Chemistry 431
Problem Set 10
Fall 2023
Solutions

1. A certain gas obeys the equation of state

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^4}$$

where a and b are numerical constants. Derive an expression for the critical volume of the gas in terms of b.
Answer:

$$\left(\frac{\partial P}{\partial V_m}\right)_T = -\frac{RT}{(V_m - b)^2} + \frac{4a}{V_m^5}$$
$$\left(\frac{\partial^2 P}{\partial V_m^2}\right)_T = \frac{2RT}{(V_m - b)^3} - \frac{20a}{V_m^6}$$

At the critical point both the first and second derivatives vanish

$$\frac{RT_c}{(V_c - b)^2} = \frac{4a}{V_c^5}$$

or

$$T_c = \left(\frac{4a}{V_c^5}\right)\left(\frac{(V_c - b)^2}{R}\right).$$

$$\frac{2R}{(V_c - b)^3}\left(\frac{4a}{V_c^5}\right)\left(\frac{(V_c - b)^2}{R}\right) = \frac{20a}{V_c^6}$$
$$\frac{8}{V_c - b} = \frac{20}{V_c}$$
$$12V_c = 20b$$
$$V_c = \frac{5}{3}b$$

2. Derive expressions for the critical pressure, temperature, volume and compression factor for the Berthelot equation of state given by

$$P = \frac{nRT}{V - nb} - \frac{an^2}{TV^2}$$

Answer:

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

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{RT}{(V-b)^2} + \frac{2a}{TV^3} \tag{1}$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_T = \frac{2RT}{(V-b)^3} - \frac{6a}{TV^4} \tag{2}$$

From Eq.(1)

$$\frac{2a}{TV^3} = \frac{RT}{(V-b)^2}$$

and

$$T^2 = \frac{2a(V-b)^2}{RV^3} \tag{3}$$

From Eq.(2)

$$\frac{2RT}{(V-b)^3} = \frac{6a}{TV^4}$$

or

$$T^2 = \frac{3a(V-b)^3}{RV^4} \tag{4}$$

Equating Eqs.(3) and (4)

$$\frac{2a(V-b)^2}{RV^3} = \frac{3a(V-b)^3}{RV^4}$$

$$2 = \frac{3(V-b)}{V}$$

or

$$V_c = 3b \tag{5}$$

From Eqs.(3) and (5)

$$T_c^2 = \frac{2a(3b-b)^2}{R(3b)^3}$$

$$= \left(\frac{8a}{27Rb}\right)^{1/2}$$

$$= \frac{2}{3}\left(\frac{2a}{3Rb}\right)^{1/2} \tag{6}$$

Using the equation of state

$$P_c = \frac{R}{2b}\frac{2}{3}\left(\frac{2a}{3Rb}\right)^{1/2} - \frac{a}{9b^2}\frac{3}{2}\left(\frac{3Rb}{2a}\right)^{1/2}$$

$$= \frac{1}{12}\left(\frac{2Ra}{3b^3}\right)^{1/2} \tag{7}$$

Then

$$z_c = \frac{P_c V_c}{RT_c} = \frac{(1/12)(2Ra/3b^3)^{1/2} 3b}{R(2a/3Rb)^{1/2}(2/3)} = \frac{3}{8} = 0.375$$

3. Use the result of problem 2 to find the reduced equation of state for a Berthelot gas.
Answer:

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

$$P = P_r P_c \qquad V = V_r V_c \qquad T = T_r T_c$$

$$P_r \frac{1}{12}\left(\frac{2aR}{3b^3}\right)^{1/2} = \frac{RT_r(2/3)(2a/3Rb)^{1/2}}{3bV_r - b} - \frac{a}{9b^2 V_r^2}\frac{3}{2}\left(\frac{3Rb}{2a}\right)^{1/2}\frac{1}{T_r}$$

Then

$$P_r = \frac{T_t}{b(3V_r - 1)}\frac{2R}{3}\left(\frac{2a}{3Rb}\right)^{1/2} 12\left(\frac{3b^3}{2aR}\right)^{1/2}$$

$$-\frac{1}{TV_r^2}\frac{3}{2}\left(\frac{3Rb}{2a}\right)^{1/2}\frac{a}{9b^2}12\left(\frac{3b^3}{2aR}\right)^{1/2}$$

$$= \frac{8T_r}{3V_r - 1} - \frac{3}{T_r V_r^2}$$

4. A certain gas obeys the equation of state

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

where a and b are numerical constants. Derive an expression for the critial volume of the gas in terms of b.
Answer:

$$\left(\frac{\partial P}{\partial V_m}\right)_T = -\frac{RT}{(V_m - b)^2} + \frac{2a}{(V_m + b)^3}$$

$$= 0 \quad \text{at} \quad T_c = \left(\frac{2a}{(V_c + b)^3}\right)\left(\frac{(V_c - b)^2}{R}\right)$$

$$\left(\frac{\partial^2 P}{\partial V_m^2}\right)_T = \frac{2RT}{(V_m - b)^3} - \frac{6a}{(V_m + b)^4}$$

$$= 0 \quad \text{at} \quad \left(\frac{2R}{(V_c - b)^3}\right)\left(\frac{2a}{(V_c + b)^3}\right)\left(\frac{(V_c - b)^2}{R}\right) = \frac{6a}{(V_c + b)^4}$$

$$\frac{2}{V_c - b} = \frac{3}{V_c + b}$$

$$V_c = 5b$$

5. Derive an expression for the critical volume of a gas that obeys the equation of state

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^6}$$

where a and b are constants.
Answer:

$$\left(\frac{\partial P}{\partial V_m}\right)_T = -\frac{RT}{(V_m - b)^2} + \frac{6a}{V_m^7}$$

$$\left(\frac{\partial^2 P}{\partial V_m^2}\right)_T = \frac{2RT}{(V_m - b)^3} - \frac{42a}{V_m^8}$$

$(\partial P/\partial V_m)_T = 0$ at

$$\frac{RT_c}{(V_c - b)^2} = \frac{6a}{V_c^7} \quad \text{or} \quad T_c = \frac{6a}{V_c^7}\frac{(V_c - b)^2}{R}$$

$(\partial^2 P/\partial V_m^2)_T = 0$ at

$$\frac{2RT_c}{(V_c - b)^3} = \frac{42a}{V_c^8}$$

Then

$$\frac{2R}{(V_c - b)^3}\frac{6a}{V_c^7}\frac{(V_c - b)^2}{R} = \frac{42a}{V_c^8}$$

$$\frac{12}{V_c - b} = \frac{42}{V_c} \quad \text{or} \quad V_c = \frac{7}{5}b$$

6. Expand the van der Waals equation of state as a virial expansion in powers of $1/V$ using the geometric series

$$\frac{1}{1-x} = 1 + x + x^2 + x^3 + \ldots$$

for $|x| < 1$. You may terminate the series after the third virial coefficient.
Answer:

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

$$= \frac{RT}{V}\left[\frac{1}{1 - b/V}\right] - \frac{a}{V^2}$$

$$PV = RT\left[1 + \frac{b}{V} + \left(\frac{b}{V}\right)^2 + \ldots\right] - \frac{a}{V}$$

$$= RT\left[1 + \frac{b - a/RT}{V} + \left(\frac{b}{V}\right)^2 \ldots\right]$$

Then

$$B(T) = b - \frac{a}{RT}$$
$$C(T) = b^2$$
$$\vdots$$

7. A gas obeys the Berthelot equation of state

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

where a and b are numerical constants. By expanding the equation of state in virial form using powers of $1/V_m$, determine an expression for the second virial coefficient of the Berthelot gas.

Answer:

$$\begin{aligned} P &= \frac{RT}{V_m\left(1 - \frac{b}{V_m}\right)} - \frac{a}{TV_m^2} \\ &= \frac{RT}{V_m}\left[1 + \frac{b}{V_m} + \left(\frac{b}{V_m}\right)^2 + \ldots\right] - \frac{a}{TV_m^2} \\ &= \frac{RT}{V_m}\left[1 + \frac{b}{V_m} + \left(\frac{b}{V_m}\right)^2 + \ldots - \frac{a}{RT^2V_m}\right] \\ &= \frac{RT}{V_m}\left[1 + \frac{b - a/RT^2}{V_m} + \left(\frac{b}{V_m}\right)^2 + \ldots\right] \end{aligned}$$

so that the second virial coefficient is

$$B(T) = b - \frac{a}{RT^2}.$$

8. The Boyle temperature of a gas is defined to be the temperature at which the second virial coefficient in the inverse volume expansion vanishes. A certain gas obeys the equation of state

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

where a and b are numerical constants. Expand the equation of state in virial form, and determine the Boyle temperature of the gas in terms of a, b and R.

Answer:

$$P = \frac{RT}{V_m}\frac{1}{1 - \frac{b}{V_m}} - \frac{a}{T^2V_m^2}$$

$$PV_m = RT\left[1+\frac{b}{V_m}+\left(\frac{b}{V_m}\right)^2+\dots\right]-\frac{a}{T^2V_m}$$

$$= RT\left[1+\frac{1}{V_m}\left(b-\frac{a}{RT^3}\right)+\left(\frac{b}{V_m}\right)^2+\dots\right]$$

Then the second virial coefficient is given by

$$B(T) = b - \frac{a}{RT^3} = 0$$

when

$$T = \left(\frac{a}{Rb}\right)^{1/3}$$

9. A certain gas obeys the equation of state

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

where a and b are numerical constants. Given the critical volume of the gas is $V_c = 5b$, derive an expression for the compression factor at the critical point.
Answer:

$$\left(\frac{\partial P}{\partial V_m}\right)_T = -\frac{RT}{(V_m-b)^2}+\frac{2a}{(V_m+b)^3}$$

$= 0$ at

$$T_c = \frac{2a}{(V_m+b)^3}\frac{(V_m-b)^2}{R} = \frac{2a}{(6b)^3}\frac{(4b)^2}{R} = \frac{4a}{27Rb}$$

$$P_c = \frac{RT_c}{V_c-b}-\frac{a}{(V_c+b)^2} = \frac{R}{4b}\frac{4a}{27Rb}-\frac{a}{36b^2} = \frac{a}{4(27)b^2}$$

$$z_c = \frac{P_cV_c}{RT_c} = \frac{a}{4(27)b^2}\frac{5b(27Rb)}{R(4a)} = \frac{5}{16}$$

10. A certain gas obeys the equation of state

$$P = \frac{RT}{V} - \frac{A}{V^2} + \frac{B}{V^3}$$

where A and B are positive constants. The critical volume is found to be $V_c = 3B/A$. Derive an expression for the compression factor z_c at the critical point thereby showing z_c to be independent of A and B.
Answer

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{RT}{V^2}+\frac{2A}{V^3}-\frac{3B}{V^4} = 0$$

at the critical point. Then

$$RT_c = \frac{2A}{V_c} - \frac{3B}{V_c^2}$$

or

$$T_c = \frac{1}{R}\left(\frac{A^2}{B} - \frac{2}{3}\frac{A^2}{B}\right) = \frac{A^2}{3RB}$$

$$P_c = \frac{RT_c}{V_c} - \frac{A}{V_c^2} + \frac{B}{V_c^3} = \frac{RA^2}{3RB}\frac{A}{3B} - \frac{A^3}{9B^2} + \frac{A^3}{27B^2} = \frac{A^3}{27B^2}$$

$$z_c = \frac{P_cV_c}{RT_c} = \frac{A^3}{27B^2}\frac{3B}{AR}\frac{3RB}{A^2} = \frac{1}{3}$$

11. The critical volume V_c of a certain gas that obeys the equation of state

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^3}$$

is $V_c = 2b$ where a and b are numerical constants and V_m is the molar volume. Derive an expression for the compression factor z_c at the critical point verifying that z_c is independent of a and b.
Answer:

$$\left(\frac{\partial P}{\partial V_m}\right)_T = -\frac{RT}{(V_m - b)^2} + \frac{3a}{V_m^4} = 0$$

at

$$\frac{RT_c}{(V_c - b)^2} = \frac{3a}{V_c^4}$$

$$\frac{RT_c}{b^2} = \frac{3a}{16b^4} \qquad T_c = \frac{3a}{16Rb^2}$$

$$P_c = R\frac{3a}{16Rb^2}\frac{1}{b} - \frac{a}{8b^3} = \frac{a}{16b^3}$$

$$z_c = \frac{P_cV_c}{RT_c} = \frac{a}{16b^3}\frac{2b}{R}\frac{16b^2R}{3a} = \frac{2}{3}$$

12. A certain gas obeys the equation of state

$$\frac{PV_m}{RT} = 1 + \frac{\alpha P}{1 + \alpha P}$$

where α is a function of temperature only. Determine the fugacity of the gas as a function of pressure.
Answer:

$$f = P\exp\left\{\int_0^P \frac{z(P,T) - 1}{P}dP\right\}$$

Now

$$z(P,T) = 1 + \frac{\alpha P}{1+\alpha P}$$

Let

$$I = \int_0^P \frac{z(P,T)-1}{P} dP = \int_0^P \frac{\alpha P}{1+\alpha P}\frac{1}{P} dP$$

$$= \alpha \int_0^P \frac{dP}{1+\alpha P}$$

Let

$$y = 1+\alpha P \qquad dP = \frac{1}{\alpha} dy$$

Then

$$I = \int_1^{(1+\alpha P)} \frac{dy}{y} = \ln(1+\alpha P)$$

Then

$$f = P\exp\{\ln(1+\alpha P)\} = P(1+\alpha P) = P + \alpha P^2$$

13. Derive an expression for the fugacity of a gas that obeys the equation of state

$$PV_m(1-bP) = RT$$

where b is a numerical constant. Determine the behavior of the fugacity as $b \to 0$ and as $P \to 0$.

Answer:

$$f = P\exp\left(\int_0^P \frac{z-1}{P}\, dP\right)$$

$$z = \frac{PV_m}{RT} \qquad \frac{PV_m}{RT}(1-bP) = z(1-bP) = 1$$

$$z = \frac{1}{1-bP} \qquad z - 1 = \frac{1}{1-bP} - 1 = \frac{1-1+bp}{1-bP} = \frac{bP}{1-bP}$$

$$\int_0^P \frac{z-1}{P}\, dP = b\int_0^P \frac{dP}{1-bP}$$

$$y = 1-bP \qquad dy = -bdP \qquad dP = -\frac{dy}{b}$$

$$\int_0^P \frac{z-1}{P}\, dP = -\int_1^{1-bP} \frac{dy}{y} = -\ln(1-bP) = \ln\frac{1}{1-bP}$$

$$f = \frac{P}{1-bP}$$

$$\lim_{b\to 0} f = P \qquad \lim_{P\to 0}\frac{f}{P} = 1$$

14. Use the virial expansion

$$PV_m = RT[1 + b(T)P + c(T)P^2 + d(T)P^3 + \ldots]$$

to derive an expression for the fugacity coefficient γ of a gas in terms of the virial coefficients. Use the result to find the value of γ in the limit that $P \to 0$.

Answer:

$$z = \frac{PV_m}{RT} = 1 + b(T)P + c(T)P^2 + d(T)P^3 \ldots$$

$$\int_0^P \frac{z-1}{P} dP = \int_0^P [b(T) + c(T)P + d(T)P^2 + \ldots]$$

$$= b(T)P + \frac{c(T)P^2}{2} + \frac{d(T)}{3}P^3 + \ldots$$

$$\gamma = \exp\left\{\int_0^P \frac{z-1}{P} dP\right\}$$

$$= \exp\left\{b(T)P + \frac{c(T)P^2}{2} + \frac{d(T)}{3}P^3 + \ldots\right\}$$

$$\lim_{P\to 0} \gamma = e^0 = 1$$