(d) Van der Waals Equation of State and Virial Coefficient

According to virial theorem the equation of state is given by

$$pV = \alpha + \frac{\beta}{V} + \frac{\gamma}{V^2} + ... \qquad ....(i)$$

Where α, β and γ are first, second and third virial coefficient.

For the Ideal gas, $\alpha = RT$ and other coefficients are zero.

Virial coefficient for Van der Waals gas

To put van der Waals equation in virial form we first rewrite it as

$$pV = RT\left(1 - \frac{b}{V}\right)^{-1} - \frac{a}{V}$$

Using binomial theorem, we have

$$\left(1 - \frac{b}{V}\right)^{-1} = 1 + \frac{b}{V} + \frac{b^2}{V^2} + ...$$

Hence

$$pV = RT + \frac{RTb - a}{V} + \frac{RTb^2}{V^2} + ... \qquad ....(ii)$$

As it will be noted, van der Waals equation has only three virial coefficients and on comparison with equation (i) yields,

$$\alpha = RT,\ \beta = RTb - a \text{ and } \gamma = RTb^2$$

At the Boyle's temperature, the second virial coefficient is zero.

Hence, $\quad RT_B b - a = 0$ or $T_B = \frac{a}{Rb}$

From the preceding, section we recall that the critical temperature of a gas obeying van der Waals equation of state is

$$T_C = \frac{8a}{27Rb}$$

on comparing these expressions, we get

$$T_B = \frac{27}{8}T_C = 3.375\ T_C$$

i.e., the Boyle's temperature, on the basis of van der Waals equation, is 3.375 times the critical temperature.