

1. Two moles of an ideal gas expand isothermally from 5.00 L to 75.0 L at 350 K.

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

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

c) Use the results from a and b to illustrate that the change in internal energy and the change in enthalpy (both state functions) depend only on the initial and final states of a system, but work and heat depend on the path taken in the process connecting the initial and final states.

2. One mole of gas is reversibly compressed from 25.0 L to 1.00 L at 300 K. Calculate the work w

[7] a) if the gas is ideal

b) if the gas obeys the equation

$$Z = \frac{pV_m}{RT} = 1 + \frac{B(T)}{V_m}$$

with $B(T) = -0.116 \text{ L mol}^{-1}$.

c) Use the results from a and b to show that attractive intermolecular forces make it “easier” (less work required) to compress a gas. Does this make sense? Comment briefly.

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

[5]
$$C_{pm}(T) = A_1 + A_2T + A_3T^2$$

with constants $A_1 = 0.5600 \text{ J K}^{-1} \text{ mol}^{-1}$

$$A_2 = 0.2756 \text{ J K}^{-2} \text{ mol}^{-1}$$

$$A_3 = -0.0001036 \text{ J K}^{-3} \text{ mol}^{-1}.$$

Ten moles of propane (assumed to be an ideal gas) is reversibly cooled from 400 K to 300 K at 1.00 bar. Calculate q , w , ΔU and ΔH .

$$P = P_{\text{ext}}$$

- Q1 a) Two moles of ideal gas expand reversibly and isothermally from 5.00 L to 75.0 L at 350 K.

isothermal ideal gas: $\Delta U = 0$ (proved $\left(\frac{\partial U}{\partial V}\right)_T = 0$ for ideal gases)

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

$$\Delta H = \Delta U + \Delta(nRT) = 0 + 0 \text{ for isothermal ideal gases}$$

↑ ↑
const. const.

$$\Delta H = 0$$

reversible ($P = P_{\text{ext}}$) expansion:

$$w = - \int P_{\text{ext}} dV = - \int \frac{nRT}{V} dV = -nRT \int_{V_i}^{V_f} \frac{1}{V} dV$$

$$= -nRT \left(\ln V \Big|_{V_i}^{V_f} \right) = -nRT (\ln V_f - \ln V_i)$$

$$w = -nRT \ln(V_f/V_i) = -(2.00 \text{ mol}) \left(8.314 \frac{\text{J}}{\text{K mol}} \right) (350 \text{ K}) \ln \left(\frac{75.0 \text{ L}}{5.00 \text{ L}} \right)$$

$$w = -15760 \text{ J}$$

$$\Delta U = q + w = 0$$

$$q = -w = 15760 \text{ J}$$

$$P_{\text{ext}} < P$$

$$P = P_f$$

- b) Two moles of ideal gas expand irreversibly and isothermally from 5.00 L to 75.0 L at 350 K.

$$\Delta U = 0$$

$$\Delta H = 0 \quad (\text{isothermal ideal gas})$$

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

$$P_f = \frac{nRT}{V_f} = \frac{(2.00 \text{ mol}) \left(0.08314 \frac{\text{L bar}}{\text{K mol}} \right) (350 \text{ K})}{75.0 \text{ L}} = 0.7760 \text{ bar}$$

(Q1 b), cont.)

$$w = -P_f(V_f - V_i)$$

convert L·bar
to $\text{m}^3 \cdot \text{Pa} = \text{J}$

$$= -(0.7760 \text{ bar})(75.0 \text{ L} - 5.00 \text{ L}) \left(\frac{10^5 \text{ Pa}}{\text{bar}} \right) \left(\frac{10^{-3} \text{ m}^3}{\text{L}} \right)$$

$$w = -5430 \text{ J}$$

$$q = 5430 \text{ J}$$

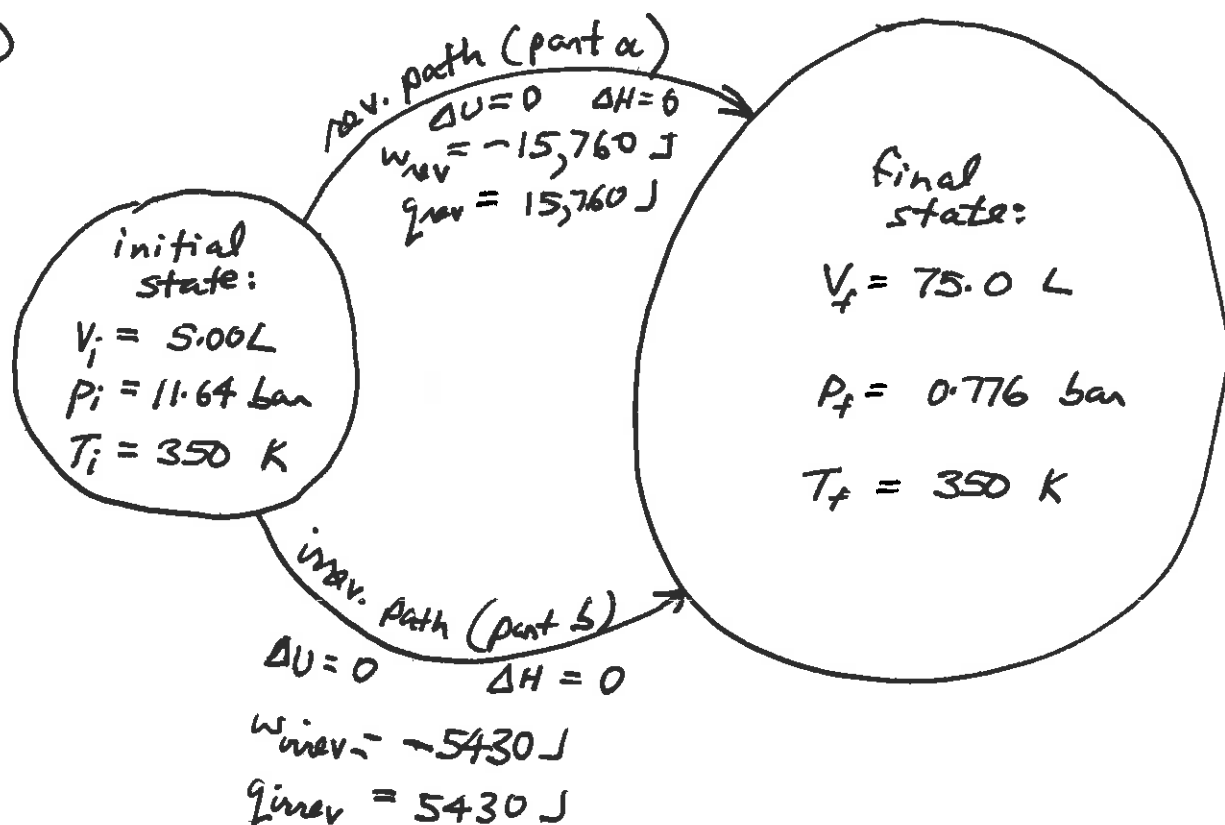
(because $\Delta U = q + w = 0$)

notice the reversibly expanding gas does more work on the surroundings than the irreversibly expanding gas:

$$w_{\text{rev}} = -15760 \text{ J}$$

$$w_{\text{irrev}} = -5430 \text{ J}$$

c)



ΔU and ΔH are path-independent (U and H are state functions)

q and w depend on the path taken
 $w_{\text{rev}} \neq w_{\text{irrev}}$
 $q_{\text{rev}} \neq q_{\text{irrev}}$

(Q2) a) One mole of an ideal gas is reversibly compressed from 25.0 L to 1.00 L at 300 K.

$$P_{\text{ext}} = P$$

$$w = -\int P_{\text{ext}} dV = -\int p dV = -\int \frac{nRT}{V} dV = -nRT \int \frac{1}{V} dV$$

$$w = -(nRT) \ln V \Big|_{V_i}^{V_f} = -nRT (\ln V_f - \ln V_i) = -nRT \ln \left(\frac{V_f}{V_i} \right)$$

$$w = -(1.00 \text{ mol}) \left(8.314 \frac{\text{J}}{\text{K mol}} \right) (300 \text{ K}) \ln \left(\frac{1.00 \text{ L}}{25.0 \text{ L}} \right)$$

$$w = 8028 \text{ J}$$

b) One mole of a gas obeying the equation of state

$$z = \frac{pV_m}{RT} = 1 + \frac{B(T)}{V_m} \quad \left[B(T) = -0.116 \frac{\text{L}}{\text{mol}} \right]$$

is reversibly compressed ($P_{\text{ext}} = P$) from 25.0 L to 1.00 L at 300 K.

$$w = -\int P_{\text{ext}} dV = -\int p dV = -\int z \frac{RT}{V_m} dV$$

$$\text{rearrange } \frac{pV_m}{RT} = \frac{pV}{nRT} = 1 + \frac{B(T)}{V_m}$$

Substitute

to get

$$p = \frac{RT}{V_m} \left(1 + \frac{B(T)}{V_m} \right) = \frac{RT}{V_m} + RT B(T) \frac{1}{V_m^2}$$

(Q2 b) cont.)

$$\text{work } w = - \int p dV = - \int \left(\frac{RT}{V_m} + \frac{RT B(T)}{V_m^2} \right) dV$$

$$w = - \int \left(\frac{nRT}{V} + \frac{n^2 RT B(T)}{V^2} \right) dV$$

$$= - \int \frac{nRT}{V} dV - \int \frac{n^2 RT B(T)}{V^2} dV$$

$n, R, T, B(T)$
constant

$$= - nRT \int \frac{dV}{V} - n^2 RT B(T) \int \frac{dV}{V^2}$$

$$= - nRT (\ln V) \Big|_{V_i}^{V_f} - nRT B(T) \left(-\frac{1}{V} \right) \Big|_{V_i}^{V_f}$$

$$= - nRT (\ln V_f - \ln V_i) - nRT B(T) \left[-\frac{1}{V_f} - \left(-\frac{1}{V_i} \right) \right]$$

$$= - nRT \ln \left(\frac{V_f}{V_i} \right) - nRT B(T) \left(\frac{1}{V_i} - \frac{1}{V_f} \right)$$

$$= -(1.00 \text{ mol}) \left(0.08314 \frac{\text{L bar}}{\text{K mol}} \right) (300 \text{ K}) \ln \left(\frac{1.00 \text{ L}}{25.0 \text{ L}} \right)$$

$$- (1.00 \text{ mol}) \left(0.08314 \frac{\text{L bar}}{\text{K mol}} \right) (300 \text{ K}) \left(-0.116 \frac{\text{L}}{\text{mol}} \right) \left(\frac{1}{25.0 \text{ L}} - \frac{1}{1.00 \text{ L}} \right)$$

$$= 80.28 \text{ L bar} - 2.78 \text{ L bar}$$

$$= 77.5 \text{ L bar}$$

conversion factor:

$$\boxed{1 \text{ L bar} \approx 100 \text{ J}}$$

$$= (77.5 \text{ L bar}) \left(10^{-3} \frac{\text{m}^3}{\text{L}} \right) \left(10^5 \frac{\text{Pa}}{\text{bar}} \right)$$

$$\boxed{w = 7750 \text{ J}}$$

(Q2 cont.)

c) ideal gas compression (part a) $w = 8028 \text{ J}$

real gas compression (part b) $w = 7750 \text{ J}$
with $B = -0.116 \text{ L mol}^{-1}$

$$\therefore Z = 1 + \frac{B}{V_m} < 1 \Rightarrow \text{attractive forces dominate}$$

Less work required to compress a real gas with attractive intermolecular forces relative to an ideal gas with no intermolecular forces

makes sense: attractive forces help to pull molecules together as they are compressed

Q3 10.0 mol propane (assumed to be an ideal gas)
reversibly cooled from 400 K to 300 K at 1.00 bar

$q?$ $w?$ $\Delta H?$ $\Delta U?$

At constant pressure (1.00 bar here) $q = \Delta H$
and $dq = dH$.

The enthalpy of the propane (treated as an ideal gas) depends only on T .
($H_m = \frac{H}{n}$)

At constant pressure:

$$\text{heat capacity } C_p = \frac{dH(T)}{dT} = n \frac{dH_m(T)}{dT} = n C_{p,m}$$

$$dq = dH = n C_{p,m} dT \quad \text{Integrate } C_{p,m} \text{ to calculate } q \text{ and } \Delta H$$

(Q3 cont.)

enthalpy change $\Delta H = \int_{H_i}^{H_f} dH = \int_{T_i}^{T_f} n C_{pm} dT$

$T_i = 400 \text{ K}$
 $T_f = 300 \text{ K}$

$$= n \int_{T_i}^{T_f} (A_1 + A_2 T + A_3 T^2) dT$$
$$= n A_1 \int dT + n A_2 \int T dT + n A_3 \int T^2 dT$$
$$= n A_1 (T) \Big|_{T_i}^{T_f} + n A_2 \left(\frac{T^2}{2} \right) \Big|_{T_i}^{T_f} + n A_3 \left(\frac{T^3}{3} \right) \Big|_{T_i}^{T_f}$$
$$= n A_1 (T_f - T_i) + \frac{n A_2}{2} (T_f^2 - T_i^2) + \frac{n A_3}{3} (T_f^3 - T_i^3)$$

$$\Delta H = (100 \text{ mol}) \left(0.5600 \frac{\text{J}}{\text{K mol}} \right) (300 - 400) \text{ K} \quad (n = 10.0 \text{ mol})$$
$$+ (100 \text{ mol}) \left(\frac{0.2756 \text{ J}}{2 \text{ K}^2 \text{ mol}} \right) (300^2 - 400^2) \text{ K}^2$$
$$+ (100 \text{ mol}) \left(\frac{-0.0001036 \text{ J}}{3 \text{ K}^3 \text{ mol}} \right) (300^3 - 400^3) \text{ K}^3$$

$$\Delta H = -560 \text{ J} - 96460 \text{ J} + 12770 \text{ J}$$

$$\Delta H = -84,250 \text{ J} = q$$

pressure p is constant (1.00 bar)

$$w = - \int p_{\text{ext}} dV = -p \int dV = -p (V_f - V_i) = -p \left(\frac{nRT_f}{p} - \frac{nRT_i}{p} \right)$$

$$w = -nR(T_f - T_i) = -(10.0 \text{ mol}) (8.314 \frac{\text{J}}{\text{K mol}}) (300 \text{ K} - 400 \text{ K})$$

$$w = 8314 \text{ J}$$

$$q + w = -84,250 \text{ J} + 8314 \text{ J} = \Delta U$$

$$\Delta U = -75,940 \text{ J}$$