

Problem Set 2

1. The Compressibility Factor for Methane can be represented by the truncated Expansion:

$$Z = 1 + BP + CP^2 + DP^3$$

If P is measured in atmospheres, the values for the constants are:

T [K]	B	C	D
200	-5.74×10^{-3}	6.86×10^{-6}	18.0×10^{-9}
1000	0.189×10^{-3}	0.275×10^{-6}	0.144×10^{-9}

Plot the values of Z as a function of P at these two temperatures in the range from 0 to 1000 atm.

2. The Second Virial Coefficient of Methane can be approximated by:

$$B'(T) = a + b e^{-c/T^2}$$

where:

$$\begin{aligned} a &= -0.1993 \text{ barr}^{-1} \\ b &= 0.2002 \text{ barr}^{-1} \\ c &= 1131 \text{ K}^2 \end{aligned}$$

for $300\text{K} < T < 600\text{K}$. What is the Boyle Temperature of Methane?

3. The Second Virial Coefficient $B'(T)$ can be obtained from measurements of the density ρ of a gas at a series of pressures. Show that the graph of P/ρ vs. P should be a straight line with slope proportional to $B'(T)$. Revisiting the Density data for Dimethyl Ether at 25°C (Handout), find the value of $B'(298.15)$.
4. Show that:

$$T \alpha = 1 + T \left(\frac{\partial \ln Z}{\partial T} \right)_P$$

and that:

$$P \kappa = 1 - P \left(\frac{\partial \ln Z}{\partial P} \right)_T$$

5. The Critical Constants for Water are 647.3K, 218.5 atm, and 55.44 cm³/mole. Calculate the values of the van der Waals constants a and b and the “van der Waals constant” R . Compare the “van der Waals constant” R with the Universal Gas Constant R . Determine the percentage error. Now compute the values of the constants a and b using only P_c , T_c and the Universal Gas Constant R . Use these results to calculate V_c . Compare this result with the correct value.
6. Use the Critical Constants for Chlorine (Cl₂), see Handout, to estimate the radius of a Cl₂ molecule assuming it is spherical.
7. As an alternative, the van der Waals constants for a gas can be estimated from the Compressibility Factor and the Boyle Temperature. If $Z = 1.00054$ at 0°C and 1 atm and the Boyle Temperature of the gas is 107K, estimate the values of the van der Waals constants a and b for the gas. (Assume the expansion for the Compressibility Factor can be truncated after the Second Virial Coefficient.)
[Ans. $a = 0.018 \text{ Pa m}^6/\text{mol}^2$ and $b = 2.0 \times 10^{-5} \text{ m}^3/\text{mol}$]
8. At what temperature does the slope of the Z vs P curve at ($P = 0$) have a maximum value for the van der Waals gas? What is the value of the maximum slope?
[Ans. $T = 2a/Rb$]
9. At high pressures, the van der Waals Eq. of State can be rearranged to the form:

$$\bar{V} = b + \frac{P}{a} \left(b + \frac{RT}{P} \right) \bar{V}^2 - \left(\frac{P}{a} \right) \bar{V}^3$$

If the quadratic and cubic terms are dropped, then we obtain $\bar{V}_0 = b$ as a first approximation to the smallest root of the equation. This would represent the volume of the liquid. Using this approximate value of \bar{V} in the higher terms, show that the next approximation for the volume of the liquid is:

$$\bar{V} = b + \frac{b^2 RT}{a}$$

From this expression show that the first approximation for the Coefficient of Thermal Expansion of a van der Waals liquid is $\alpha = bR/a$.

10. Show that according to the van der Waals Eq. of State the Compressibility Factor at the Critical Point is:

$$Z = 3/8$$

11. Calculate the P vs. V Isotherm for Benzene (C₆H₆) at 360K using the van der Waals Eq. of State ($a = 18 \text{ L}^2\text{atm}$, $b = 0.1154 \text{ L/mole}$). Plot the resulting curve to $\bar{V} = 30 \text{ L/mole}$.
- Crudely estimate the Vapor Pressure for Benzene at 360K using this graph.
 - Obtain the slope $(\partial V/\partial P)_T$ for $P = 1\text{atm}$. Use this to calculate the Coefficient of Compressibility κ of the liquid at this pressure.

12. At low pressures, the Berthelot equation has the form:

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

The Berthelot parameters can be estimated from Critical Point data:

$$a = (27/64) R^2 T_c^3 / P_c$$

$$b = R T_c / 8 P_c$$

Gas density data for SO₂ at 273.15K is:

P (atm)	0.25	0.50	1.00
ρ (g/L)	0.71878	1.44614	2.92655

Compare these values with those calculated using the Equation of State of D. Berthelot. (Use appropriate reference sources to obtain the Critical Point for SO₂.)

13. Read the papers of Beattie and Bridgeman outlining their Equation of State.
- What features do Beattie and Bridgeman consider desirable in an Equation of State?
 - What is the largest average deviation of the “pressure calculated by the Equation of State” from the observed pressure for Ethyl Ether?
 - What is the average deviation for the ten gases considered in the second paper?
 - What is the lowest “Maximum” pressure considered for the comparison of Beattie and Bridgeman’s Equation of State with experimental data?
14. Use the Principle of Corresponding States to determine the Molar Volume of Ammonia at 212°C and 224 atm. Critical Constants for Ammonia are:

$$\begin{aligned} T_c &= 405.5 \text{ K} \\ P_c &= 112.2 \text{ atm} \\ V_c &= 72.02 \text{ cm}^3/\text{mole} \end{aligned}$$

[Ans. $V = 0.101 \text{ L}$]