

From Atkins and de Paula's *Physical Chemistry*, 8th ed.

2.3(b) A sample consisting of 2.00 mol He is expanded isothermally at 22°C from 22.8 dm³ to 31.7 dm³ (a) reversibly, (b) against a constant external pressure equal to the final pressure of the gas, and (c) freely (against zero external pressure). For the three processes calculate q , w , ΔU , and ΔH .

In all 3 cases, the initial states are the same and the final states are the same. $\therefore \Delta U$ (and ΔH , which we'll discuss later) must also be the same.

Specifically, $\Delta U = nC_{v,m}\Delta T = 0$ since $\Delta T = 0$

(a) Reversibly is when $p_{\text{ext}} = p_{\text{sys}}$ (move in a moment)

$$\text{so } w = -nRT \ln\left(\frac{V_f}{V_i}\right) = -(2.00 \text{ mol}) \left(\frac{8.31447 \text{ J}}{\text{mol K}}\right) (295.15 \text{ K}) \\ \times \ln\left(\frac{31.7 \text{ dm}^3}{22.8 \text{ dm}^3}\right) = \boxed{-1.617 \text{ kJ}}$$

$$\text{and } \boxed{q = -w = +1.617 \text{ kJ}}$$

(b) $p_{\text{ext}} = p_f$ throughout expansion,

$$\text{and } p_f = \frac{nRT}{V_f} = (2.00 \text{ mol}) \left(\frac{0.082058 \text{ K atm}}{\text{mol K}}\right) \left(\frac{295.15 \text{ K}}{31.7 \text{ K}}\right) \\ = 1.528 \text{ atm}$$

$$\text{so } w = -p_{\text{ext}} \Delta V = (-1.528 \text{ atm}) \underbrace{(31.7 - 22.8) \text{ K}}_{\text{down to 2 sf!}} \left(\frac{101.325 \text{ J}}{\text{K atm}}\right)$$

$$\boxed{w = -1.378 \text{ kJ}} \Rightarrow \boxed{q = +1.378 \text{ kJ}}$$

