

7.4: The Third Law of Thermodynamics

In chapter 4, we have discussed how to calculate reaction enthalpies for any reaction, given the formation enthalpies of reactants and products. In this section, we will try to do the same for reaction entropies. In this case, however, our task is simplified by a fundamental law of thermodynamics, introduced by Walther Hermann Nernst (1864–1941) in 1906.¹ The statement that was initially known as Nernst's Theorem is now officially recognized as the third fundamental law of thermodynamics, and it has the following definition:

Definition: Third Law of Thermodynamics

The entropy of a perfectly ordered, pure, crystalline substance is zero at $T = 0$ K.

This law sets an unambiguous zero of the entropy scale, similar to what happens with absolute zero in the temperature scale. The absolute value of the entropy of every substance can then be calculated in reference to this unambiguous zero. As such, absolute entropies are always positive. This is in stark contrast to what happened for the enthalpy. An unambiguous zero of the enthalpy scale is lacking, and standard formation enthalpies (which might be negative) must be agreed upon to calculate relative differences.

In simpler terms, given a substance i , we are not able to measure absolute values of its enthalpy H_i (and we must resort to known enthalpy differences, such as $\Delta_f H^\ominus$ at standard pressure). At the same time, for entropy, we can measure S_i thanks to the third law, and we usually report them as S_i^\ominus . A comprehensive list of standard entropies of inorganic and organic compounds is reported in appendix 16. Reaction entropies can be calculated from the tabulated standard entropies as differences between products and reactants, using:

$$\Delta_{\text{rxn}} S^\ominus = \sum_i \nu_i S_i^\ominus,$$

with ν_i being the usual stoichiometric coefficients with their signs given in [Definition: Signs of the Stoichiometric Coefficients](#).

The careful wording in the definition of the third law [Definition: Third Law of Thermodynamics](#) allows for the fact that some crystal might form with defects (i.e., not as a perfectly ordered crystal). In this case, a residual entropy will be present even at $T = 0$ K. However, this residual entropy can be removed, at least in theory, by forcing the substance into a perfectly ordered crystal.²

An interesting corollary to the third law states that it is impossible to find a procedure that reduces the temperature of a substance to $T = 0$ K in a finite number of steps.

1. Walther Nernst was awarded the 1920 Nobel Prize in Chemistry for his work in thermochemistry.
2. A procedure that—in practice—might be extremely difficult to achieve.

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