Chemistry 431
Problem Set 4
Fall 2023

1. The pressure of a Van der Waals gas as a function of T and V is given by

$$P = \frac{RT}{V-b} - a\left(\frac{1}{V}\right)^2$$

where a and b are constants and the number of moles has been set to 1 for this problem. The internal energy U as a function of T and V for a Van der Waals gas is given by

$$U = C_V T - a\frac{1}{V}$$

   (a) Explictly evaluate $(\partial T/\partial V)_P$ for the Van der Waals gas and derive an expression for $(\partial V/\partial T)_P$ and from the explicitly evaluated derivative.

   (b) Explicitly calculate $(\partial U/\partial T)_V$, $(\partial T/\partial V)_U$ and $(\partial V/\partial U)_T$ for the Van der Waals gas. Demonstrate that

$$\left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_U \left(\frac{\partial V}{\partial U}\right)_T = -1$$

   (c) Evaluate $(\partial U/\partial T)_P$ for the Van der Waals gas.

2. (a) Give the total differential of the internal energy U of a system where U is taken to be a function of T and V.

   (b) Consider a system where only PV-work is done and $P_{ext} = P$. Use the result from part "a" to show the expression for the heat is given by

$$đq = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] dV$$

   (c) Use part "b" to prove that the expression for $đq$ is not an exact differential.

3. For any substance, show that

$$\left(\frac{\partial U}{\partial P}\right)_V = \frac{\kappa C_V}{\beta}$$

4. Show that

$$\left(\frac{\partial U}{\partial T}\right)_P = C_V + \kappa V \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial U}{\partial V}\right)_T$$

where C_V is the constant volume heat capacity and κ is the isothermal compressibility.

5. Show that

$$\left(\frac{\partial H}{\partial P}\right)_V = \frac{C_P\kappa}{\beta} + \left(\frac{\partial H}{\partial P}\right)_T$$

where κ is the isothermal compressiblilty and β is the isobaric coefficient of thermal expansion.

6. Show that for any substance

$$\left(\frac{\partial U}{\partial H}\right)_P = \frac{C_V}{C_P} + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial H}\right)_P$$

and give the numerical value for $\left(\frac{\partial U}{\partial H}\right)_P$ for an ideal monatomic gas.

7. Show that for any substance

$$\left(\frac{\partial H}{\partial U}\right)_V = \frac{C_P}{C_V} - C_P\mu_{JT}\left(\frac{\partial P}{\partial U}\right)_V$$

where the Joule-Thomson coefficient is defined by

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H .$$

8. Show that

$$\left(\frac{\partial H}{\partial P}\right)_U = C_P\left[\left(\frac{\partial T}{\partial P}\right)_U - \mu_{JT}\right]$$

9. Show that for any substance

$$\left(\frac{\partial H}{\partial V}\right)_U = C_P\left(\frac{\partial T}{\partial V}\right)_U - \frac{\left(\frac{\partial H}{\partial P}\right)_T\left(\frac{\partial U}{\partial V}\right)_P}{\left(\frac{\partial U}{\partial P}\right)_V}$$

10. Show that for any substance at temperature T, pressure P, volume V and internal energy U

$$\left(\frac{\partial P}{\partial V}\right)_U = \left(\frac{\partial P}{\partial V}\right)_T - \frac{1}{C_V}\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial U}{\partial V}\right)_T$$

where C_V is the constant volume heat capacity.

11. The heat capacity of CO_2 is $C_{P,m} = 2.09$ J mol^{-1} K^{-1}. When 50. grams of CO_2 at 25.°C and 1.0 bar pressure are isothermally compressed to 10.0 bar, ΔH for the process is -23.18 J. Calculate the Joule-Thomson coefficient, μ_{JT}, for CO_2.