Topic 4I - Global Changes in Entropy

Spontaneous Processes

Spontaneous processes are ones that occur without the need for an external stimulus and proceed toward a state of maximum "microstates" (W), *i.e.*, maximum entropy:

$$S = k_B \ln W$$

where k_B is Boltzmann's constant $(1.38 \times 10^{-23} \text{ J/K})$

Spontaneous processes result in an overall <u>increase</u> in entropy of the <u>universe</u> (system + surroundings):

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$$

For any physical or chemical process, ΔS_{surr} is determined primarily by the flow of energy as <u>heat</u> into or out of the system (*i.e.*, out of or into the surroundings). For <u>exothermic</u> processes $(\Delta H < 0)$, $\Delta S_{surr} > 0$. For <u>endothermic</u> processes $(\Delta H > 0)$, $\Delta S_{surr} < 0$.

Exothermic processes are almost always spontaneous $(\Delta S_{univ} > 0)$. Why?

Endothermic processes can only be spontaneous if the increase that occurs in S_{sys} is sufficiently large to offset the decrease in S_{surr}.
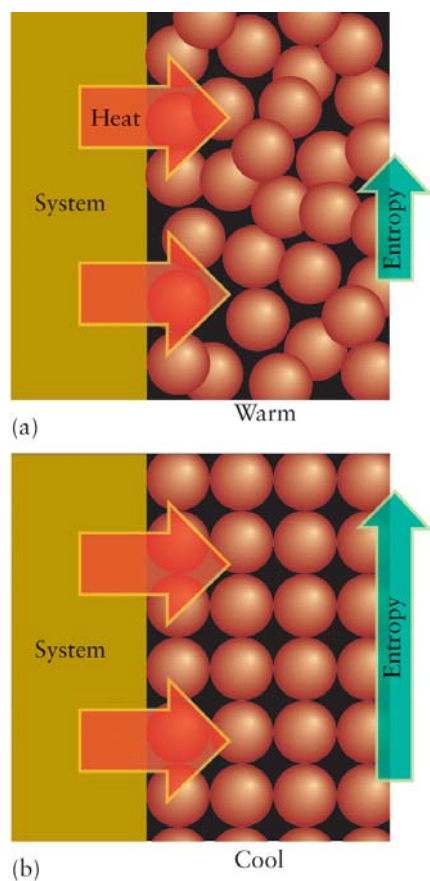
FIGURE 9.16 (a) When a given quantity of heat flows into hot surroundings, it produces very little additional chaos and the increase in entropy is small. (b) When the surroundings are cool, however, the same quantity of heat can make a considerable difference to the disorder, and the change in entropy of the surroundings is correspondingly large.
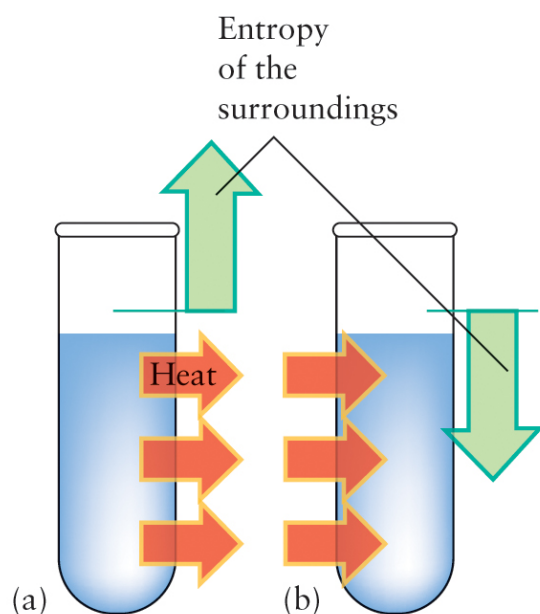
FIGURE 9.17 (a) In an exothermic process, heat escapes into the surroundings and increases their entropy. (b) In an endothermic process, the entropy of the surroundings decreases. The red arrows represent the transfer of heat between system and surroundings, and the green arrows indicate the entropy change of the surroundings.
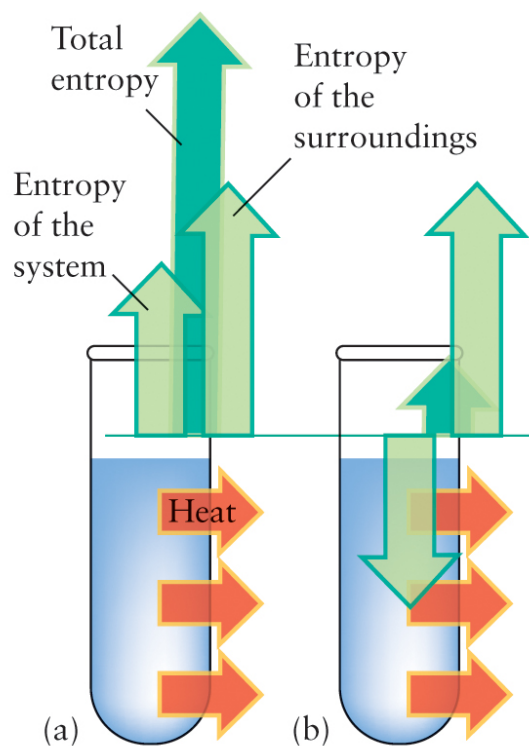
FIGURE 9.18 In an exothermic reaction, (a) the overall entropy change is certainly positive when the entropy of the system increases. (b) The overall entropy change may also be positive when the entropy of the system decreases. The reaction is spontaneous in both cases.
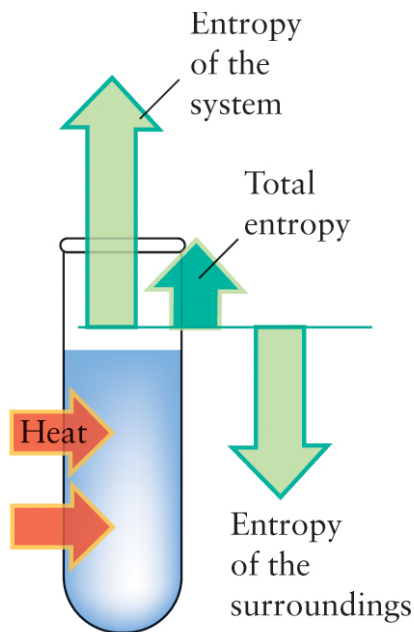
FIGURE 9.19 An endothermic reaction is spontaneous only if the entropy of the system increases enough to overcome the decrease in entropy of the surroundings.

The **First Law of Thermodynamics** defines the conservation of energy during processes, but provides no information about the spontaneity or "likelihood" of a process.

The driving force for a spontaneous process is an increase in the randomness or disorder of the <u>universe</u> (not just of the system).

Spontaneous processes are ones that proceed toward states of highest probability (largest number of microstates). The quantitative measure of this randomness or disorder is **Entropy**. Thus,

In any real (*i.e.*, irreversible) spontaneous process, the entropy of the universe (system + surroundings) must <u>increase</u>.

Statements of the Second Law of Thermodynamics

In any spontaneous process, the entropy of the universe (*i.e.*, system + surroundings) <u>increases</u>.

In any cyclic process, the transfer of heat from a cooler body to a warmer one cannot occur with 100% efficiency.

In a <u>reversible</u> process, the total entropy of the universe (system + surroundings) is <u>unchanged</u>.

In an <u>irreversible</u> (i.e., real) process, the total entropy of the universe <u>increases</u>.

[According to the First Law of Thermodynamics, you can't win; you can only break even.]

[According to the Second Law of Thermodynamics, you can't even break even.]

Interplay of ΔS_{sys} and ΔS_{surr} in Determining the Sign of ΔS_{univ}			
Signs of Entropy Changes			
ΔS_{sys}	ΔS_{surr}	ΔS_{univ}	Process Spontaneous?
+	+	+	Yes
−	−	−	No (reaction will occur in opposite direction)
+	−	?	Yes, if ΔS_{sys} has a larger magnitude than ΔS_{surr}
−	+	?	Yes, if ΔS_{surr} has a larger magnitude than ΔS_{sys}

Interplay of ΔS_{sys} and ΔS_{surr} in determining the sign of ΔS_{univ}

$\Delta S_{tot} = 0$

$\Delta S_{tot} > 0$

(a) Reversible process   **(b) Irreversible process**
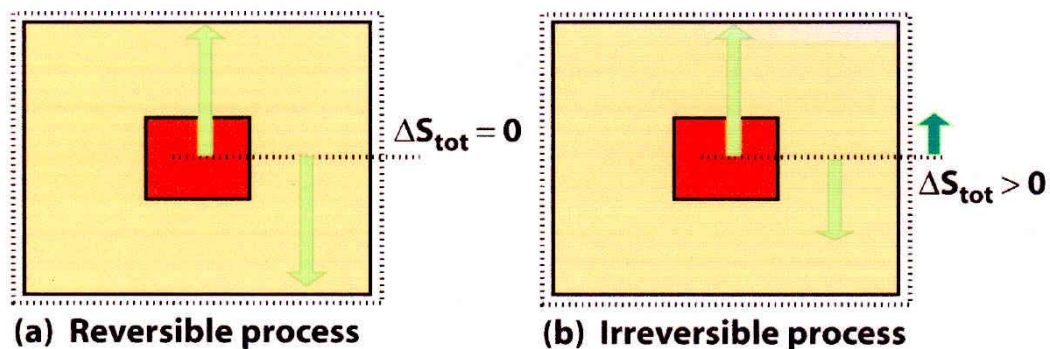
FIGURE 7.18 (a) When a process takes place reversibly—that is, when the system is at equilibrium with its surroundings—the change in entropy of the surroundings is the negative of the change in entropy of the system and the overall change is zero. (b) For an irreversible change between the same two states of the system, the final state of the surroundings is different from the final state in part (a), and the change in the system is not canceled by the entropy change of the surroundings. Overall, there is an increase in entropy.

Entropy changes for the reversible *vs.* irreversible isothermal expansion of 1.0 mole of an ideal gas from 8.0 L to 20.0 L
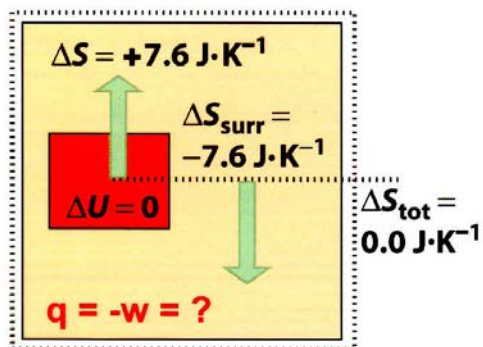
(a) **Nonspontaneous process** (reversible)
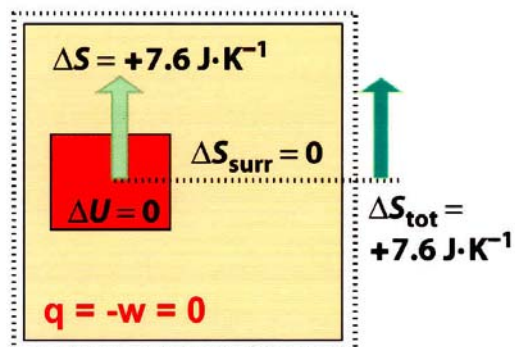
(b) **Spontaneous process** (irreversible; free expansion)

$$\Delta S_{sys} = nR \ln\left(\frac{V_2}{V_1}\right) = 1 \times 8.314 \times \ln\left(\frac{20}{8}\right) = 7.6 \text{ J / K}$$

Entropy of Other Reversible Processes

For a phase transition (melting, boiling, sublimation):

$$\Delta S_{fus} = \frac{q_{rev}}{T} = \frac{\Delta H_{fus}}{T_{MP}} \qquad \Delta S_{surr} = ?$$

$$\Delta S_{vap} = \frac{q_{rev}}{T} = \frac{\Delta H_{vap}}{T_{BP}} \qquad \Delta S_{surr} = ?$$

For reversible, non-isothermal processes at constant V:

$$dq_{rev} = nC_v dT$$

$$\Delta S_{T_1 \rightarrow T_2} = \frac{dq_{rev}}{T} = \int_{T_1}^{T_2} \frac{nC_v}{T} dT = nC_v \ln\left(\frac{T_2}{T_1}\right)$$

For reversible, non-isothermal processes at constant P:

$$\Delta S_{T_1 \rightarrow T_2} = nC_p \ln\left(\frac{T_2}{T_1}\right)$$

Some Changes in which the Entropy Increases

(a) Melting; $S_{liquid} > S_{solid}$

$$\Delta S_{fus} = \frac{\Delta H_{fus}}{T_{MP}}$$

(b) Vaporization; $S_{vapor} > S_{liquid}$

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T_{BP}}$$

$$\Delta S_{sol} = \frac{\Delta H_{sol}}{T}$$

(c) Dissolving; $S_{solution} > S_{solvent} + S_{solute}$

(d) Warming; $S_{hot\ gas} > S_{cold\ gas}$

$$\Delta S = \int_{T_1}^{T_2} \frac{nC_v}{T} dT$$

$$= nC_v \ln\left(\frac{T_2}{T_1}\right)$$