Affinity for Spontaneous Reaction:

Dependence on Pressure

The Gibbs energy of a given closed system is defined by equation (a) where $\xi$ describes the chemical composition.

$$G(T, p, \xi)$$ (a)

We consider the dependence of Gibbs energy on pressure and extent of reaction at fixed temperature $T$.

$$\frac{\partial}{\partial p} \left( \frac{\partial G}{\partial \xi} \right) = \frac{\partial}{\partial \xi} \left( \frac{\partial G}{\partial p} \right)$$ (b)

But volume $V = \left( \frac{\partial G}{\partial p} \right)_{T, \xi}$ and affinity $A = -\left( \frac{\partial G}{\partial \xi} \right)_{T, p}$.

Volume $V$ and affinity $A$ are given by first differentials of the Gibbs energy, $G$.

Then

$$-\left( \frac{\partial A}{\partial p} \right)_{T, \xi} = \left( \frac{\partial V}{\partial \xi} \right)_{T, p}$$ (c)

Here $\left( \frac{\partial V}{\partial \xi} \right)_{T, p}$ is the volume of reaction, being the increase volume accompanying unit increase in extent of reaction, $\xi$. 