

- 1) Calculate the molar entropy of a constant volume sample of nitrogen, N₂, at 350 K given that it is 191.61 J K⁻¹ mol⁻¹ at 298 K.

E3.2(c) If we assume that neon is a perfect gas then $C_{V,m}$ may be taken to be constant and given by

$$\begin{aligned} C_{V,m} &= C_{p,m} - R; & C_{p,m} &= 29.125 \text{ J K}^{-1} \text{ mol}^{-1} \text{ [Table 2.6]} \\ & & &= (29.125 - 8.314) \text{ J K}^{-1} \text{ mol}^{-1} \\ & & &= 20.811 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

Integrating, we obtain

$$\begin{aligned} S_m(500 \text{ K}) &= S_m(298 \text{ K}) + C_{V,m} \ln \frac{T_f}{T_i} \\ &= (191.61 \text{ J K}^{-1} \text{ mol}^{-1}) + (20.811 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \left(\frac{350 \text{ K}}{298 \text{ K}} \right) \\ &= (191.61 + 3.35) \text{ J K}^{-1} \text{ mol}^{-1} = \boxed{194.96 \text{ J K}^{-1} \text{ mol}^{-1}} \end{aligned}$$

- 2) Calculate ΔS (for the system) when the state of 2.50 moles of nitrogen, assumed to be an ideal gas, is changed from 25 °C and 2.00 atm to 125 °C and 8.00 atm.

E3.3(c) However the change occurred ΔS has the same value as if the change happened by reversible heating at constant pressure (step 1) followed by reversible isothermal compression (step 2)

$$\Delta S = \Delta S_1 + \Delta S_2$$

For the first step

$$\Delta S_1 = \int \frac{dq_{\text{rev}}}{T} = \int \frac{C_{p,m} dT}{T} = C_{p,m} \ln \frac{T_f}{T_i}$$

$$\Delta S_1 = (2.50 \text{ mol}) \times \left(\frac{7}{2} \right) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln \frac{(125 + 273) \text{ K}}{(25 + 273) \text{ K}} = 21.05 \text{ J K}^{-1}$$

and for the second

$$\Delta S_2 = \int \frac{dq_{\text{rev}}}{T} = \frac{q_{\text{rev}}}{T}$$

$$\text{where } q_{\text{rev}} = -w = \int p dV = nRT \ln \frac{V_f}{V_i} = nRT \ln \frac{p_i}{p_f}$$

$$\text{so } \Delta S_2 = nR \ln \frac{p_i}{p_f} = (2.50 \text{ mol}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln \frac{2.00 \text{ atm}}{8.00 \text{ atm}} = -28.81 \text{ J K}^{-1}$$

$$\Delta S = (21.05 - 28.81) \text{ J K}^{-1} = \boxed{-7.8 \text{ J K}^{-1}}$$

- 3) Consider a system consisting of 3.0 moles of $\text{CO}_2(\text{g})$, initially at 35°C and 9.0 atm and confined to a cylinder of cross-section 100.0 cm^2 . The sample is allowed to expand adiabatically against an external pressure of 2.5 atm until the piston has moved outwards through 25 cm. Assume that carbon may be considered an ideal gas with a $C_{V,m} = 28.8\text{ J K}^{-1}\text{ mol}^{-1}$, and calculate (a) q , (b) w , (c) ΔU , (d), ΔT , (e) ΔS .

E3.6(c) (a) $q = 0$ [adiabatic]

$$(b) w = -p_{\text{ex}}\Delta V = -(2.5\text{ atm}) \times \left(\frac{1.01 \times 10^5\text{ Pa}}{\text{atm}} \right) \times (100.0\text{ cm}^2) \times (25\text{ cm}) \times \left(\frac{1\text{ m}^3}{10^6\text{ cm}^3} \right)$$

$$= -517.6\text{ J} = \boxed{-518\text{ J}}$$

$$(c) \Delta U = q + w = 0 - 518\text{ J} = \boxed{-518\text{ J}}$$

$$(d) \Delta U = nC_{V,m}\Delta T$$

$$\Delta T = \frac{\Delta U}{nC_{V,m}} = \frac{-518\text{ J}}{(2.5\text{ mol}) \times (28.8\text{ J K}^{-1}\text{ mol}^{-1})}$$

$$= \boxed{-7.2\text{ K}}$$

(e) Entropy is a state function, so we can compute it by any convenient path. Although the specified transformation is adiabatic, a more convenient path is constant-volume cooling followed by isothermal expansion. The entropy change is the sum of the entropy changes of these two steps:

$$\Delta S = \Delta S_1 + \Delta S_2 = nC_{V,m} \ln\left(\frac{T_f}{T_i}\right) + nR \ln\left(\frac{V_f}{V_i}\right) \quad [3.19 \ \& \ 3.13]$$

$$T_f = 308.2\text{ K} - 7.2\text{ K} = 301.2\text{ K}$$

$$V_i = \frac{nRT}{p_i} = \frac{(2.5\text{ mol}) \times (8.206 \times 10^{-2}\text{ dm}^3\text{ atm K}^{-1}\text{ mol}^{-1}) \times (308.2\text{ K})}{9.0\text{ atm}}$$

$$= 7.025\text{ dm}^3$$

$$V_f = 7.025\text{ dm}^3 + (100\text{ cm}^2) \times (15\text{ cm}) \times \left(\frac{1\text{ dm}^3}{1000\text{ cm}^3} \right)$$

$$= 7.025\text{ dm}^3 + 2.5\text{ dm}^3 = 9.53\text{ dm}^3$$

$$\Delta S = (2.5\text{ mol}) \times \left\{ (28.8\text{ J K}^{-1}\text{ mol}^{-1}) \times \ln\left(\frac{301}{308}\right) \right.$$

$$\left. + (8.314\text{ J K}^{-1}\text{ mol}^{-1}) \times \ln\left(\frac{9.53}{7.025}\right) \right\}$$

$$= 2.5\text{ mol}(-0.662\text{ J K}^{-1}\text{ mol}^{-1} + 2.536\text{ J K}^{-1}\text{ mol}^{-1}) = \boxed{4.7\text{ J K}^{-1}}$$

- 4) The enthalpy of vaporization of ethanol is 43.5 kJ mol^{-1} at its normal boiling point of 352 K . Calculate (a) the entropy of vaporization of ethanol at this temperature and (b) the entropy of the surroundings.

E3.7(c) (a) $\Delta_{\text{vap}}S = \frac{\Delta_{\text{vap}}H}{T_b} = \frac{43.5 \times 10^3 \text{ J mol}^{-1}}{352 \text{ K}} = +123.6 \text{ J K}^{-1} = \boxed{124 \text{ J K}^{-1}}$
 (b) If vaporization occurs reversibly, as is generally assumed

$$\Delta S_{\text{sys}} + \Delta S_{\text{sur}} = 0 \quad \text{so} \quad \Delta S_{\text{sur}} = \boxed{-124 \text{ J K}^{-1}}$$

- 5) Calculate the maximum non-expansion work per mole that be obtained from a fuel cell in which the chemical reaction is the combustion of ethanol at 298 K .

E3.14(c) $\text{C}_2\text{H}_5\text{OH}(l) + 3\text{O}_2(g) \rightarrow 2\text{CO}_2(g) + 3\text{H}_2\text{O}(l)$
 $\Delta_r G^\ominus = \sum_{\text{Products}} \nu \Delta_f G^\ominus - \sum_{\text{Reactants}} \nu \Delta_f G^\ominus$ [3.40]
 $\Delta_r G^\ominus = 2\Delta_f G^\ominus(\text{CO}_2, g) + 3\Delta_f G^\ominus(\text{H}_2\text{O}, l) - \Delta_f G^\ominus(\text{C}_2\text{H}_5\text{OH}, l)$
 $= \{2 \times (-394.36) + (3 \times -237.13) - (-174.78)\} \text{ kJ mol}^{-1} = -1325.33 \text{ kJ mol}^{-1}$

Therefore, the maximum non-expansion work is $\boxed{1325.33 \text{ kJ mol}^{-1}}$ since $|w_{\text{add}}| = |\Delta G|$.

- 6) Calculate the Carnot efficiency of a primitive steam engine operating on steam at $180 \text{ }^\circ\text{C}$ and discharging at $100 \text{ }^\circ\text{C}$. (b) Repeat the calculation for a modern steam turbine with steam at $360 \text{ }^\circ\text{C}$ and $100 \text{ }^\circ\text{C}$.

E3.15(c) $\varepsilon_{\text{rev}} = 1 - \frac{T_c}{T_h}$ [3.10]
 $\varepsilon = 1 - \frac{373 \text{ K}}{353 \text{ K}} = \boxed{0.18}$ (18 per cent efficiency for the old steam engine)
 $\varepsilon = 1 - \frac{453 \text{ K}}{633 \text{ K}} = \boxed{0.41}$ (41 per cent efficiency for the modern turbine)

- 7) Suppose that 2.5 moles of Ar(g) occupies 72 dm³ at 298 K and expands to 100 dm³. Calculate ΔG for the process.

$$\text{E3.16(c)} \quad \Delta G = nRT \ln\left(\frac{p_f}{p_i}\right) [3.56] = nRT \ln\left(\frac{V_i}{V_f}\right) \text{ [Boyle's law]}$$

$$\Delta G = (2.5 \text{ mol}) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times \ln\left(\frac{72}{100}\right) = \boxed{-2.0 \text{ kJ}}$$