

Section 16.3

The Second and Third Laws of Thermodynamics



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Learning Objectives



- State and explain the second and third laws of thermodynamics
- Calculate entropy changes for phase transitions and chemical reactions under standard conditions

The Second Law of Thermodynamics



- Processes that involve an increase in entropy of the system ($\Delta S > 0$) are very often spontaneous. But not always.
- To identify a property that reliably predicts spontaneity we must also consider the effect a process has on the surroundings.
- Together the change of entropy of a system and the surroundings encompasses the change to the universe.

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

Heat Flow and ΔS



- Consider the three possible outcomes of the process of heat flow between two objects, the *system* and the *surroundings*.
 - 1) The objects are at different temperatures
 - Heat flows from the hotter to the cooler object.
 - This is always spontaneous.
 - 2) The objects are at different temperatures
 - Heat flows from the cooler to the hotter object.
 - This is never observed to occur spontaneously.
 - 3) The objects are at essentially the same temperature, $T_{\text{sys}} \approx T_{\text{surr}}$
 - This means the system is at equilibrium.

Outcome One



- Designating the hotter object as the system and invoking the definition of entropy yields the following:

$$\Delta S_{\text{sys}} = \frac{-q_{\text{rev}}}{T_{\text{sys}}} \quad \text{and} \quad \Delta S_{\text{surr}} = \frac{q_{\text{rev}}}{T_{\text{surr}}}$$

- The magnitudes of $-q_{\text{rev}}$ and q_{rev} are equal
- Since $T_{\text{sys}} > T_{\text{surr}}$, the entropy decrease of the system will be less than the entropy increase of the surroundings. The entropy of the universe will increase:

$$|\Delta S_{\text{sys}}| < |\Delta S_{\text{surr}}|$$
$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$$

Outcome Two



- Designating the hotter object as the system and invoking the definition of entropy yields the following:

$$\Delta S_{\text{sys}} = \frac{q_{\text{rev}}}{T_{\text{sys}}} \quad \text{and} \quad \Delta S_{\text{surr}} = \frac{-q_{\text{rev}}}{T_{\text{surr}}}$$

- The arithmetic signs of q_{rev} denote the gain of heat by the system and the loss of heat by the surroundings.
- The direction of the heat flow will yield a negative value for ΔS_{univ} .
- This process involves a decrease in the entropy of the universe.*

Outcome Three



- The objects are at essentially the same temperature, $T_{\text{sys}} \approx T_{\text{surr}}$, the magnitudes of the entropy changes are essentially the same for both the system and the surroundings.

$$|\Delta S_{\text{sys}}| \approx |\Delta S_{\text{surr}}|$$

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$$

Second Law of Thermodynamics



- *All spontaneous changes cause an increase in the entropy of the universe.*

The Second Law of Thermodynamics

$\Delta S_{\text{univ}} > 0$	spontaneous
$\Delta S_{\text{univ}} < 0$	nonspontaneous (spontaneous in opposite direction)
$\Delta S_{\text{univ}} = 0$	at equilibrium

A Convenient Approximation



- Determining the *reversible heat* transferred can be practically very difficult.
- However, because the surroundings usually represents a huge thermal sink, the heat transferred from or to the surroundings can all be considered reversible.
- This allows us a convenient approximation.

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T}$$

The Third Law of Thermodynamics



- Consider the entropy of a pure, perfectly crystalline solid at absolute zero (0 K).
 - This system would have zero kinetic energy.
 - There is one possible location for each atom or molecule ($W = 1$).

$$S = k \ln W = k \ln(1) = 0$$

- This limiting condition represents the **third law of thermodynamics**
 - *The entropy of a pure, perfect crystalline substance at 0 K is zero.*

Standard Entropies



- Careful calorimetric measurements can be made to determine the temperature dependence of a substance's entropy and to derive absolute entropy values under specific conditions.
- **Standard entropies** (S°) are for one mole of substance under standard conditions
 - A pressure of 1 bar and a temperature of 298.15 K

Standard Entropy Change



- The **standard entropy change** (ΔS°) for a reaction may be computed using:

$$\Delta S^\circ = \sum \nu S^\circ(\text{products}) - \sum \nu S^\circ(\text{reactants})$$

- where ν represents stoichiometric coefficients in the balanced equation representing the process.



$$= [xS^\circ(\text{C}) + yS^\circ(\text{D})] - [mS^\circ(\text{A}) + nS^\circ(\text{B})]$$

Finding Standard Entropies



- A table of standard entropy values for various substances can be found in [Appendix G](#).
- Don't forget that these values are only valid at standard temperatures and pressures.

Substance	S° (J mol ⁻¹ K ⁻¹)
carbon	
C(s, graphite)	5.740
C(s, diamond)	2.38
CO(g)	197.7
CO ₂ (g)	213.8
CH ₄ (g)	186.3
C ₂ H ₄ (g)	219.3
C ₂ H ₆ (g)	229.2
CH ₃ OH(l)	126.8
C ₂ H ₅ OH(l)	160.7
hydrogen	
H ₂ (g)	130.7
H(g)	114.7
H ₂ O(g)	188.8
H ₂ O(l)	70.0
HCl(g)	186.8
H ₂ S(g)	205.7
oxygen	
O ₂ (g)	205.2