ENTROPY CHANGES IN MACROSCOPIC SYSTEMS

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Reference: Daniel V. Schroeder, *An Introduction to Thermal Physics*, (Addison-Wesley, 2000) - Problems 3.10 - 3.11.

The original definition of entropy was in terms of heat flow, rather than the multiplicity of states in a system. If an amount of heat Q flows into a substance at a constant temperature T, the change in entropy is

$$\Delta S = \frac{Q}{T} \tag{1}$$

If heat flows *out* of the substance, then Q is negative and the system loses entropy. In order for a system to maintain a constant temperature when it gains or loses heat, it must differ from the types of systems we've considered up to now. One possibility is that the amount of heat gained is very small compared to the existing internal energy of the system so that the added heat makes a negligible difference to the temperature. Such a system is called a *heat reservoir*. Another example is a phase change, as when ice melts into liquid water, as during a phase change, heat is gained or lost and the substance doesn't change its temperature.

Example 1. Suppose a 30 g ice cube at 0° C = 273 K is placed on a table in a room at 25° C = 298 K. The ice will first melt into water, still at 273 K (because it's a phase change), then the water will warm up to 298 K. All of this heat is transferred from the air in the room, which we can consider to be a heat reservoir at a constant temperature of 298 K. The changes in entropy are then:

The latent heat of fusion of water at 273 K is 334 J g^{-1}, so the amount of heat required to melt the ice is

$$Q = 334 \times 30 = 10020 \text{ J} \tag{2}$$

Since it occurs at a constant temperature, the entropy change of the water is

$$\Delta S_1 = \frac{Q}{T} = \frac{10020}{273} = 36.7 \text{ J K}^{-1} \tag{3}$$

As the water warms up, it absorbs heat, but the temperature varies. We can then use our relation between entropy and heat capacity, along with the fact that the specific heat capacity of water is roughly constant over the liquid range at 1 cal $\mathrm{g}^{-1}\mathrm{K}^{-1} = 4.181$ J $\mathrm{g}^{-1}\mathrm{K}^{-1}$ to get

$$\begin{aligned}
\Delta S_2 &= C_V \int_{T_i}^{T_f} \frac{1}{T} dT && (4)\\
&= C_V \ln \frac{T_f}{T_i} && (5)\\
&= (4.181 \times 30) \ln \frac{298}{273} && (6)\\
&= 11.0 \text{ J K}^{-1} && (7)
\end{aligned}$$

Thus the total entropy increase of the water is

$$\Delta S_{H_2O} = 47.7 \text{ J K}^{-1} \tag{8}$$

The total amount of heat transferred to the water from the room's air is

$$Q = 10020 + 4.181 \times 30 \times (298 - 273) = 13155.75 \text{ J} \tag{9}$$

This happens at a constant room temperature of 298 K so the entropy lost by the room is

$$\Delta S_{room} = -\frac{13155.75}{298} = -44.1 \text{ J K}^{-1} \tag{10}$$

The net entropy change of the universe is therefore

$$\Delta S = \Delta S_{H_2O} + \Delta S_{room} = +3.6 \text{ J K}^{-1} \tag{11}$$

which is positive, as required by the second law of thermodynamics.

Example 2. To draw a bath (in the days before hot and cold running water, presumably) we mix 50 litres of hot water at 55° C $= 328$ K with 25 litres of cold water at 10° C $= 283$ K. The final temperature of the water is the weighted average:

$$T_f = \frac{50 \times 328 + 25 \times 283}{75} = 313 \text{ K} (= 40^\circ \text{ C}) \tag{12}$$

To find the entropy change, we can use 5. The hot water cools down and thus loses heat, so its entropy change is

$$\begin{aligned}
\Delta S_{hot} &= 4.181 \times 5 \times 10^4 \times \ln \frac{313}{328} && (13)\\
&= -9786 \text{ J K}^{-1} && (14)
\end{aligned}$$

The entropy gained by the cold water is

$$\Delta S_{cold} = 4.181\times 2.5\times 10^{4}\times \ln\frac{313}{283} \quad (15)$$

$$= +10532 \text{ J K}^{-1} \quad (16)$$

Thus the net entropy change is

$$\Delta S = +746 \text{ J K}^{-1} \quad (17)$$

which is again positive.

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