Affinity for Spontaneous Reaction: Stability

A given closed system at temperature T and pressure p undergoes a spontaneous change in chemical composition. Chemical reaction is driven by the affinity for spontaneous change such that the Gibbs energy decreases.

Thus \[ A = -\left( \frac{\partial G}{\partial \xi} \right)_{T,p} \] (a)

The plot of Gibbs energy G against composition \( \xi \) shows a gradual decrease until G reaches a minimum where the affinity A is zero at chemical equilibrium. An imagined plot beyond equilibrium would show an increase in Gibbs energy. In other words spontaneous chemical reaction stops at the point where G is a minimum (at fixed T and p). If the chemical reaction stops, the rate of chemical reaction is zero. We link the thermodynamic definition of chemical equilibrium and the definition of chemical equilibrium which emerges from the Law of Mass Action with reference to the kinetics of chemical reaction.

An accompanying plot shows a gradually decreasing affinity when plotted against \( \xi \), passing zero at \( \xi_{eq} \). The gradient of the plot in the neighbourhood of equilibrium is negative;

i.e. \[ \left( \frac{\partial A}{\partial \xi} \right)_{T,p} < 0 \] (b)

Equation (b) is the thermodynamic condition for a stable chemical equilibrium. The composition does not change no matter how long we wait. Indeed that is the experience of chemists and equation (b) expresses quantitatively this observation.

One might ask--- how does the system 'know' it is at a minimum in Gibbs energy?

Within the system, any fluctuation in composition leads to an increase in Gibbs energy. This tendency is opposed spontaneously; i.e. these fluctuations are opposed.