The direction of processes

Entropy inequality (second law) is often explained as a condition determining the direction of processes. Usually, it is said of spontaneous processes, which should be understood as processes running *per se*, without any additional forces applied to them after their initiation. For example, hydrochloric acid reacts (very) spontaneously with sodium hydroxide (forming table salt and water) when mixed; when the two substances are placed in separated containers, no reaction occurs.

Another "spontaneous" process is observed when two bodies at different temperatures are brought into contact. Then, the initially hotter body cools while the initially colder body heats, until their temperatures are equal (equilibrium). No one has ever observed that the initially hotter body grows hotter and the initially colder body grows colder, though this process would not violate energy conservation (first law).

Let us look at temperature equilibration through the lens of entropy inequality. The two bodies in contact are uniform and thermally isolated from their surroundings (cf. figure), and the only possible energy transfer between them is by means of heat. The total couple is thus adiabatic: $\dot{S} > 0$. Due to its link to heat(ing), the entropy is additive (cf. also sec. 2.3 in the book): $\dot{S} = \dot{S}_1 + \dot{S}_2$. No energy is lost, no work is performed, and thus the first law says that $Q_{f1} = -Q_{f2}$. The entropy of each uniform body is supposed to fulfil the second law, eq. (9.48) in the book: $\dot{S}_i = Q_{fi}/T$. Combining all the expressions given, we get:

$$\dot{S}_1 + \dot{S}_2 = Q_{f1}/T_1 + Q_{f2}/T_2 = Q_{f1}/T_1 - Q_{f1}/T_2 > 0. \tag{1}$$

And finally,

$$Q_{f1}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) > 0. \tag{2}$$

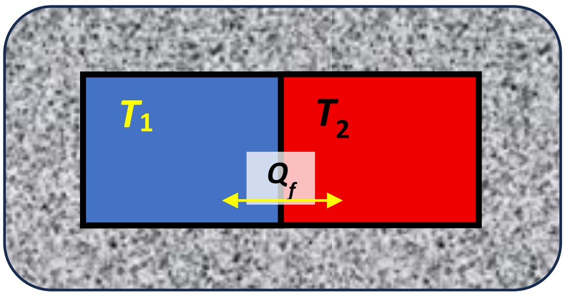
From (2) it follows that

$$T_1 > T_2 \Rightarrow \frac{1}{T_1} < \frac{1}{T_2} \Rightarrow Q_{f1} < 0, \tag{3a}$$

or

$$T_1 < T_2 \Rightarrow \frac{1}{T_1} > \frac{1}{T_2} \Rightarrow Q_{f1} > 0, \tag{3b}$$

Eq. (3) gives the proper directions of energy transfer by heat in the analyzed example, in terms of the proper signs of Q_{fi}.



Our demonstration was simplified; we used several assumptions. Nevertheless, it shows how entropy inequality works as a criterion of direction.