Answer on Question #77196 - Chemistry - Physical Chemistry

Question:

For a reaction in equilibrium at temperature T0, show that if the reaction is endothermic, heating to a higher temperature T1 causes some reactant to spontaneously convert to product, by making use of the integrated Gibbs-Helmholtz equation

Solution:

For the thermodynamic function of the state (f) and its natural variables (x, y)

$$f - x\left(\frac{\delta f}{\delta x}\right)_y = -x^2\left(\frac{\delta\left(\frac{f}{x}\right)}{\delta x}\right)_y = \left(\frac{\delta\left(\frac{f}{x}\right)}{\delta\left(\frac{1}{x}\right)}\right)_y ;$$

$$G - T\left(\frac{\delta G}{\delta T}\right)_P = -T^2\left(\frac{\delta\left(\frac{G}{T}\right)}{\delta T}\right)_P = \left(\frac{\delta\left(\frac{G}{T}\right)}{\delta\left(\frac{1}{T}\right)}\right)_P ;$$

(δG/δT)P = –S, and G ≡ H – TS;

$$H = G - T\left(\frac{\delta G}{\delta T}\right)_P = -T^2\left(\frac{\delta\left(\frac{G}{T}\right)}{\delta T}\right)_P = \left(\frac{\delta\left(\frac{G}{T}\right)}{\delta\left(\frac{1}{T}\right)}\right)_P .$$

This is the Gibbs-Helmholtz equation. If we apply this equation to the initial and final states of the process, which occurs at a constant temperature and pressure, and take the difference, we get:

$$\Delta H = \Delta G - T\left(\frac{\delta \Delta G}{\delta T}\right)_P = -T^2\left(\frac{\delta\left(\frac{\Delta G}{T}\right)}{\delta T}\right)_P = \left(\frac{\delta\left(\frac{\Delta G}{T}\right)}{\delta\left(\frac{1}{T}\right)}\right)_P .$$