

1. Use $df = (2x^2/y)dx - (2x^2/y^3)dy$ to decide if the function $f(x,y)$ exists. [2]
2. Use $dV_m = (R/p)dT - (RT/p^2)dp$ to decide if the function $V_m(T,p)$ exists. [2]
3. a) The following equations for $C_p - C_V$ are both correct.

$$C_p - C_V = \left[p + \left(\frac{\partial U}{\partial V} \right)_T \right] \left(\frac{\partial V}{\partial T} \right)_p \quad (1)$$

[3]

$$C_p - C_V = T \left(\frac{\partial p}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_p \quad (2)$$

But which equation [(1) or (2)] is more convenient for calculating $C_p - C_V$? Explain.

b) Prove $C_p - C_V = R$ for an ideal gas.

4. For the reversible adiabatic expansion or compression of an ideal gas with constant heat capacity, we proved $p_i V_i^\gamma = p_f V_f^\gamma$. Use this result to show

[2]

$$p_i^{1-\gamma} T_i^\gamma = p_f^{1-\gamma} T_f^\gamma$$

Hint: $pV^\gamma = p^{1-\gamma} p^\gamma V^\gamma = p^{1-\gamma} (pV)^\gamma$

5. 1.00 mole of N_2 (assumed to be an ideal gas with $C_{V,m} = 5R/2$) initially at 300 K and 140 bar expands adiabatically to a final pressure of 1.00 bar.

[9]

a) Calculate T_{final} , q , w , ΔU and ΔH if the expansion is reversible ($p_{\text{external}} = p$).

b) Calculate T_{final} , q , w , ΔU and ΔH if the expansion is irreversible with $p_{\text{external}} = 1.00$ bar.

6. Adiabatic expansions are widely used to liquefy gases. Will the adiabatic expansions described in Question 5 produce any liquid N_2 ? Justify your answer.

[2]

Data: the boiling point of liquid N_2 at 1.00 bar is 77 K.

(Q1)

$$df = \frac{2x^2}{y} dx - \frac{2x^2}{y^3} dy$$

f is a function of x, y (i.e., the function $f(x, y)$ exists)

$$\text{if } \left(\frac{\partial}{\partial y} \frac{2x^2}{y} \right)_x \stackrel{?}{=} \left(\frac{\partial}{\partial x} - \frac{2x^2}{y^3} \right)_y$$

$$LS = \left(\frac{\partial}{\partial y} \frac{2x^2}{y} \right)_x = 2x^2 \left(\frac{\partial}{\partial y} \frac{1}{y} \right)_x = 2x^2 \left(\frac{\partial}{\partial y} \frac{1}{y} \right)_x$$

$$LS = 2x^2 \left(-\frac{1}{y^2} \right)$$

$$RS = \left(\frac{\partial}{\partial x} - \frac{2x^2}{y^3} \right)_y = -\frac{2}{y^3} \frac{\partial x^2}{\partial x} = -\frac{2}{y^3} 2x$$

$$LS \neq RS$$

$f(x, y)$ does not exist

significance:

To calculate f for the change $x_i, y_i \rightarrow x_f, y_f$ the intermediate values of x, y along the path from x_i, y_i to x_f, y_f must be specified.

Q2

$$dV_m = \frac{R}{P} dT - \frac{RT}{P^2} dP$$

V_m is a function of T, P if

$$\left(\frac{\partial \frac{R}{P}}{\partial P} \right)_T \stackrel{?}{=} \left(\frac{\partial \left(-\frac{RT}{P^2} \right)}{\partial T} \right)_P$$

$$LS = \left(\frac{\partial \frac{R}{P}}{\partial P} \right)_T$$

$$= R \left(\frac{\partial P^{-1}}{\partial P} \right)_T$$

$$= R(-1)P^{-2}$$

$$RS = \left(\frac{\partial \left(-\frac{RT}{P^2} \right)}{\partial T} \right)_P = -\frac{R}{P^2} \left(\frac{\partial T}{\partial T} \right)_P$$

$$= -RP^{-2}$$

$LS = RS \Rightarrow$ the function $V_m(T, P)$ exists

(sure! $V_m = RT/P$)

Q3 a) For the purpose of calculating $C_p - C_v$

eq. 2 $C_p - C_v = T \left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_P$ is more reliable

than eq. 3 $C_p - C_v = \left[p + \left(\frac{\partial U}{\partial V} \right)_T \right] \left(\frac{\partial V}{\partial T} \right)_P$

because all of the quantities on the RS of eq. 2 are easily measured (p, V, T) or easily calculated from equations of state (see part b).

In eq. 3, $(\partial U / \partial V)_T$ is not directly measurable.

b) $C_p - C_v$ for an ideal gas ($pV = nRT$)?

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

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

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

$$= \frac{nRT}{V} (1) \frac{nR}{P} (1) = p(1) \frac{nR}{P}$$

$$\boxed{C_p - C_v = nR} \quad \div n \Rightarrow \boxed{C_{pm} - C_{vm} = R}$$

Q4 Convert $P_i V_i^\gamma = P_f V_f^\gamma$ to an equation in terms of P_i, T_i and P_f, T_f

given: $P_i V_i^\gamma = P_f V_f^\gamma$ (note $P_i = P_i^{1-\gamma} P_i^\gamma$)

$$P_i^{1-\gamma} P_i^\gamma V_i^\gamma = P_f^{1-\gamma} P_f^\gamma V_f^\gamma$$

$$P_i^{1-\gamma} (P_i V_i)^\gamma = P_f^{1-\gamma} (P_f V_f)^\gamma$$

$$P_i^{1-\gamma} (nRT_i)^\gamma = P_f^{1-\gamma} (nRT_f)^\gamma$$

$$P_i^{1-\gamma} \cancel{(nR)^\gamma} T_i^\gamma = P_f^{1-\gamma} \cancel{(nR)^\gamma} T_f^\gamma$$

$$P_i^{1-\gamma} T_i^\gamma = P_f^{1-\gamma} T_f^\gamma$$

for the reversible
adiabatic
expansion/compression
of an ideal gas

Q5 Adiabatic expansion of 1.00 mole of N_2 from $T_i = 300$ K and $P_i = 140$ bar to the final pressure $P_f = 1.00$ bar.

$$C_{vm} = \frac{5}{2} R \quad (3 \text{ translations, } 2 \text{ rotations, } \frac{R}{2} \text{ each})$$

$$C_{pm} = C_{vm} + R = \frac{7}{2} R$$

heat capacity ratio $\gamma = \frac{C_p}{C_v} = \frac{C_{pm}/n}{C_{vm}/n} = \frac{C_{pm}}{C_{vm}} = \boxed{\frac{7}{5}}$

(Q5 cont.)

a) reversible adiabatic expansion from 300 K, 140 bar to a final pressure of 1.00 bar

from Question 4: $P_i^{1-\gamma} T_i^\gamma = P_f^{1-\gamma} T_f^\gamma$

$$T_f^\gamma = T_i^\gamma \frac{P_i^{1-\gamma}}{P_f^{1-\gamma}} = T_i^\gamma \left(\frac{P_i}{P_f} \right)^{1-\gamma}$$

$$T_f = (T_f^\gamma)^{1/\gamma} = \left[T_i^\gamma \left(\frac{P_i}{P_f} \right)^{1-\gamma} \right]^{1/\gamma}$$

$$= T_i^{\gamma \cdot \frac{1}{\gamma}} \left(\frac{P_i}{P_f} \right)^{\frac{(1-\gamma)}{\gamma}} = T_i \left(\frac{P_i}{P_f} \right)^{\frac{1-\gamma}{\gamma}}$$

$$= (300 \text{ K}) \left(\frac{140 \text{ bar}}{1.00 \text{ bar}} \right)^{\frac{1-\frac{7}{5}}{\frac{7}{5}}} = (300 \text{ K}) 140^{-2/7}$$

$$T_f = 73.1 \text{ K}$$

$$q = 0 \text{ (adiabatic)} \quad (\therefore \Delta U = \overset{0}{q} + w = w)$$

$$dU_m = C_{vm} dT \text{ (ideal gas)} \quad \Delta U_m = \int_{T_i}^{T_f} C_{vm} dT$$

$$\Delta U_m = C_{vm} (T_f - T_i) = \frac{5}{2} (8.314 \frac{\text{J}}{\text{K mol}}) (73.1 - 300) \text{ K}$$

$$\Delta U_m = -4716 \text{ J mol}^{-1} = w$$

$$\Delta H_m = C_{pm} (T_f - T_i) = \frac{7}{2} (8.314 \frac{\text{J}}{\text{K mol}}) (73.1 - 300) \text{ K} = \boxed{\Delta H_m = -6602 \frac{\text{J}}{\text{mol}}}$$

(Q5 a cont.)

another way to calculate the final temperature =

$$V_{mi} = \frac{RT_i}{P_i} = \frac{(0.08314 \text{ L bar K}^{-1} \text{ mol}^{-1}) 300 \text{ K}}{140 \text{ bar}}$$

$$V_{mi} = 0.1782 \text{ L mol}^{-1}$$

$$P_i V_{mi}^\gamma = P_f V_{mf}^\gamma \quad (\text{reversible adiabatic expansion})$$

$$V_{mf}^\gamma = \frac{P_i}{P_f} V_{mi}^\gamma \quad (V_{mf}^\gamma)^{1/\gamma} = \left(\frac{P_i}{P_f} V_{mi}^\gamma \right)^{1/\gamma}$$

$$V_{mf} = \left(\frac{P_i}{P_f} \right)^{1/\gamma} V_{mi} \quad \gamma = \frac{7}{5} \quad \frac{1}{\gamma} = \frac{5}{7}$$

$$V_{mf} = \left(\frac{140 \text{ bar}}{1 \text{ bar}} \right)^{5/7} 0.1782 \text{ L mol}^{-1}$$

$$V_{mf} = 6.079 \text{ L mol}^{-1}$$

$$T_f = \frac{P_f V_{mf}}{R} = \frac{(1 \text{ bar})(6.079 \text{ L mol}^{-1})}{0.08314 \text{ L bar K}^{-1} \text{ mol}^{-1}}$$

$$T_f = 73.1 \text{ K}$$

(same result obtained using $P_i T_i^{1-\gamma} = P_f T_f^{1-\gamma}$)

(Q5 cont.)

b) irreversible adiabatic expansion of N_2
from 300 K, 140 bar to a final pressure
of 1.00 bar against constant external pressure

$$P_{\text{external}} = 1.00 \text{ bar (constant)}$$

$$dU = d\overset{\nearrow 0 \text{ (adiabatic)}}{q} + dw \quad (\text{First Law})$$

$$C_v dT = 0 - P_{\text{external}} dV \quad (\text{ideal gas: } dU = C_v dT)$$
$$\int_{T_i}^{T_f} C_v dT = - \int P_{\text{external}} dV \quad (C_v, P_{\text{external}} \text{ constant})$$

$$C_v(T_f - T_i) = -P_{\text{external}}(V_f - V_i) \quad (\div n)$$

$$C_{vm}(T_f - T_i) = -P_f(V_{fm} - V_{mi}) \quad (P_{\text{external}} = P_f)$$

$$C_{vm}T_f + P_f V_{mf} = C_{vm}T_i + P_f V_{mi} = C_{vm}T_i + \frac{P_f}{P_i} P_i V_{mi}$$

$$C_{vm}T_f + RT_f = C_{vm}T_i + \frac{P_f}{P_i} RT_i$$

$$T_f (C_{vm} + R) = \left(C_{vm} + \frac{P_f R}{P_i} \right) T_i$$

$$T_f = \frac{C_{vm} + \frac{P_f R}{P_i}}{C_{vm} + R} T_i = \frac{\frac{5}{2}R + \frac{1.00 \text{ bar}}{140 \text{ bar}} R}{\frac{5}{2}R + R} T_i$$

$$T_f = \frac{\frac{5}{2} + \frac{1.00}{140}}{\frac{5}{2} + 1} 300 \text{ K}$$

$$T_f = \boxed{214.9 \text{ K}}$$

(Q5 b cont.)

irreversible adiabatic expansion: $T_i = 300\text{ K}$, $T_f = 214.9\text{ K}$

$$q = 0 \text{ so } \Delta U = W$$

$$dU = C_v dT \quad (\text{ideal gas})$$

$$\Delta U = \int_{T_i}^{T_f} C_v dT = C_v \int_{T_i}^{T_f} dT = C_v (T_f - T_i)$$

per mole:

$$\Delta U_m = C_{v,m} (T_f - T_i) = \frac{5}{2} (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (214.9 - 300) \text{ K}$$

$$\Delta U_m = -1769 \text{ J mol}^{-1} = W$$

$$\Delta H_m = C_{p,m} (T_f - T_i) = (C_{v,m} + R) (T_f - T_i)$$

$$= \frac{7}{2} (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (214.9 - 300) \text{ K}$$

$$\Delta H_m = -2476 \text{ J mol}^{-1}$$

(Q6) Will the adiabatic expansions described in Question 5 produce any liquid N_2 ?

a) reversible adiabatic expansion has $T_f = 73.1\text{ K}$ at $1.00\text{ bar} \Rightarrow$ this temperature is slightly below the boiling point, so a little $\text{N}_2(\text{l})$ will form

b) irreversible adiabatic expansion to 214.9 K at 1.00 bar
 $T = 214.9\text{ K}$ is above the boiling point \Rightarrow no liquid N_2