Chemistry 431
Problem Set 4
Fall 2023
Solutions

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.
Answer:

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

$$T = \frac{V-b}{R}\left[P + \frac{a}{V^2}\right]$$

$$\left(\frac{\partial T}{\partial V}\right)_P = \frac{1}{R}\left[P + \frac{a}{V^2}\right] - \frac{2a}{V^3}\left(\frac{V-b}{R}\right)$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \left[\frac{1}{R}\left(P + \frac{a}{V^2}\right) - \frac{2a}{V^3}\left(\frac{V-b}{R}\right)\right]^{-1}$$

(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

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

Answer:

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

$$\left(\frac{\partial U}{\partial T}\right)_V = C_V$$

$$T = \frac{U + a/V}{C_V}$$

$$\left(\frac{\partial T}{\partial V}\right)_U = -\frac{a}{C_V V^2}$$

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

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

$$\left(\frac{\partial V}{\partial U}\right)_T = \frac{a}{(C_V T - U)^2}$$

$$\left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_U \left(\frac{\partial V}{\partial U}\right)_T = C_V\left(-\frac{a}{C_V V^2}\right)\left(\frac{a}{(C_V T - U)^2}\right)$$

$$= -\frac{a^2}{V^2(C_V T - U)^2}$$

But

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

so that

$$\left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_U \left(\frac{\partial V}{\partial U}\right)_T = -\frac{a^2}{V^2}\frac{V^2}{a^2} = -1$$

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

$$dU = C_V dT + \frac{a}{V^2}dV$$

$$\left(\frac{\partial U}{\partial T}\right)_P = C_V + \frac{a}{V^2}\left(\frac{\partial V}{\partial T}\right)_P$$

$$= C_V + \frac{a}{V^2}\left[\frac{1}{R}\left(P + \frac{a}{V^2}\right) - \frac{2a}{V^3}\left(\frac{V-b}{R}\right)\right]^{-1}$$

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.
Answer:

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

(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

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

Answer:

$$\begin{aligned} dU &= đq + đw \\ &= đq - PdV \end{aligned}$$

or

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

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

$$\left(\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial T}\right)_V\right)_T \neq \left(\frac{\partial}{\partial T}\left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]\right)_V$$

3. For any substance, show that

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

Answer:

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

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

$$\frac{\kappa}{\beta} = -\left[\frac{(\partial V/\partial P)_T}{(\partial V/\partial T)_P}\right] = \left(\frac{\partial T}{\partial P}\right)_V$$

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

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.
Answer:

$$dU = C_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

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

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

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

But

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

and

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

Then

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

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.

Answer:

$$\begin{aligned} dH &= \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \\ &= C_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \end{aligned}$$

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

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

$$\left(\frac{\partial T}{\partial P}\right)_V = -\frac{\left(\frac{\partial V}{\partial P}\right)_T}{\left(\frac{\partial V}{\partial T}\right)_P} = -\frac{-V\kappa}{V\beta} = \frac{\kappa}{\beta}$$

Then

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

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.

Answer:

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

$$= C_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

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

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

For an ideal gas $(\partial U/\partial V)_T$=0 and

$$\left(\frac{\partial U}{\partial H}\right)_P = \frac{C_V}{C_P} = \frac{3/2nR}{5/2nR} = \frac{3}{5}$$

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

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

Answer:

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP = C_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

$$\left(\frac{\partial H}{\partial U}\right)_V = C_P \left(\frac{\partial T}{\partial U}\right)_V + \left(\frac{\partial H}{\partial P}\right)_T \left(\frac{\partial P}{\partial U}\right)_V = \frac{C_P}{C_V} + \left(\frac{\partial H}{\partial P}\right)_T \left(\frac{\partial P}{\partial U}\right)_V$$

$$\left(\frac{\partial H}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_H \left(\frac{\partial T}{\partial H}\right)_P = -1$$

$$\left(\frac{\partial H}{\partial P}\right)_T = -\left(\frac{\partial H}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_H = -C_P \mu_{JT}$$

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

8. Show that

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

Answer:

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP = C_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

$$\left(\frac{\partial H}{\partial P}\right)_U = C_P\left(\frac{\partial T}{\partial P}\right)_U + \left(\frac{\partial H}{\partial P}\right)_T$$

$$\left(\frac{\partial H}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_H \left(\frac{\partial T}{\partial H}\right)_P = -1$$

$$\left(\frac{\partial H}{\partial P}\right)_T = -\left(\frac{\partial T}{\partial P}\right)_H \left(\frac{\partial H}{\partial T}\right)_P = -\mu_{JT} C_P$$

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

9. Show that for any substance

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

Answer:

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

$$= C_P\, dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

$$\left(\frac{\partial H}{\partial V}\right)_U = C_P\left(\frac{\partial T}{\partial V}\right)_U + \left(\frac{\partial H}{\partial P}\right)_T \left(\frac{\partial P}{\partial V}\right)_U$$

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

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

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

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.
Answer:

$$dP = \left(\frac{\partial P}{\partial V}\right)_T dV + \left(\frac{\partial P}{\partial T}\right)_V dT$$

$$\left(\frac{\partial P}{\partial V}\right)_U = \left(\frac{\partial P}{\partial V}\right)_T + \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_U$$

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

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

Then

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

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.
Answer:

$$\mu_{JT} = -\frac{1}{C_P}\left(\frac{\partial H}{\partial P}\right)_T$$

$$n_{CO_2} = (50 \text{ g})\left(\frac{\text{mol}}{44 \text{ g}}\right) = 1.14 \text{ mol}$$

$$\mu_{JT} = -\frac{(-23.18 \text{ J})/(9 \text{ bar})}{(1.14 \text{ mol})(2.09 \text{ J mol}^{-1}\text{K}^{-1})} = 1.08\text{K bar}^{-1}$$