1. a) The gas is heated from 300 K to 450 K at a constant external pressure of 1.00 bar.

\[ V_i = \frac{nRT_i}{P_i} = \frac{1 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{K}^{-1} \times 300 \text{ K}}{10^5 \text{ Pa}} = 2.49 \times 10^{-2} \text{ m}^3 \]

\[ V_f = \frac{T_f}{T_i} V_i = \frac{450 \text{ K}}{300 \text{ K}} \times 2.49 \times 10^{-2} \text{ m}^3 = 3.74 \times 10^{-2} \text{ m}^3 \]

\[ w = -P_{\text{external}} \Delta V = -10^5 \text{ Pa} \times (3.74 \times 10^{-2} \text{ m}^3 - 2.49 \times 10^{-2} \text{ m}^3) = -1.25 \times 10^3 \text{ J} \]

\[ \Delta U = nC_{v,m} \Delta T = 1 \text{ mol} \times \frac{3 \times 8.314 \text{ J mol}^{-1} \text{K}^{-1}}{2} \times 150 \text{ K} = 1.87 \times 10^3 \text{ J} \]

\[ q = \Delta H = \Delta U - w = 1.87 \times 10^3 \text{ J} + 1.25 \times 10^3 \text{ J} = 3.12 \times 10^3 \text{ J} \]

\[ \Delta S = nC_{p,m} \ln \left( \frac{T_f}{T_i} \right) = 1 \text{ mol} \times \left( \frac{3}{2} + 1 \right) \times 8.314 \text{ J mol}^{-1} \text{K}^{-1} \times \ln \left( \frac{450 \text{ K}}{300 \text{ K}} \right) = 8.43 \text{ J K}^{-1} \]

b) The gas is heated to 450 K at a constant volume corresponding to the initial volume.

\[ w = 0 \text{ because } \Delta V = 0. \]

\[ \Delta U = q = nC_{v,m} \Delta T = 1 \text{ mol} \times \frac{3 \times 8.314 \text{ J mol}^{-1} \text{K}^{-1}}{2} \times 150 \text{ K} = 1.87 \times 10^3 \text{ J} \]

\[ \Delta H = nC_{p,m} \Delta T = 1 \text{ mol} \times \frac{5 \times 8.314 \text{ J mol}^{-1} \text{K}^{-1}}{2} \times 150 \text{ K} = 3.12 \times 10^3 \text{ J} \]

\[ \Delta S = nC_{v,m} \ln \left( \frac{T_f}{T_i} \right) = 1 \text{ mol} \times \left( \frac{3}{2} + 1 \right) \times 8.314 \text{ J mol}^{-1} \text{K}^{-1} \times \ln \left( \frac{450 \text{ K}}{300 \text{ K}} \right) = 5.06 \text{ J K}^{-1} \]

c) The gas undergoes a reversible isothermal expansion at 300 K until the pressure is half of its initial value.

\[ \Delta U = \Delta H = 0 \text{ because } \Delta T = 0. \]

\[ w_{\text{reversible}} = -q = -nRT \ln \frac{V_f}{V_i} = -1 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{K}^{-1} \times 300 \text{ K} \times \ln 2 = -1.73 \times 10^3 \text{ J} \]

\[ \Delta S = \frac{q_{\text{reversible}}}{T} = \frac{1.73 \times 10^3 \text{ J}}{300 \text{ K}} = 5.76 \text{ J K}^{-1} \]
2. The state of the surroundings for each part is as follows:

a. 450 K, 1 bar  
b. 450 K, 1 bar  
c. 300 K, 0.500 bar

a) The gas is heated to 450 K at a constant pressure of 1.00 bar. From 1a) we get $q$,

$$\Delta S_{\text{surroundings}} = \frac{-q}{T_{\text{surroundings}}} = \frac{-3.12 \times 10^3 J}{450 \text{ K}} = -6.93 \text{ J K}^{-1}$$

$$\Delta S_{\text{total}} = \Delta S + \Delta S_{\text{surroundings}} = 8.43 \text{ J K}^{-1} - 6.93 \text{ J K}^{-1} = 1.50 \text{ J K}^{-1}$$

The process is spontaneous.

b) The gas is heated to 450 K at a constant volume corresponding to the initial volume.

$$\Delta S_{\text{surroundings}} = \frac{-q}{T_{\text{surroundings}}} = \frac{-1.87 \times 10^3 J}{450 \text{ K}} = -4.16 \text{ J K}^{-1}$$

$$\Delta S_{\text{total}} = \Delta S + \Delta S_{\text{surroundings}} = 5.06 \text{ J K}^{-1} - 4.16 \text{ J K}^{-1} = 0.90 \text{ J K}^{-1}$$

The process is spontaneous.

c) The gas undergoes a reversible isothermal expansion at 300 K until the pressure is half of its initial value.

$$\Delta S_{\text{surroundings}} = \frac{q}{T} = \frac{-1.73 \times 10^3 J}{300 \text{ K}} = -5.76 \text{ J K}^{-1}$$

$$\Delta S_{\text{total}} = \Delta S + \Delta S_{\text{surroundings}} = 5.76 \text{ J K}^{-1} - 5.76 \text{ J K}^{-1} = 0$$

There is no natural direction of change in this process because it is reversible.
3.
a) The heat input is the same for a reversible and an irreversible process.

\[ dq = dq_{\text{reversible}} = nC_{p,m}dT \]

\[ \Delta S = n \int \frac{C_{p,m}}{T} dT = nC_{p,m} \ln \frac{T_f}{T_i} \]

\[ = 1 \text{ mol} \times 753 \text{ J mol}^{-1} \text{ K}^{-1} \ln \frac{373.15 \text{ K}}{273.15 \text{ K}} \]

\[ = 23.49 \text{ J K}^{-1} \]

b)

\[ \Delta S_{\text{fusion}} = \frac{\Delta H_{\text{fusion}}}{T_{\text{fusion}}} = \frac{6009 \text{ J}}{273.15 \text{ K}} = 22.00 \text{ J K}^{-1} \]

\[ \Delta S_{\text{vaporization}} = \frac{\Delta H_{\text{vaporization}}}{T_{\text{vaporization}}} = \frac{40656 \text{ J}}{373.15 \text{ K}} = 108.95 \text{ J K}^{-1} \]

\[ \Delta S_{\text{total}} = \Delta S_{\text{fusion}} + \Delta S_{\text{vaporization}} + \Delta S_{\text{heating}} = (22.00 + 108.95 + 23.49) \text{ J K}^{-1} \]

\[ = 154.4 \text{ J K}^{-1} \]

4.

From equation 4.60 in Levine,

\[ \Delta S = \int_{T_i}^{T_f} \frac{C_p}{T} dT = \int V \alpha dP. \]

According to the problem statement we can assume \( C_p \) is a constant, which is found in the Appendix and since \( \kappa = 0 \) it means \( V \) doesn't change with \( P \) at constant \( T \), so can \( V \) be taken outside the pressure integral. The appendix has \( C_p \) for water. Then the integrals are simple and

\[ \Delta S = \int_{T_i}^{T_f} \frac{C_p}{T} dT = \int V \alpha dP \approx nC_{p,m} \ln \frac{T_f}{T_i} - nV_m \alpha (P_f - P_i) \]

\[ = 1 \text{ mol} \times 75.3 \text{ J mol}^{-1} \text{ K}^{-1} \times \ln \frac{450 \text{ K}}{298 \text{ K}} \]

\[ -1 \text{ mol} \times \frac{18.02 \times 10^3 \text{ kg mol}^{-1}}{997 \text{ kg m}^{-3}} \times 2.07 \times 10^{-4} \text{ K}^{-1} \times (800-1) \text{ bar} \times 10^5 \text{ Pa bar}^{-1} \]

\[ = 31.0 \text{ J K}^{-1} - 0.299 \text{ J K}^{-1} = 30.7 \text{ J K}^{-1} \]