From H E Stanley, Introduction to Phase Transitions and Critical Phenomena, OUP 1971, p 71-72.

Eq. (5.8) below is a re-expression of the van der Waals equation for one mole of gas.

5.3. The van der Waals critical point: P_c, V_c, and T_c

The P–V isotherm for $T = T_c$ is characterized by a horizontal tangent and an inflection point when $P = P_c$ and $V = V_c$. Hence we may obtain the three parameters P_c, V_c, and T_c (which define the critical point) by solving simultaneously the three equations:

(i) $(\partial P/\partial V)_{T=T_c} = 0$,
(ii) $(\partial^2 P/\partial V^2)_{T=T_c} = 0$, and
(iii) the van der Waals equation (5.4),

where in all three equations we set $P = P_c$, $V = V_c$, and $T = T_c$.

An alternative procedure is to observe that we may equate coefficients of identical powers of V in the two equations:

$$(V - V_c)^3 = V^3 - 3V^2V_c + 3V\,V_c^2 - V_c^3 = 0 \tag{5.7}$$

and

$$V^3 - (\mathscr{b} + \mathscr{R}T_c/P_c)\,V^2 + (a/P_c)V - a\mathscr{b}/P_c = 0 \tag{5.8}$$

Equation (5.8) merely states that for $P = P_c$ and $T = T_c$, all three roots of eqn (5.7) are the same and in fact are equal to the critical volume V_c. We thereby obtain the three equations:

$$-3V_c = -(\mathscr{b} + \mathscr{R}T_c/P_c), \tag{5.9}$$

$$+3V_c^2 = a/P_c, \tag{5.10}$$

and

$$-V_c^3 = -a\mathscr{b}/P_c. \tag{5.11}$$

Equations (5.10) and (5.11) may be combined to yield

$$P_c = a/27\mathscr{b}^2 \tag{5.12}$$

and

$$V_c = 3\mathscr{b}. \tag{5.13}$$

Finally, substitution of (5.12) and (5.13) into (5.9) results in

$$\mathscr{R}T_c = 8a/27\mathscr{b}. \tag{5.14}$$