1. 

a) 
\[ w_{ab} = -nRT_{hot} \ln \frac{V_b}{V_a} \]
\[ w_{bc} = nC_{V,m} \left( T_{cold} - T_{hot} \right) \]
\[ w_{cd} = -nRT_{cold} \ln \frac{V_d}{V_c} \]
\[ w_{da} = nC_{V,m} \left( T_{hot} - T_{cold} \right) = -w_{bc} \]

b) 
\[ w_{\text{total}} = -nRT_{hot} \ln \frac{V_b}{V_a} - nRT_{cold} \ln \frac{V_d}{V_c} \]

c) Use the adiabat relations for ideal gas:
\[ T_{cold} \gamma^{-1} = T_{hot} \] \[ \text{and} \] \[ T_{hot} \gamma^{-1} = T_{cold} \gamma^{-1} \]
Solve these for \( T_{cold} / T_{hot} \) and equate the results,
\[ \frac{T_{cold}}{T_{hot}} = \left( \frac{V_b}{V_a} \right)^{\gamma^{-1}} = \left( \frac{V_c}{V_d} \right)^{\gamma^{-1}}. \] Therefore, \( \frac{V_b}{V_c} = \frac{V_a}{V_d} \) or \( \frac{V_c}{V_d} = \frac{V_b}{V_a} \)

Therefore
\[ w_{\text{total}} = -nRT_{hot} \ln \frac{V_b}{V_a} - nRT_{cold} \ln \frac{V_d}{V_c} = -nR \left( T_{hot} - T_{cold} \right) \ln \frac{V_b}{V_a} \]

d) The heat withdrawn from the hot reservoir (isothermal process) where \( \Delta U_{ab} = 0 \) must be \( q_{\text{ab}} = -w_{\text{ab}} = nRT_{hot} \ln \frac{V_b}{V_a} \)

e) The efficiency is
\[ e = \frac{w_{\text{cycle}}}{q_{\text{ab}}} = \frac{(T_{hot} - T_{cold})}{T_{hot}} = 1 - \frac{T_{cold}}{T_{hot}} < 1. \]
2.

a) First calculate $V_c$ and $V_d$.

$$\frac{T_c}{T_b} = \left(\frac{V_c}{V_b}\right)^{\frac{1}{\gamma}}; \quad \frac{V_c}{V_b} = \left(\frac{T_c}{T_b}\right)^{\frac{1}{\gamma}}$$

$$\frac{V_c}{V_b} = \left(\frac{423 \text{ K}}{873 \text{ K}}\right)^{\frac{1}{\gamma}} = \left(\frac{423 \text{ K}}{873 \text{ K}}\right)^{\frac{3}{2}} = 2.9649; \quad V_c = 10.000 \text{ L} \times 2.9649 = 29.649 \text{ L}$$

$$\frac{T_d}{T_a} = \left(\frac{V_d}{V_a}\right)^{\frac{1}{\gamma}}; \quad \frac{V_d}{V_a} = \left(\frac{T_d}{T_a}\right)^{\frac{1}{\gamma}}$$

$$\frac{V_d}{V_a} = \left(\frac{423 \text{ K}}{873 \text{ K}}\right)^{\frac{1}{\gamma}} = \left(\frac{423 \text{ K}}{873 \text{ K}}\right)^{\frac{3}{2}} = 2.9649; \quad V_d = 3.500 \text{ L} \times 2.9649 = 10.377 \text{ L}$$

b) We next calculate $w$ for each step in the cycle, and for the total cycle.

$$w_{ab} = -nRT_a \ln \frac{V_b}{V_a} = -1 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 873 \text{ K} \times \ln \frac{10.0 \text{ L}}{3.50 \text{ L}} = -7.62 \times 10^3 \text{ J}$$

$$w_{bc} = nC_{V,m} (T_c - T_b) = 1 \text{ mol} \times \frac{3}{2} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times (423 \text{ K} - 873 \text{ K}) = -5.61 \times 10^3 \text{ J}$$

$$w_{cd} = -nRT_c \ln \frac{V_d}{V_c} = -1 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 423 \text{ K} \times \ln \frac{10.377 \text{ L}}{29.649 \text{ L}} = +3.69 \times 10^3 \text{ J}$$

$$w_{da} = nC_{V,m} (T_d - T_a) = 1 \text{ mol} \times \frac{3}{2} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times (873 \text{ K} - 423 \text{ K}) = +5.61 \times 10^3 \text{ J}$$

$$w_{total} = -7.62 \times 10^3 \text{ J} - 5.61 \times 10^3 \text{ J} + 3.69 \times 10^3 \text{ J} + 5.61 \times 10^3 \text{ J} = -3.93 \times 10^3 \text{ J}$$

$$e = 1 - \frac{T_{cold}}{T_{hot}} = 1 - \frac{423 \text{ K}}{873 \text{ K}} = 0.515; \quad q = \frac{w}{e} = 1.94 \times 10^3 \text{ J}$$

Therefore, 1.94 kJ of heat must be extracted from the surroundings to do 1.00 kJ of work in the surroundings.
3. Going through each step in Problem 2 yields (it is an ideal gas):

\[ a \rightarrow b \quad \Delta U = \Delta H = 0 \text{ because } \Delta T = 0. \quad q = -w = 7.62 \times 10^3 J \]

\[ b \rightarrow c \quad \Delta U = w = -5.61 \times 10^3 J \text{ because } q = 0 \quad \Delta H = \Delta U + nR\Delta T = -5.61 \times 10^3 J - 3.74 \times 10^3 J = -9.35 \times 10^3 J \]

\[ c \rightarrow d \quad \Delta U = \Delta H = 0 \text{ because } \Delta T = 0. \quad q = -w = -3.69 \times 10^3 J \]

\[ d \rightarrow a \quad \Delta U = w = 5.61 \times 10^3 J \text{ because } q = 0 \quad \Delta H = \Delta U + nR\Delta T = 9.35 \times 10^3 J \]

\[ q_{total} = 7.62 \times 10^3 J - 3.69 \times 10^3 J = 3.93 \times 10^3 J = -w_{total} \]

\[ \Delta U_{total} = \Delta H_{total} = 0 \]

4.

\[ a \rightarrow b \quad \Delta S_{sys} = -\Delta S_{surroundings} = \frac{q_{reversible}}{T} = \frac{7.62 \times 10^3 J}{873 K} = 8.73 J K^{-1} \quad \Delta S_{univ} = 0 \]

\[ b \rightarrow c \quad \Delta S_{sys} = -\Delta S_{surroundings} = 0 \text{ because } q_{reversible} = 0 \quad \Delta S_{univ} = 0 \]

\[ c \rightarrow d \quad \Delta S_{sys} = -\Delta S_{surroundings} = \frac{q_{reversible}}{T} = \frac{-3.692 \times 10^3 J}{423 K} = -8.73 J K^{-1} \quad \Delta S_{univ} = 0 \]

\[ d \rightarrow a \quad \Delta S_{sys} = -\Delta S_{surroundings} = 0 \text{ because } q_{reversible} = 0 \quad \Delta S_{univ} = 0. \]

For the cycle, \( \Delta S_{sys} = -\Delta S_{surroundings} = \Delta S_{univ} = 0. \)

5.

a) \( \eta = \frac{q_{cold}}{w_{cycle}} = \frac{-q_{cold}}{-\left(q_{cold} + q_{hot}\right)} = \frac{T_{cold}}{T_{hot} - T_{cold}} \)

b) For the freezer \( \eta = \frac{255 K}{294 K - 255 K} = 6.5 \)

For the refrigerator \( \eta = \frac{277 K}{294 K - 277 K} = 16.3 \)

The freezer is more expensive to operate than the refrigerator by the ratio 16.3/6.5 = 2.5.