

Exercise

3A.2(b) Efficiency, η , is $\frac{\text{work performed}}{\text{heat absorbed}} = \frac{|w|}{q_h} = \frac{0.71 \text{ kJ}}{2.71 \text{ kJ}} = 0.262$. For an ideal

Heat engine we have $\eta_{\text{rev}} = 1 - \frac{T_c}{T_h}$ [3A.10] $= 0.262 = 1 - \frac{T_c}{273.16 \text{ K}}$. Solving for T_c , we

obtain $T_c = 201.6 \text{ K}$ as the temperature of the organic liquid.

3A.9(b) Since the masses are equal and the heat capacity is assumed constant, the final temperature will be the average of the two initial temperatures,

$$T_f = \frac{1}{2}(100^\circ \text{C} + 25^\circ \text{C}) = 62.5^\circ \text{C}$$

The heat capacity of each block is $C = mC_s$ where C_s is the specific heat capacity.

So,

$$\Delta H(\text{individual}) = mC_s \Delta T = 10.0 \times 10^3 \text{ g} \times 0.449 \text{ J K}^{-1} \text{ g}^{-1} \times (\pm 37.5 \text{ K}) = \pm 168 \text{ kJ}$$

These two enthalpy changes add up to zero: $\Delta H_{\text{tot}} = 0$

$$\Delta S = mC_s \ln\left(\frac{T_f}{T_i}\right); \quad 100^\circ \text{C} = 373.2 \text{ K}; \quad 25^\circ \text{C} = 298.2 \text{ K}; \quad 62.5^\circ \text{C} = 335.7 \text{ K}$$

$$\Delta S_1 = (10.0 \times 10^3 \text{ g}) \times (0.449 \text{ J K}^{-1} \text{ g}^{-1}) \times \ln\left(\frac{335.7}{298.2}\right) = 532 \text{ J K}^{-1}$$

$$\Delta S_2 = (10.0 \times 10^3 \text{ g}) \times (0.449 \text{ J K}^{-1} \text{ g}^{-1}) \times \ln\left(\frac{335.7}{373.2}\right) = -475 \text{ J K}^{-1}$$

$$\Delta S_{\text{total}} = \Delta S_1 + \Delta S_2 = 57 \text{ J K}^{-1}$$

3A.11(b) (i) $\Delta_{\text{vap}} S = \frac{\Delta_{\text{vap}} H}{T_b} = \frac{35.27 \times 10^3 \text{ J mol}^{-1}}{(64.1 + 273.15) \text{ K}} = +104.58 \text{ J K}^{-1} = 104.6 \text{ J K}^{-1}$

(ii) If vaporization occurs reversibly, as is generally assumed

$$\Delta S_{\text{sys}} + \Delta S_{\text{sur}} = 0 \quad \text{so} \quad \Delta S_{\text{sur}} = -104.6 \text{ J K}^{-1}$$

Comment. This calculation has been based on the assumption that the heat capacities remain constant over the range of temperatures involved and that the enthalpy of vaporization at 298.15 K given in Table 3A.2 can be applied to the vaporization at 373.15 K. Neither one of these assumptions are strictly valid. Therefore, the calculated value is only approximate.

$$3A.12(b) \quad \Delta S = nC_p(\text{H}_2\text{O},s)\ln\frac{T_f}{T_i} + n\frac{\Delta_{\text{fus}}H}{T_{\text{fus}}} + nC_p(\text{H}_2\text{O},l)\ln\frac{T_f}{T_i} + n\frac{\Delta_{\text{vap}}H}{T_{\text{vap}}} + nC_p(\text{H}_2\text{O},g)\ln\frac{T_f}{T_i}$$

$$n = \frac{15.0 \text{ g}}{18.02 \text{ g mol}^{-1}} = 0.832 \text{ mol}$$

$$\begin{aligned} \Delta S &= 0.832 \text{ mol} \times 38.02 \text{ J K}^{-1} \text{ mol}^{-1} \times \ln\frac{273.15}{261.15} + 0.832 \text{ mol} \times \frac{6.008 \text{ kJ/mol}^{-1}}{273.15 \text{ K}} \\ &+ 0.832 \text{ mol} \times 75.291 \text{ J K}^{-1} \text{ mol}^{-1} \times \ln\frac{373.15}{273.15} \\ &+ 0.832 \text{ mol} \times \frac{40.657 \text{ kJ/mol}^{-1}}{373.15 \text{ K}} + 0.832 \text{ mol} \times 33.58 \text{ J K}^{-1} \text{ mol}^{-1} \times \ln\frac{378.15}{373.15} \end{aligned}$$

$$\boxed{\Delta S = 130.3 \text{ J K}^{-1}}$$

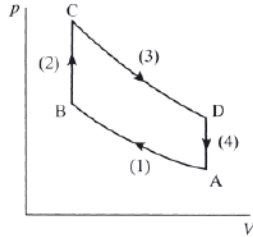
$$3B.2(b) \quad (i) \quad \begin{aligned} \Delta_r S^\ominus &= S_m^\ominus(\text{Zn}^{2+}, \text{aq}) + S_m^\ominus(\text{Cu}, \text{s}) - S_m^\ominus(\text{Zn}, \text{s}) - S_m^\ominus(\text{Cu}^{2+}, \text{aq}) \\ &= [-112.1 + 33.15 - 41.63 + 99.6] \text{ J K}^{-1} \text{ mol}^{-1} = \boxed{-21.0 \text{ J K}^{-1} \text{ mol}^{-1}} \end{aligned}$$

$$(ii) \quad \begin{aligned} \Delta_r S^\ominus &= 12S_m^\ominus(\text{CO}_2, \text{g}) + 11S_m^\ominus(\text{H}_2\text{O}, \text{l}) - S_m^\ominus(\text{C}_{12}\text{H}_{22}\text{O}_{11}, \text{s}) - 12S_m^\ominus(\text{O}_2, \text{g}) \\ &= [(12 \times 213.74) + (11 \times 69.91) - 360.2 - (12 \times 205.14)] \text{ J K}^{-1} \text{ mol}^{-1} \\ &= \boxed{+512.0 \text{ J K}^{-1} \text{ mol}^{-1}} \end{aligned}$$

Problem

3A.2 The Otto cycle is represented in Fig. 3.1. Assume one mole of air.

Figure 3A.1



$$\eta = \frac{|w_{\text{cycle}}|}{|q_2|} \quad [3A.8]$$

$$w_{\text{cycle}} = w_1 + w_3 = \Delta U_1 + \Delta U_3 \quad [q_1 = q_3 = 0] = C_V(T_B - T_A) + C_V(T_D - T_C)$$

$$q_2 = \Delta U_2 = C_V(T_C - T_B)$$

$$\eta = \frac{|T_B - T_A + T_D - T_C|}{|T_C - T_B|} = 1 - \left(\frac{T_D - T_A}{T_C - T_B} \right)$$

We know that

$$\frac{T_A}{T_B} = \left(\frac{V_B}{V_A} \right)^{\gamma} \quad \text{and} \quad \frac{T_D}{T_C} = \left(\frac{V_C}{V_D} \right)^{\gamma} \quad [2E.2a]$$

Since $V_B = V_C$ and $V_A = V_D$, $\frac{T_A}{T_B} = \frac{T_D}{T_C}$, or $T_D = \frac{T_A T_C}{T_B}$

Then
$$\eta = 1 - \frac{\frac{T_A T_C}{T_B} - T_A}{T_C - T_B} = 1 - \frac{T_A}{T_B} \quad \text{or} \quad \boxed{\eta = 1 - \left(\frac{V_B}{V_A} \right)^{\gamma}}$$

Given that $C_{p,m} = \frac{7}{2}R$, we have $C_{V,m} = \frac{5}{2}R$ [2D.11] and $c = \frac{2}{5}$

For $\frac{V_A}{V_B} = 10$, $\eta = 1 - \left(\frac{1}{10} \right)^{2/5} = \boxed{0.47}$

$$\Delta S_1 = \Delta S_3 = \Delta S_{\text{sur},1} = \Delta S_{\text{sur},3} = \boxed{0} \quad [\text{adiabatic reversible steps}]$$

$$\Delta S_2 = C_{V,m} \ln \left(\frac{T_C}{T_B} \right)$$

At constant volume $\left(\frac{T_C}{T_B} \right) = \left(\frac{p_C}{p_B} \right) = 5.0$

$$\Delta S_2 = \left(\frac{5}{2} \right) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (\ln 5.0) = \boxed{+33 \text{ J K}^{-1}}$$

$$\Delta S_{\text{sur},2} = -\Delta S_2 = \boxed{-33 \text{ J K}^{-1}}$$

$$\Delta S_4 = -\Delta S_2 \left[\frac{T_C}{T_D} = \frac{T_B}{T_A} \right] = \boxed{-33 \text{ J K}^{-1}}$$

$$\Delta S_{\text{sur},4} = -\Delta S_4 = \boxed{+33 \text{ J K}^{-1}}$$