# Question #75493

# Description:

1. Write Onne's equation. Using van der Waals' equation, obtain an expression of Boyle temperature (Tb) in terms of van der Waals' constants and hence show that the Boyle's temperature is related to critical temperature (Tc) through the relation **Tb =3.375Tc.**

**Solution.**

Use van der Waals' equation:

$\left(P+\frac{a}{{V_m}^2}\right)(V_m-b)=RT$ **(1)**

P is the pressure , Vm is molar volume, R is the universal gas constant, T is the absolute temperature, a,b constant van der Waals' equation, find the function P=P(V,T), , as a result we get and let T= const

$P=\frac{RT}{(V_m-b)}-\frac{a}{{V_m}^2}$ **(2)**

Tc-temperature at which the difference between liquid and gas disappears, on the isotherms it corresponds to the inflection point (T=Tc), its condition for the function of two variables is

$$\left(\frac{\partial P}{\partial V}\right)_{T=const}=0,\qquad \left(\frac{\partial^2 P}{\partial V^2}\right)_{T=const}=0$$

We compute derivatives of 1 and 2 order

$$\left(\frac{\partial P}{\partial V}\right)_{T=const}=-\frac{RT_c}{(V_m-b)^2}+\frac{2a}{{V_m}^3}=0,\qquad \left(\frac{\partial^2 P}{\partial V^2}\right)_{T=const}=+\frac{2RT_c}{(V_m-b)^3}-\frac{6a}{{V_m}^4}=0$$

whence it follows that

$RT_c=\frac{2a}{{V_m}^3}(V_m-b)^2$ **(3)**

and substituting in the derivatives of **2** order

$$\frac{2}{(V_m-b)^3}\frac{2a}{{V_m}^3}(V_m-b)^2-\frac{6a}{{V_m}^4}=\frac{4a}{(V_m-b)\ \ {V_m}^3}-\frac{6a}{{V_m}^4}=0,$$

$$\frac{2}{(V_m-b)}-\frac{3}{V_m}=0,\frac{2V_m-3V_m+3b}{(V_m-b)\ \ V_m}=0,\qquad -V_m+3b=0,\ V_m=3b$$

molar volume corresponds to the critical volume, then Tc

$$RT_c=\frac{2a}{(3b)^3}(3b-b)^2=\frac{8a}{27b},T_c=\frac{8a}{27bR}$$

on the other hand, multiplying the pressure by temperature corresponds to the Onne's or virial equation, and the definition of temperature Tb (at a temperature of Boyle's gas compressibility does not depend on the pressure):

$$PV_m=RT+\frac{B_2}{V_m}+\frac{B_3}{(V_m)^2}+\cdots,T_b=T\ if\ B_2=0,\ \left(\frac{\partial PV_m}{\partial(\frac{1}{V})}\right)_{T=const}=0 \quad \textbf{(4)}$$

we rewrite equation (2) as

$$PV_m = \frac{RT}{\left(1-\frac{b}{V_m}\right)} - \frac{a}{V_m} = RT\left(1+\frac{b}{V_m}+..\right) - \frac{a}{V_m} = RT + \frac{RTb}{V_m}+..-\frac{a}{V_m} = RT + \frac{bRT-a}{V_m}+..$$

where $\frac{RT}{\left(1-\frac{b}{V_m}\right)} = RT\left(1+\frac{b}{V_m}+..\right)$

there is decomposition into Taylor series, comparing the latter with the equation Onne's we obtain and equation (4)

$$B_2 = bRT_b - a = 0, T_b = \frac{a}{bR}$$

and

$$T_c = \frac{8a}{27bR}$$

Then

$$\frac{T_b}{T_c} = \frac{27}{8} = 3.3750$$

**Answer: Tb =3.375Tc.**

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