At the critical point ($T = T_c$, $V = V_c$) both derivatives are zero:

$$-\frac{RT_c}{(V_c - b)^2} + \frac{2a}{V_c^3} = 0,$$

$$\frac{2RT_c}{(V_c - b)^3} - \frac{6a}{V_c^4} = 0.$$

These may be solved for a and b:

$$a = \frac{9RT_c V_c}{8}, \quad b = \frac{V_c}{3}, \tag{2.38}$$

which gives the parameters a and b in terms of the critical volume and critical temperature. We substitute these values into the van der Waals equation at $V = V_c$, $T = T_c$, to obtain the pressure at the critical point:

$$P_c = \frac{RT_c}{V_c - b} - \frac{a}{V_c^2} = \frac{3RT_c}{8V_c}.$$

This result can also be written as

$$\frac{P_c V_c}{RT_c} = \frac{3}{8}, \tag{2.39}$$

and shows that the critical compressibility factor according the van der Waals equation is $Z_c = 3/8 = 0.375$. This value is rather high (most critical compressibility factors are in the range $0 - 0.3$) and a sign that the van der Waals equation will probably be not very accurate. We solve eq. (2.39) for the critical volume,

$$V_c = \frac{3RT_c}{P_c}$$

8 Pc ("8" missing from denominator)

and substitute this value into eq. (2.38):

$$a = \frac{27}{64}\frac{(RT_c)^2}{P_c}, \quad b = \frac{RT_c}{8P_c}.$$

These now give the parameters a and b in terms of critical pressure and critical temperature. With these values, the van der Waals equation will place the critical point exactly at the experimental critical temperature and critical pressure of the fluid; however, the critical volume from the van der Waals equation will not match the experimental critical volume unless the critical compressibility of the fluid happens to be 0.375. The main point, however, is that the van der Waals equation produces reasonable results at various pressures and temperatures using only two critical constants as a guide (see Example 2.11).

Soave-Redlich-Kwong (SRK) Equation of State The Soave-Redlich-Kwong equation of state is given by

$$P = \frac{RT}{V - b} - \frac{a}{V(V + b)}, \tag{2.40}$$