Chemistry 431
Problem Set 10
Fall 2023

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.

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

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

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

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.

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.

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

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

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

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.

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.

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.

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.

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.

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.

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 $P \to 0$.

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 $P \to 0$.