

1. (20%) Show that the second virial coefficient for a van der Waals gas is given by

$$B(T) = \frac{1}{RT} \left(\frac{\partial z}{\partial \frac{1}{V_m}} \right)_T = b - \frac{a}{RT}$$

Rather than differentiating with respect to $\frac{1}{V_m}$, we introduce the variable $u = \frac{1}{V_m}$

Sol:

Using this variable, the virial expansion takes the form

$$P = RT \left([P(u)]_{u=0} + \left[\frac{dP(u)}{du} \right]_{u=0} u + \frac{1}{2!} \left[\frac{d^2 P(u)}{du^2} \right]_{u=0} u^2 + \dots \right)$$

Therefore, the second virial coefficient is $B(T) = \frac{1}{2RT} \left[\frac{d^2 P(u)}{du^2} \right]_{u=0}$.

We carry out this differentiation for the van der Waals equation written in terms of the variable u .

$$\begin{aligned} P &= \frac{RT}{V_m - b} - \frac{a}{V_m^2} = \frac{RT}{1/u - b} - au^2 \\ \frac{dP}{du} &= -\frac{RT}{(1/u - b)^2} \frac{d(1/u)}{du} - 2au = \frac{RT}{u^2(1/u - b)^2} - 2au = \frac{RT}{(1 - ub)^2} - 2au \\ \frac{d^2 P}{du^2} &= \frac{2bRT}{(1 - ub)^3} - 2a \end{aligned}$$

$$\lim_{u \rightarrow 0} \frac{2bRT}{(1 - ub)^3} - 2a = 2bRT - 2a \text{ and}$$

$$B(T) = \frac{1}{2RT} \left[\frac{d^2 P(u)}{du^2} \right]_{u=0} = b - \frac{a}{RT}$$

2. (20%) At what temperature does the slope of the z versus P curve as $P \rightarrow 0$ have its maximum value for a vander Waals gas? What is the value of the maximum slope?

Sol:

$$\left(\frac{\partial z}{\partial P}\right)_{T,P \rightarrow 0} = \frac{1}{RT} \left(b - \frac{a}{RT}\right)$$

For a van der Waals gas

$$\left(\frac{\partial}{\partial T} \left(\frac{\partial z}{\partial P}\right)_T\right)_{P \rightarrow 0} = -\frac{1}{RT^2} \left(b - \frac{a}{RT}\right) + \frac{1}{RT^3} = -\frac{1}{RT^2} \left(b - \frac{2a}{RT}\right)$$

Setting this derivative equal to zero gives

$$b - \frac{2a}{RT_{\max}} = 0 \quad T_{\max} = \frac{2a}{Rb}$$

$$\text{The maximum slope is } \frac{1}{RT_{\max}} \left(b - \frac{a}{RT_{\max}}\right) = \frac{b}{2a} \left[b - a \left(\frac{b}{2a}\right)\right] = \frac{b^2}{4a}.$$

3. (20%) For a Van der Waals gas, $Z = \frac{V_m}{(V_m - b)} - \frac{a}{RTV_m}$.

Expand the first term of this expression in a Taylor series in the limit $V_m \gg b$ to

obtain $Z \approx 1 + \frac{b - \frac{a}{RT}}{V_m}$

Sol:

$$f(x) = f(0) + \left(\frac{df(x)}{dx}\right)_{x=0} x + \dots$$

In this case, $f(x) = \frac{1}{1-x}$ and $x = \frac{b}{V_m}$.

$$z = \frac{V_m}{V_m - b} - \frac{a}{RTV_m} = \frac{1}{1 - \frac{b}{V_m}} - \frac{a}{RTV_m}$$

Because $\frac{1}{1-x} \approx 1 + x + \frac{x^2}{2} + \dots$

$$\frac{1}{1 - \frac{b}{V_m}} \approx 1 + \frac{b}{V_m}$$

$$z \approx 1 + \frac{b}{V_m} - \frac{a}{RTV_m} = 1 + \frac{1}{V_m} \left(b - \frac{a}{RT}\right)$$

4.(20%) Show that the slope of Z as a function of P as $P \rightarrow 0$ is related to the van der waals parameters by:

$$\lim_{P \rightarrow 0} \left(\frac{\partial Z}{\partial P} \right)_T = \frac{1}{RT} \left(b - \frac{a}{RT} \right)$$

Sol:

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

$$Z = \frac{PV_m}{RT} = \frac{V_m}{V_m - b} - \frac{a}{V_m RT}$$

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

5.(20%) For $T > T_B$ the equation of state $P(V_m - b) = RT$ is an improvement over the ideal gas law because it takes the finite volume of the molecules into account.

Derive an expression for the fugacity coefficient for a gas that obeys this equation of state. (fugacity coefficient : f/p)

Sol:

Following the EOS which is given by this example:

$$P = \frac{RT}{V_m - b} \Rightarrow PV_m = RT - bP \text{ or } PV_m = \frac{V_m RT}{V_m - b}$$

$$Z = \frac{PV_m}{RT} = 1 + \frac{bP}{RT} \quad \text{or} \quad \frac{V_m}{V_m - b} \quad (\text{here } V_m \text{ is the function of } P)$$

$$Z - 1 = \frac{bP}{RT} \quad \text{or} \quad \frac{b}{V_m - b} = \frac{bP}{RT} \quad (\text{because } V_m = \frac{RT}{P} + b)$$

so fugacity coefficient can be calculated by:

$$\ln \gamma = \ln \frac{f}{p} = \int_0^p \frac{z-1}{P} dp = \int_0^p \frac{b}{RT} dp = \frac{bP}{RT}$$

$$\gamma = e^{\frac{bP}{RT}} \approx 1 + \frac{bP}{RT} = Z$$

because when $T > T_b$, most of gases has $\gamma > 1$

so it is a good approximation (which means the attractive force is not important when T is large)