a. Use a reversible expansion; $\Delta S = q_{\text{rev}}/T$; $q_{\text{rev}} = nRT \ln(P_1/P_2)$

$$\Delta S_{\text{syst}} = nRT \ln(2) = 17.29 \text{ J K}^{-1}; \Delta S_{\text{surr}} = -nRT \ln(2) = -17.29 \text{ J K}^{-1};$$

$$\Delta S_{\text{tot}} = \Delta S_{\text{syst}} + \Delta S_{\text{surr}} = 0$$

b. Do the expansion against $P = 0$, $W = 0$;

$\Delta S_{\text{syst}} = 17.29$ since it must be the same as in part (a).

$\Delta S_{\text{surr}} = 0$ since there is no interaction with the surroundings;

$$\Delta S_{\text{tot}} = \Delta S_{\text{syst}} + \Delta S_{\text{surr}} = 17.29 + 0 = 17.29 \text{ J K}^{-1}.$$

c. $w_{\text{irrev}} = P_2(V_2 - V_1) = nP_2(RT/P_2 - RT/P_1) = nRT(1 - \frac{1}{2}) = 3716.4 \text{ J}$

$w_{\text{irrev}} = q = -q_{\text{surr}}; \Delta S_{\text{syst}} = -17.29$, same as in (a).

For the surroundings, first do a reversible expansion to an intermediate pressure such that $q_{\text{rev}} = 3716.4 \text{ J}$. Then complete the expansion against zero pressure so that $q = w = 0$ and $\Delta S_{\text{surr}} = 0$ for the rest of the process. For the first (rev.) portion of the process

$$\Delta S_{\text{surr}} = -3716.4/298 = -12.47 \text{ J K}^{-1} \text{ and this is the entire } \Delta S_{\text{surr}}$$

$$\Delta S_{\text{tot}} = \Delta S_{\text{syst}} + \Delta S_{\text{surr}} = 17.29 - 12.47 = 4.82 \text{ J K}^{-1}.$$

Note that for the reversible process $\Delta S_{\text{tot}}$ is zero while for the irreversible processes it is greater than zero.

I. ice(263 K) $\rightarrow$ ice(273 K): $\Delta S_1 = n33 \ln(273/263) = 1.231n$

II. ice(273 K) $\rightarrow$ H$_2$O(273 K): $\Delta S_{II} = 6010n/273 = 22.015n$

III. H$_2$O(273 K) $\rightarrow$ H$_2$O(373 K): $\Delta S_{III} = n75 \ln(373/273) = 23.408n$

IV. H$_2$O(373 K) $\rightarrow$ gas(373 K): $\Delta S_{IV} = 40670n/373 = 109.035n$

$\Delta S_{\text{tot}} = \Delta S_1 + \Delta S_{II} + \Delta S_{III} + \Delta S_{IV} = 155.589(1000/18) = 8649.4 \text{ J K}^{-1}$

6. H$_2$O(1liq): $S^o(298) = 69.940 \text{ J K}^{-1} \text{ mol}^{-1}$;

For the reaction: H$_2$O(1liq, 298K) $\rightarrow$ H$_2$O(gas, 373 K)

$\Delta S = 75 \ln(373/298) + 40670/373 = 125.87 = S^o(g, 373) - S^o(1liq, 298)$

$S^o(g, 373) = 125.87 + 69.94 = 195.81 \text{ J K}^{-1} \text{ mol}^{-1}$