

Question #61126, Chemistry / Physical Chemistry / Completed

Question:

Explain Nernst heat theorem.

Answer:

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

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

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

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

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

In other words, the Nernst heat theorem says that as absolute zero is approached, the entropy change ΔS for a chemical or physical transformation approaches 0. This can be expressed mathematically as follow

$$\lim_{T \rightarrow 0} \Delta S = 0$$

The above equation is a modern statement of the theorem.

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