\right)_V = m = -M\frac{P_c}{T_c} \qquad\qquad at \qquad V = V_c \tag{14}$$

$$\left(\frac{d^2P}{dT^2}\right)_V = 0 \qquad\qquad at \qquad V = V_c \tag{15}$$

where T_B is Boyle temperature $T_B = 30 + 2.42T_c - 5.67 \times 10^{-4}T_c^2$ and $T' = (0.9869 - 0.6751Z_c)T_c$ as Martin[3] gives. Z_c is the compressibility factor at critical point.
The solution of （7）－（15） except (10) is

$$f_1(T_c) = -\frac{20RT_cV_c}{17} + \frac{9V_c(17P_cV_c - 5RT_c)(77V_c^6 - 247V_c^4g + 72V_c^2g^2 - 4g^3)}{34(60V_c^6 - 213V_c^4g + 72V_c^2g^2 - 4g^3)} \tag{16}$$

$$f_2(T_c) = \frac{25RT_cV_c^2}{51}$$
$$- \frac{V_c^2(7P_cV_c - 5RT_c)(153V_c^{10} + 153V_c^8g + 444V_c^6g^2 - 1056V_c^4g^3 + 288V_c^2g^4 - 16g^5)}{17g^2(60V_c^6 - 213V_c^4g + 72V_c^2g^2 - 4g^3)} \tag{17}$$

$$f_3(T_c) = -\frac{RT_cV_c^5}{51} + \frac{V_c^5(17P_cV_c - 5RT_c)(315V_c^6 - 315V_c^4\boldsymbol{g} + 72V_c^2\boldsymbol{g}^2 - 4\boldsymbol{g}^3)}{34(60V_c^6 - 213V_c^4\boldsymbol{g} + 72V_c^2\boldsymbol{g}^2 - 4\boldsymbol{g}^3)} \tag{18}$$

$$f_4(T_c) = \frac{9V_c^{12}(17P_cV_c - 5RT_c)e^{\boldsymbol{g}/V_c^2}}{\boldsymbol{g}^2(60V_c^6 - 213V_c^4\boldsymbol{g} + 72V_c^2\boldsymbol{g}^2 - 4\boldsymbol{g}^3)} \tag{19}$$

$$C_0 = -\frac{T'^5 T_B^5 T_c^5 [f_1(T_c)P_c(T'-T_B) + R^2T'^2(T_B - T_c)(Z_c - 1)]}{P_c(T_B^5 T_c^5(T_B - T_c) + T'^6(T_B^5 - T_c^5) + T'^5(T_c^6 - T_B^6)]} \tag{20}$$

$$B_0 = \frac{f_1(T_c) - C_0(1/T_B^5 - 1/T_c^5)}{R(T_c - T_B)} \tag{21}$$

$$A_0 = B_0RT_c - C_0/T_c^5 - f_1(T_c) \tag{22}$$

$$c = f_4(T_c)T_c^5 \tag{23}$$

$$b = \frac{m}{R}V_c^3 - V_c^2 - B_0V_c \tag{24}$$

$$a = bRT_c - f_2(T_c) \tag{25}$$

$$\boldsymbol{a} = \frac{f_3(T_c)}{a} \tag{26}$$

where for water $\boldsymbol{g} = 0.86\ V_c^2$, $m = 7.61\ P_c/T_c$, here $\boldsymbol{g}$ is an empirical parameter because equation (10) cannot be used directly as Martin-Hou[3] studied because there have some inequality, and no other additional equation are applied to solve $\boldsymbol{g}$. m is defined as $m = (dP/dT)_{Vc} = -MP_c/T_c$.

Through the equations above one can see that all the constants but one of the BWR equation are obtained in form of T_c, P_c, and V_c. This BWR equation is used to calculate the thermodynamic properties of water. The relative pressure (P_r) range is 0.0046-4.53; the relative density (r_r) range is 0.0016-3.25. As can be seen from **Figure 1**, the equation can be applied to a wider range of temperature with relatively acceptable deviations (the *PVT* data of water are provided by IAPWS[4]). Also from **Figure 1** one can see that this equation can best describe the behavior of gas below critical point and gas that is near or high above critical temperature. The drawback of this method for BWR equation is that when near critical temperature and the pressure is getting high the deviation is also getting high. The reason may lie in the fact that all the conditions that applied to the BWR equation is just for gas region or near critical point, so it is not very suitable for liquid and compressed gas. If there is some limitation equation that can best describe the behavior of liquid, the results will be better.

Figure 1   The deviation of volume of water calculated by equation (1)
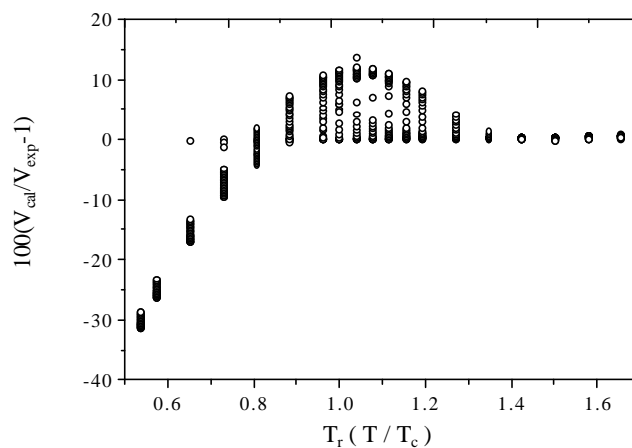
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