

## 11.4: Genesis of the Third Law - the Nernst Heat Theorem

The third law arises in a natural way in the development of statistical thermodynamics. It is probably fair to say that the classical thermodynamic treatment of the third law was shaped to a significant degree by the statistical thermodynamic treatment that developed about the same time. Nevertheless, we can view the third law as an inference from thermochemical observations.

Walther Nernst was the first to recognize the principle that underlies the third law. From published experimental results, Nernst inferred a postulate known as the **Nernst heat theorem**. The experimental results that inspired Nernst were measurements of enthalpy and Gibbs free energy differences,  $\Delta_r H$  and  $\Delta_r G$ , for particular reactions at a series of temperatures. (We define  $\Delta_r H^\circ$  in [Section 8.6](#). We define  $\Delta_r H$  the same way, except that the reactants and products are not all in their standard states. Likewise,  $\Delta_r G$  and  $\Delta_r S$  are differences between Gibbs free energies and entropies of reactants and products. We give a more precise definition for  $\Delta_r G^\circ$  in [Section 13.2](#).) As the temperature decreased to a low value, the values of  $\Delta_r H$  and  $\Delta_r G$  converged. Since  $T\Delta_r S = \Delta_r H - \Delta_r G$ , this observation was consistent with the fact that the temperature was going to zero. However, Nernst concluded that the temperature factor in  $T\Delta_r S$  was not, by itself, adequate to explain the observed dependence of  $\Delta_r H - \Delta_r G$  on temperature. He inferred that the entropy change for these reactions decreased to zero as the temperature decreased to absolute zero and postulated that this observation would prove to be generally valid. The Nernst heat theorem asserts that the entropy change for any reaction of pure crystalline substances goes to zero as the temperature goes to zero.

Subsequently, Max Planck suggested that the entropy of reaction goes to zero because of a still more basic phenomenon: the entropy of every crystalline substance goes to zero as the temperature goes to zero. Further investigation then showed that Planck's formulation fails for substances like carbon monoxide, in which the crystalline solid does not become perfectly ordered at the temperature goes to zero. The Lewis and Randall statement refines the Planck formulation by recognizing that non-zero entropies will be observed at absolute zero for solids that are not crystalline and for crystalline solids that are not perfectly ordered. The Lewis and Randall statement also makes a choice (implicit also in the Planck formulation) of the zero point for the entropies of chemical substances—namely, “some crystalline state” of each element at absolute zero. This choice ensures that, at any temperature greater than zero, the entropy of every substance will be greater than zero.

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