264.

Problem 26.43 (RHK)

A mixture of 1.78 kg *of water and* 262 g *of ice at* 0^0C *is, in a reversible process, brought to a final equilibrium state where the water ice/ratio, by mass is* 1:1 *at* 0^0C. *We have to calculate* (a) *the change of entropy of the system during the process.* (b) *The system is then returned to the first equilibrium state, but in an irreversible way* (*by using a Bunsen burner, for instance*). *We have to calculate the entropy change of the system during this process.* (c) *We have to show that the answer is consistent with the second law of thermodynamics.*

Solution:

(a)

Amount of water present, $m_{water} = 1.78$ kg,

Amount of ice present, $m_{ice} = 0.262$ kg.

Therefore,

$m_{water} + m_{ice} = 2.042$ kg.

Amount of water that will have to be freezed for water and ice to become 1:1 by mass,

$\Delta m_{water} = \left(1.78 - 2.042/2\right)$ kg $= 0.759$ kg.

Heat of fusion of water, $L_{fusion} = 333$ kJ kg^{-1}.

The amount of heat to be added to the mixture of ice and water for freezing 0.759 kg of water into ice at $0^{0}\mathrm{C}$ will be

$Q = -0.759 \times 333 \times 10^{3}$ J $= -252.7 \times 10^{3}$ kJ.

That is 252.7 kJ of heat will have to be extracted from the ice-water mixture so that the ratio of ice to water becomes 1:1. The change in the entropy of the system will be

$$\Delta S = \frac{-252.7 \times 10^{3}}{273} \text{ J K}^{-1} = -925.5 \text{ J K}^{-1}.$$

The entropy of the system has decreased as water has been transformed into a more ordered crystalline state.

(b)

Now when 0.759 kg of ice is melted by adding heat using say a Bunsen burner, the thermodynamic process is irreversible. The amount of heat to be added to the system for bringing the system back into its initial state will also be 252.7 kJ. And the change in entropy (by using a reversible path connecting the two states) will be

$$\Delta S_{irreversible} = \frac{252.7 \times 10^{3}}{273}\ \text{J K}^{-1} = 925.8\ \text{J K}^{-1}.$$

The statement of the second law of thermodynamics is that in any thermodynamic process that proceeds from one equilibrium state to another, the entropy of the system plus that of the environment either remains unchanged or increases.

The change in entropy that we have worked out is not the total change of entropy of the system and that of the environment taken together. Therefore, there is no inconsistency with the second law of thermodynamics.