Q- A certain gas has the equation of state $P = \frac{RT}{V_m - bT} - \frac{a}{V_m^3}$

Here V_m is molar volume and a and b are constants.

Find a and b in terms of critical volume V_c and critical temperature T_c

(The volume is the molar volume means the quantity of the gas is one mole or n = 1)

Here the pressure is given as a function of molar volume and temperature. If we consider the temperature constant, the equation will give the relation between the pressure and volume of the gas at constant temperature and its plot will be isothermal.

If we take the temperature of the gas T equal to critical temperature T_C, the pressure of the gas will be minimum and hence the rate of change of pressure per unit volume i.e. dP/dV (the slop of the PV plot) will be zero. Hence differentiating the equation of state, we get

$$\frac{dP}{dV_m} = RT_C * \frac{d}{dt}(V_m - b\,T_C)^{-1} - \frac{d}{dt}\,a\,V_m^{-3} = 0$$

Or $\frac{dP}{dV_m} = RT_C * (-1)(V_m - b\,T_C)^{-2} - a(-3)V_m^{-4} = 0$

or $\frac{dP}{dV_m} = -\frac{RT_C}{(V_m - b\,T_C)^2} + \frac{3\,a}{V_m^4} = 0$ --------------------------- (1)

or $\frac{RT_C}{(V_m - b\,T_C)^2} = \frac{3\,a}{V_m^4}$ --------------------------- (2)

As the critical point the point of inflection, the rate of change of slope will also be zero or the second derivative of the pressure is zero and hence we get by differentiating equation (1)

$$\frac{d^2P}{dV_m^2} = \frac{d}{dV_m}\left(\frac{RT_C}{(V_m - b\,T_C)^2} - \frac{3\,a}{V_m^4}\right) = 0$$

Or $RT_C \frac{d}{dV_m}(V_m - b\,T_C)^{-2} - 3a\frac{d}{dV_m}\,V_m^{-4} = 0$

Or $RT_C(-2)(V_m - b\,T_C)^{-3} - 3a(-4)\,V_m^{-5} = 0$

Or $\frac{2RT_C}{(V_m - b\,T_C)^3} = \frac{12a}{V_m^5}$ --------------------------- (3)

Now dividing equation (2) by equation (3) we get

$$\frac{(V_m - b\,T_C)}{2} = \frac{V_m}{4}$$

Or $2(V_m - b\,T_C) = V_m$

Or $V_m = 2b\,T_C$

Or $b = \frac{V_m}{2\,T_C}$

As this volume is at the critical temperature it is critical volume and we can write

$$b = \frac{V_C}{2\,T_C}$$

Now substituting the value of b in equation (2) and writing V_m as critical volume we get

$$\frac{RT_C}{(V_m - b\,T_C)^2} = \frac{3\,a}{V_m^4}$$

Or $\frac{RT_C}{\left(V_C - \frac{V_C}{2\,T_C}T_C\right)^2} = \frac{3\,a}{V_C^4}$

Or $\frac{RT_C}{\left(V_C - \frac{V_C}{2}\right)^2} = \frac{3\,a}{V_C^4}$

Or $\frac{4RT_C}{(V_C)^2} = \frac{3\,a}{V_C^4}$

Gives $a = \frac{4RT_C V_C^2}{3}$