

1. (4 Points) In class lecture, we discussed one particular equation of state (EOS), the ideal gas EOS. Another EOS is the van der Waals EOS which attempts to describe non-ideal (real) gases. The form of the van der Waals EOS is:

$$P(T, \bar{V}) = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2}$$

P is pressure, T is absolute temperature, and  $\bar{V}$  is molar volume. What is the order of this polynomial equation with respect to molar volume for a single component species? Please derive an explicit functional form to support your answer.

Solution:

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

$$P(\bar{V} - b)(\bar{V}^2) = RT\bar{V}^2 - a(\bar{V} - b)$$

$$P\bar{V}^3 - Pb\bar{V}^2 = RT\bar{V}^2 - a(\bar{V} - b)$$

$$P\bar{V}^3 - (Pb + RT)\bar{V}^2 + a\bar{V} - ab = 0$$

*Third order*  
*cubic*

2. (3 Points) A mixture of  $2.50 \times 10^{-3}$  grams of  $O_2$ ,  $3.51 \times 10^{-3}$  moles of  $N_2$ , and  $4.67 \times 10^{20}$  molecules of CO are placed in a vessel of volume 4.65 Liters at 15.4 Celsius. What is the total pressure in the vessel at this temperature and composition?

Solution:

$$N_{Total} = N_{O_2} + N_{N_2} + N_{CO}$$

$$N_{Total} = (0.00250 \text{ gr } O_2) \left( \frac{1 \text{ mol}}{(2)(15.9994) \text{ gr}} \right) + 0.00351 + \left( \frac{4.67 \times 10^{20}}{6.023 \times 10^{23}} \right)$$

$$N_{Total} = 0.000078129 + 0.00351 + 0.000775361$$

$$N_{Total} = 0.004363490 \text{ moles}$$

$$P_{Total} = \left( \frac{N_{Total} RT}{V} \right) = \left( \frac{(0.004363490)(0.08206 \text{ L atm mol}^{-1} \text{K}^{-1})(15.4 + 273.15)}{(4.65 \text{ L})} \right)$$

$$P_{Total} = 0.0217 \text{ atm}$$

**3 (1 Point).** Consider a state function  $\bar{U}(T, \bar{V})$  where the independent variables are the usual state properties we measure for a pure fluid, single-phase system. Provide an expression for the total differential of  $\bar{U}(T, \bar{V})$ .

Solution:

$$d\bar{U}(T, \bar{V}) = \left( \frac{\partial \bar{U}}{\partial \bar{V}} \right)_T d\bar{V} + \left( \frac{\partial \bar{U}}{\partial T} \right)_{\bar{V}} dT$$

1. (4 Points). Prove the equality:

$$\left(\frac{\partial C_V}{\partial V}\right)_T = T \left(\frac{\partial^2 P}{\partial T^2}\right)_V$$

Remember that U is a state function (hence its total differential is an exact differential). Also, the following relation may be useful:  $\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P$ .

Solution:

$$\begin{aligned} \left(\frac{\partial C_V}{\partial V}\right)_T &= \left(\frac{\partial}{\partial V} \left(\frac{\partial U}{\partial T}\right)_V\right)_T = \left(\frac{\partial}{\partial T} \left(\frac{\partial U}{\partial V}\right)_T\right)_V \\ &= \left(\frac{\partial}{\partial T} \left(T \left(\frac{\partial P}{\partial T}\right)_V - P\right)\right)_V \\ &= T \left(\frac{\partial^2 P}{\partial T^2}\right)_V + \left(\frac{\partial P}{\partial T}\right)_V - \left(\frac{\partial P}{\partial T}\right)_V \\ &= T \left(\frac{\partial^2 P}{\partial T^2}\right)_V \end{aligned}$$

2. (3 Point). For a change of 1 bar pressure at 298.15K, what is the fractional change in volume of a sample of water? Consider the fractional change relative to the initial sample volume.

Solution:

$$\left(\frac{dV}{V}\right) = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P + \frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T$$

$$\left(\frac{dV}{V}\right) = \alpha \Delta T - \kappa_T \Delta P$$

$$\ln\left(\frac{V_2}{V_1}\right) = \alpha \Delta T - \kappa_T \Delta P$$

$$f = \frac{\Delta V}{V_1} = \frac{V_2 - V_1}{V_1} = \frac{V_2}{V_1} - 1$$

$$\frac{V_2}{V_1} = f + 1$$

$$\ln(f + 1) = \alpha \Delta T - \kappa_T \Delta P$$

$$f + 1 = e^{\alpha \Delta T - \kappa_T \Delta P} = e^{0 - (0.0000457 \text{ bar}^{-1})(1 \text{ bar})} = 0.9999543$$

$$f = 0.9999543 - 1 = -0.0000457$$

$$|f| = 0.0000457$$

There is a 0.00457% drop in the volume after the 1 bar pressure change. This is an example of why water is considered an incompressible fluid at normal thermodynamic conditions. This assumes constant expansion coefficients over this pressure change.

**3. (1 Point).**

**A.** The Joule-Thomson coefficient for an ideal gas is zero. True or False? True

**B.** Ideal Gas enthalpy is a function of Temperature?