

The Second Law of Thermodynamics

So far, our quest has been to find a criterion to predict spontaneity. **The second law of thermodynamics** provides such a criterion that relates entropy to spontaneity, which states *that the entropy of the universe increases in a spontaneous process and remains unchanged in an equilibrium process*. The universe is made up of system and the surroundings, and the change in the entropy of the universe (ΔS_{univ}) is sum of the entropy changes in the system (ΔS_{sys}) and the surroundings (ΔS_{surr}), which is expressed by the following mathematical equation:

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

Then the second law of thermodynamics states that

Spontaneous process: $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$

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

Nonspontaneous process: $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} < 0$

For a spontaneous process, the second law does not place any conditions for ΔS_{sys} or ΔS_{surr} as long as the sum is greater than zero, i.e., either ΔS_{sys} or ΔS_{surr} can be negative but not both. On the other hand, in an equilibrium process, the sum of the entropies must be zero, which means that the magnitudes ΔS_{sys} and ΔS_{surr} must be the same with opposite sign. In the nonspontaneous process, however, the sum must be less than zero, which means that either one or both can be negative.

Entropy Changes in Chemical Reactions

If we want to use the second law of thermodynamics to determine whether a process is spontaneous, both ΔS_{sys} and ΔS_{surr} must be measured because the second law refers to the entropy of the universe, not that of the system or the surroundings. In reality, it is difficult to measure ΔS_{surr} , and due that we will concentrate only on ΔS_{sys} . In terms of chemical reactions, ΔS_{sys} is nothing but the change in standard entropy of reaction ($\Delta S^0_{\text{reaction}}$).

Let us represent the chemical reaction in the following general form and calculate $\Delta S^0_{\text{reaction}}$.

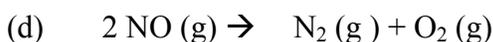


The standard entropy change of reaction is the difference between the standard entropies of products and reactants. Thus

$$\Delta S^0_{\text{reaction}} = [c \times S^0(C) + d \times S^0(D) + \dots] - [a \times S^0(A) + b \times S^0(B) + \dots]$$

Example

From the standard entropy values, calculate the standard entropy changes for the following reactions at 25°C.



Answer

$$\begin{aligned} \text{(a) } \Delta S^{\circ}_{\text{reaction}} &= [2 \times S^{\circ} (\text{KCl}(\text{s})) + 3 \times S^{\circ} (\text{O}_2 (\text{g}))] - [2 \times S^{\circ} (\text{KClO}_3(\text{s}))] \\ &= (2 \times 82.68 \text{ J/K.mol} + 3 \times 205.0 \text{ J/K.mol}) - (2 \times 142.97 \text{ J/K.mol}) \\ &= 494.42 \text{ J/K.mol} \end{aligned}$$

Thus, the entropy of the reaction increases as seen by the formation of oxygen gas.

$$\begin{aligned} \text{(b) } \Delta S^{\circ}_{\text{reaction}} &= [2 \times S^{\circ} (\text{NH}_3 (\text{g}))] - [1 \times S^{\circ} (\text{N}_2 (\text{g})) + 3 \times S^{\circ} (\text{H}_2 (\text{g}))] \\ &= (2 \times 193 \text{ J/K.mol}) - (1 \times 192 \text{ J/K.mol} + 3 \times 131 \text{ J/K.mol}) \\ &= -199 \text{ J/K.mol} \end{aligned}$$

The entropy of the system decreases because 4 moles of gases (1 mol nitrogen and 3 mol hydrogen) react and form 2 moles of ammonia. The physical states of all the substances are the same except the fact that the product has less number of moles, hence it becomes more order.

$$\begin{aligned} \text{(c) } \Delta S^{\circ}_{\text{reaction}} &= [2 \times S^{\circ} (\text{HF}(\text{g}))] - [1 \times S^{\circ} (\text{H}_2 (\text{g})) + 1 \times S^{\circ} (\text{F}_2 (\text{g}))] \\ &= (2 \times 173.5 \text{ J/K.mol}) - (1 \times 131.0 \text{ J/K.mol} + 203.4 \text{ J/K.mol}) \\ &= 12.6 \text{ J/K.mol} \end{aligned}$$

Here 2 moles of reactants in gaseous form (1 mol hydrogen gas and 1 mol fluorine gas) form 2 mol of product (hydrogen fluoride) also in gaseous form. The number of moles did not change and hence one would think that change in entropy should be zero.

However, the above calculation indicates that the final value is not exactly zero but close to zero. The sign on the entropy change could be positive or negative.

$$\begin{aligned} \text{(d) } \Delta S^{\circ}_{\text{reaction}} &= [1 \times S^{\circ} (\text{N}_2 (\text{g})) + 1 \times S^{\circ} (\text{O}_2 (\text{g}))] - [2 \times S^{\circ} (\text{NO} (\text{g}))] \\ &= (1 \times 191.5 \text{ J/K.mol} + 1 \times 205.0 \text{ J/K.mol}) - (2 \times 210.6 \text{ J/K.mol}) \\ &= -24.7 \text{ J/K.mol} \end{aligned}$$

In this example, the change in entropy of reaction is negative in spite of the fact that the same number of moles is involved on both sides of the reaction. But, the change is small.

In general, we may say that **if the total number of moles of reactants is the same as the total number of moles of products, the entropy change of reaction is not zero, but close to zero with either positive or negative sign.**
