

## 16.1: Nernst's Heat Theorem

At the beginning of the twentieth century, Walther Nernst (Nobel Prize in Chemistry 1920) had investigated heat capacities and heats of reaction at progressively lower temperatures. As a result of his studies, he enunciated an important principle that initially was restricted to the behaviour of reactions involving solids and liquids but which is now believed to apply to all processes and substances.

The subject of chemical thermodynamics is dealt with more fully in Chapter 17, but for the present we shall note that some chemical reactions require an input of heat to initiate them; other chemical reactions generate heat. The former are known as *endothermic* reactions; the latter are *exothermic* reactions. If the reaction takes place at constant pressure (i.e. on an open laboratory bench) the heat gained or lost is an increase or decrease in *enthalpy*  $H$ . The *heat of reaction* is usually given as  $\Delta H$ , being positive for an endothermic reaction (in which the system gains heat) and negative for an exothermic reaction. It should be noted that spontaneous reactions are by no means always exothermic; some spontaneous reactions result in the absorption of heat from their surroundings and in a corresponding increase of enthalpy.

Nernst had noticed that, at progressively lower temperatures, the change in enthalpy and the change in the Gibbs function during a chemical reaction become more and more equal. And (as we shall see, what amounts to the same thing) the *rate of change of the Gibbs function with temperature* becomes less and less as the temperature is lowered. That this amounts to the same thing is evident from the Gibbs-Helmholtz relation

$$\Delta H = \Delta G - T \left( \frac{\partial(\Delta G)}{\partial T} \right)_P. \quad (16.1.1)$$

What Nernst proposed was that, in the limit, as the temperature approaches zero, the changes in the enthalpy and Gibbs function are equal – or, what amounts to the same thing, the temperature rate of change of the Gibbs function at constant pressure approaches zero at zero temperature. And since

$$\left( \frac{\partial(\Delta G)}{\partial T} \right)_P = -\Delta S, \quad (16.1.2)$$

this implies that *chemical reactions at a temperature of absolute zero take place with no change of entropy*. This is *Nernst's Heat Theorem*.

Planck later extended this to suppose that, not only does  $\Delta G \rightarrow \Delta H$ , but that, as  $T \rightarrow 0$ , the enthalpy and the Gibbs function of the system approach each other asymptotically in such a manner that, in the limit, as  $T \rightarrow 0$ ,  $G \rightarrow H$  and  $(\partial G/\partial T)_P \rightarrow 0$ .

This has a number of consequences. For example, until now, we had defined only what is meant by a *change in entropy*. In particular, in order to state what *the* entropy of a system is at some temperature, we would need to know what the entropy is at a temperature of zero kelvin. In Sections 12.8 and 12.9 we attempted to calculate the change in the Helmholtz and Gibbs functions as a system was changed from one state to another. We found that the right hand sides of equations 12.9.9 and 12.9.11 for calculating the changes in these functions contained the entropy. We later went on to show how we could calculate the difference in entropy in some state to that at zero temperature, but there was still a matter of an arbitrary constant, namely – what is the entropy at zero temperature? We now have the answer, resulting *from the observed behaviour of*  $(\partial G/\partial T)_P [= -S]$  as the temperature approaches zero – namely that the arbitrary constant is no longer arbitrary, and the entropy approaches zero as the temperature approaches zero.

Another consequence is

---

This page titled [16.1: Nernst's Heat Theorem](#) is shared under a [CC BY-NC](#) license and was authored, remixed, and/or curated by [Jeremy Tatum](#).