# CHAPTER OVERVIEW

## 6: The Third Law and Cryogenics

The third law of thermodynamics concerns the entropy of perfectly-ordered crystals at zero kelvins.

When a chemical reaction or phase transition is studied at low temperatures, and all substances are pure crystals presumed to be perfectly ordered, the entropy change is found to approach zero as the temperature approaches zero kelvins:

$$\lim_{T \to 0} \Delta S = 0 \tag{6.0.1}$$
$$\text{(pure, perfectly-ordered crystals)}$$

Equation 6.0.1 is the mathematical statement of the *Nernst heat theorem* or **third law of thermodynamics**. It is true in general only if each reactant and product is a pure crystal with identical unit cells arranged in perfect spatial order.

> Nernst preferred to avoid the use of the entropy function and to use in its place the partial derivative $-(\partial A / \partial T)_V$ (Eq. 5.4.9). The original 1906 version of his heat theorem was in the form $\lim_{T \to 0} (\partial \Delta A / \partial T)_V = 0$ (William H. Cropper, *J. Chem. Educ.*, **64**, 3–8, 1987).

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