

1. One mole of an ideal gas is compressed isothermally from 1.00 bar and 25.0 L to 100.0 bar and 0.250 L.

[8]

a) Calculate  $q$ ,  $w$ ,  $\Delta U$  and  $\Delta H$  if the compression is

i) irreversible with  $p_{\text{external}} = 100.0$  bar

ii) reversible ( $p_{\text{external}} = p$ )

b) Use the results from part a) to illustrate that the enthalpy and internal energy are state functions, but heat and work are path-dependent.

2. One mole of a gas obeying the van der Waals equation

[7]

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

with  $a = 5.580 \text{ L}^2 \text{ bar mol}^{-2}$  and  $b = 0.0651 \text{ L mol}^{-1}$  is compressed reversibly and isothermally from 25.0 L and 0.991 bar to 0.250 L and 45.6 bar at 300 K.

a) Calculate  $q$ ,  $w$ ,  $\Delta U$  and  $\Delta H$ .

b) Do attractive forces (represented by the van der Waals  $a$  coefficient) increase or decrease the amount of work required to compress the gas? Justify your answer.

c) Do repulsive forces (represented by van der Waals  $b$  coefficient) increase or decrease the amount of work required to compress the gas? Justify your answer.

The following equations may be used to answer this question:

$$\int_{V_{m1}}^{V_{m2}} \frac{1}{V_m - b} dV_m = \ln \left( \frac{V_{m2} - b}{V_{m1} - b} \right) \quad \int_{V_{m1}}^{V_{m2}} \frac{1}{V_m^2} dV_m = \frac{1}{V_{m1}} - \frac{1}{V_{m2}} \quad \left( \frac{\partial U_m}{\partial V_m} \right)_T = \frac{a}{V_m^2}$$

3. The heat capacity of propane at 1.00 bar is accurately represented by the equation

[5]

$$C_{pm}(T) = A_1 + A_2 T + A_3 T^2$$

with constants  $A_1 = 0.56 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $A_2 = 0.27559 \text{ J K}^{-2} \text{ mol}^{-1}$ ,  $A_3 = -0.00010355 \text{ J K}^{-3} \text{ mol}^{-1}$ .

a) Calculate  $C_p$  for 10.00 moles of propane at 300 K and 1.00 bar. Why does the heat capacity of propane *increase* as the temperature is raised?

b) 10.00 moles of propane (assumed to be an ideal gas) is reversibly heated from 300 K to 500 K at 1.00 bar. Calculate  $q$ ,  $w$ ,  $\Delta U$  and  $\Delta H$ .

1. a) i)  $P_{\text{ext}} = 1.00 \text{ bar}$  (irreversible compression)

$$w = - \int_{V_i}^{V_f} P_{\text{ext}} dV = - P_{\text{ext}} \int_{V_i}^{V_f} dV = - P_{\text{ext}} (V_f - V_i)$$

$$w = -(100.0 \text{ bar})(0.250 - 25.0) \text{ L}$$

$$= +2475 \text{ L bar} = 2475 \text{ L bar} \left( \frac{10^{-3} \text{ m}^3}{\text{L}} \right) \left( \frac{10^5 \text{ Pa}}{\text{bar}} \right)$$

$$w = 247.5 \text{ kJ}$$

$U$  is constant for an isothermal ideal gas  
[recall  $(\partial U / \partial V)_T = 0$  if  $pV = nRT$ ]

$$\Delta U = 0$$

$$\Delta U = q + w$$

$$q = \Delta U - w = -w$$

$$q = -247.5 \text{ kJ}$$

$$H = U + pV \quad \text{so}$$

$$\Delta H = \Delta(U + pV)$$

$$= \Delta U + \Delta(pV)$$

$$= \Delta U + \Delta(nRT) = 0 + 0$$

$$\Delta H = 0$$

notice  $q \neq \Delta H$  (pressure not constant)

$$T = \frac{pV}{nR} = \frac{(1.00 \text{ bar})(25.0 \text{ L})}{(1.00 \text{ mol})(0.08314 \text{ L bar K}^{-1} \text{ mol}^{-1})}$$

$$T = 300.7 \text{ K}$$

(1. cont.) a) ii)  $P_{\text{ext}} = P$  (reversible compression)

$$w = - \int P_{\text{ext}} dV = - \int P dV = - \int \frac{nRT}{V} dV$$

$$w = - nRT \int_{V_i}^{V_f} \frac{dV}{V} = - nRT \ln\left(\frac{V_f}{V_i}\right)$$

$$w = -(1.00 \text{ mol})(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(300.7 \text{ K}) \ln\left(\frac{0.250 \text{ L}}{25.0 \text{ L}}\right)$$

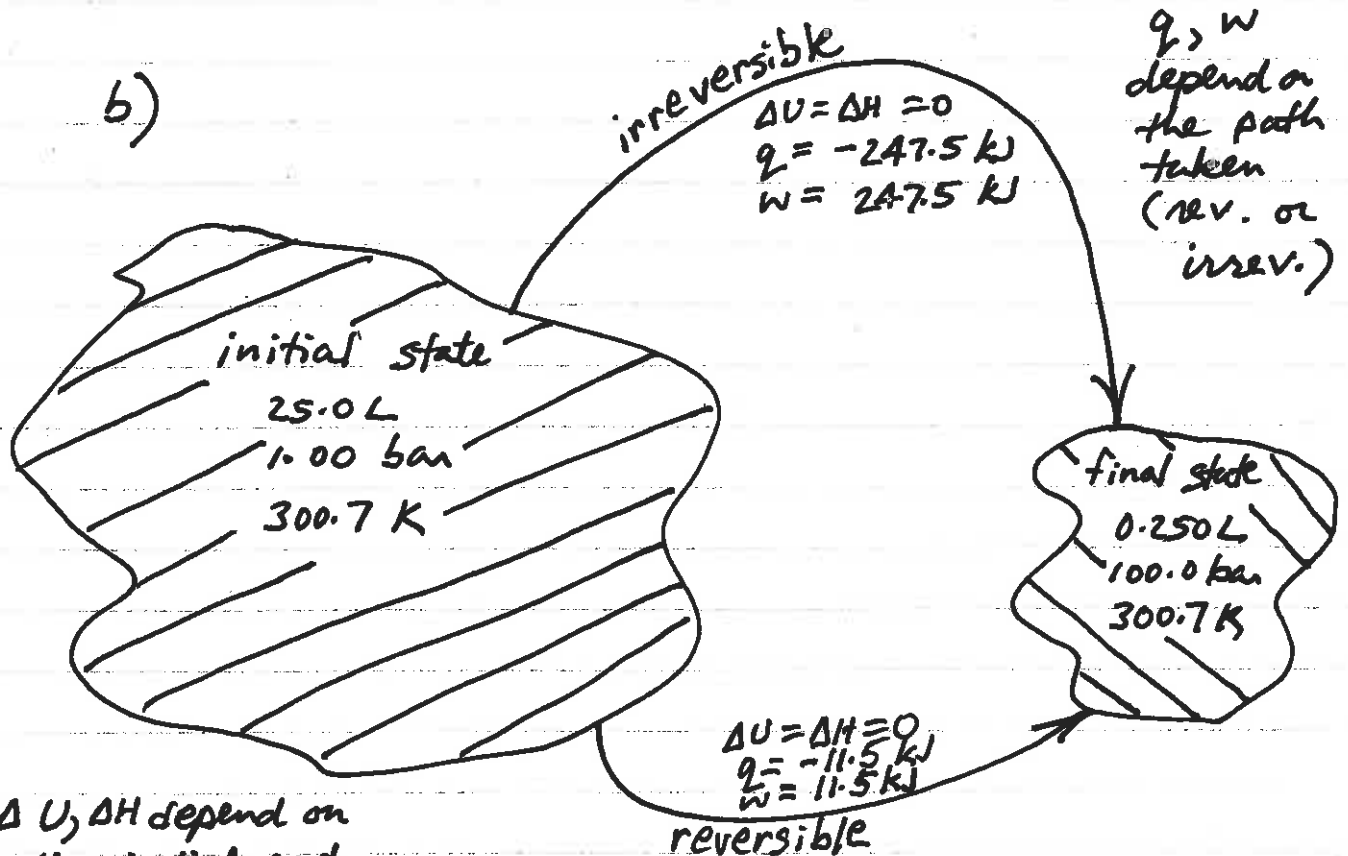
$$w = 11.5 \text{ kJ}$$

$$\Delta U = 0$$

$$\Delta H = 0$$

$$q = -11.5 \text{ kJ}$$

b)



2. a)  $w = - \int p_{\text{ext}} dV = - \int p dV$  (reversible)

for one mole:

$$w = - \int \left( \frac{RT}{V_m - b} - \frac{a}{V_m^2} \right) dV_m$$

watch the sign (positive) here!

$$w = - RT \int_{V_{m1}}^{V_{m2}} \frac{dV_m}{V_m - b} + a \int_{V_{m1}}^{V_{m2}} \frac{dV_m}{V_m^2}$$

$$w = - RT \ln \left( \frac{V_{m2} - b}{V_{m1} - b} \right) + a \left( \frac{1}{V_{m1}} - \frac{1}{V_{m2}} \right)$$

$$= \left( -0.08314 \frac{\text{L bar}}{\text{K mol}} \right) (300\text{K}) \ln \left( \frac{0.250 - 0.0651}{25.0 - 0.0651} \right)$$

$$+ 5.580 \frac{\text{L}^2 \text{bar}}{\text{mol}^2} \left( \frac{1}{25.0\text{L}} - \frac{1}{0.250\text{L}} \right)$$

$$= 122.3 - 22.1 \text{ L bar}$$

$$w = 100.2 \text{ L bar} \left( \frac{10^{-3} \text{ m}^3}{\text{L}} \right) \left( \frac{10^5 \text{ Pa}}{\text{bar}} \right)$$

$$w = 10.02 \text{ kJ}$$

$$dU_m = \left( \frac{\partial U_m}{\partial T} \right)_{V_m} dT + \left( \frac{\partial U_m}{\partial V_m} \right)_T dV_m = \frac{a}{V_m^2} dV_m$$

(isothermal)

$$\Delta U_m = \int_{U_{m1}}^{U_{m2}} dU_m = \int_{V_{m1}}^{V_{m2}} \frac{a}{V_m^2} dV_m = a \int_{V_{m1}}^{V_{m2}} \frac{dV_m}{V_m^2} = -22.1 \text{ L bar}$$

$$\Delta U_m = -2.21 \text{ kJ} \quad (\text{not zero, not an ideal gas})$$

(2 cont.)  $\Delta U_m = q + w$   $q = \Delta U_m - w$

$q = -2.21 - 10.02 \text{ kJ}$   $q = -12.23 \text{ kJ}$

$\Delta H = \Delta(U + pV) = \Delta U + \Delta(pV)$

$\Delta H_m = \Delta U_m + \Delta(pV_m) = \Delta U_m + p_f V_{mf} - p_i V_{mi}$   
 $= \Delta U_m + [(45.6)(0.250) - (0.991)(25.0)] \text{ L bar mol}^{-1}$   
 $= \Delta U_m + (-13.38 \text{ L bar})$   
 $= -2.21 \text{ kJ} - 1.338 \text{ kJ mol}^{-1}$

$\Delta H_m = -3.548 \text{ kJ mol}^{-1}$

b) repulsion effect on compression work:

compare  $-RT \int_{V_m}^{V_{m-b}} \frac{dV_m}{V_m - b} = 12.23 \frac{\text{kJ}}{\text{mol}}$  including b positive

with  $-RT \int_{V_m}^{V_{mi}} \frac{dV_m}{V_m} = -(8.314)(300) \ln\left(\frac{0.250}{25.0}\right) = 11.49 \frac{\text{kJ}}{\text{mol}}$   
 (b=0, ideal gas, no repulsion) negative

more work required to compress a gas with repulsive forces operating

c) attractive effect on compression work:

contributes  $-\int_{V_{mi}}^{V_{mf}} \left(-\frac{a}{V_m^2}\right) dV_m = -2.21 \frac{\text{kJ}}{\text{mol}}$  negative

reduces the work required to compress the gas

3. a) at 300 K:

$C_p$  and  $C_{pm}$  increase as the temperature is raised because propane molecules vibrate more actively, absorbing extra heat

$$\begin{aligned}C_{pm} &= A_1 + A_2 T + A_3 T^2 \\&= 0.56 + 0.27559(300) - (0.00010355) 300^2 \\&= 0.56 + 82.677 - 9.320 \\&= 73.92 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

$$C_p = n C_{pm} = (10.00 \text{ mol})(73.92 \text{ J K}^{-1} \text{ mol}^{-1}) = \boxed{739.2 \text{ J K}^{-1}}$$

b) for 1.00 mol:  $\left( C_{pm} = \frac{dq_{p,p}}{dT} \text{ at const. pressure} \right)$

$$q_m = \int_{T_i}^{T_f} C_{pm} dT = \int_{T_i}^{T_f} (A_1 + A_2 T + A_3 T^2) dT$$

$$= A_1 \int_{T_i}^{T_f} dT + A_2 \int_{T_i}^{T_f} T dT + A_3 \int_{T_i}^{T_f} T^2 dT$$

$$= A_1 T \Big|_{T_i}^{T_f} + A_2 \frac{T^2}{2} \Big|_{T_i}^{T_f} + A_3 \frac{T^3}{3} \Big|_{T_i}^{T_f}$$

$$= A_1 (T_f - T_i) + \frac{A_2}{2} (T_f^2 - T_i^2) + \frac{A_3}{3} (T_f^3 - T_i^3)$$

$$= 0.56(500 - 300) + \frac{0.27559}{2}(500^2 - 300^2) - \frac{0.00010355}{3}(500^3 - 300^3)$$

$$= 112.0 + 22.047 - 3.383$$

$$\boxed{q_m = 18.78 \text{ kJ mol}^{-1} = \Delta H_m}$$

(heating at const.  $p$ )

$$w_m = - \int p_{\text{ext}} dV_m = - \int p dV_m \text{ (reversible)}$$

$$w_m = - p dV_m \text{ (} p \text{ constant)}$$

(3 b cont.)

$$w_m = -p(V_{mf} - V_{mi})$$

$$P_f = P_i = P$$

$$= -p \left( \frac{RT_f}{P_f} - \frac{RT_i}{P_i} \right)$$

$$= -R(T_f - T_i)$$

$$= -(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(500 - 300) \text{ K}$$

$$w_m = -1.663 \text{ kJ mol}^{-1}$$

$$\Delta U_m = q_m + w_m = 18.78 - 1.66 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta U_m = 17.12 \text{ kJ mol}^{-1}$$

$$q = nq_m = (10.0 \text{ mol})(18.78 \text{ kJ mol}^{-1})$$

$$q = 187.8 \text{ kJ} = \Delta H$$

$$w = nw_m = -(10.0 \text{ mol})(1.663 \text{ kJ mol}^{-1})$$

$$w = -16.63 \text{ kJ}$$

$$\Delta U = n\Delta U_m$$

$$\Delta U = 171.2 \text{ kJ}$$