Reversible Change

In thermodynamics the term 'reversible' means that in such a system the affinity for spontaneous change $A$ is zero; we can in fact characterise the composition of the system by the symbol $\xi_{eq}$, indicating a time independent extent of chemical reaction. The composition of the system does not change because the affinity for spontaneous change is zero.

For a reversible change the affinity for spontaneous change is zero at all stages. The composition is represented by $\xi_{eq}$, and the rate of change $d\xi_{eq}/dt$ is zero, at defined $T$ and $p$. We represent the volume of the system using following equation.

$$V = V[T, p, \xi_{eq}, A = 0]$$

This equation means that the volume, a dependent variable, is unambiguously defined by the set of variables in the square brackets, $[...]$. The pressure is changed from $p$ to $p + \Delta p$, such that the new equilibrium composition is $\xi + \Delta \xi$ where the affinity for spontaneous change is zero.

$$V = V[T, (p + \Delta p), \xi_{eq}(p + \Delta p), A = 0]$$

Under these circumstances the change from $V(p)$ to $V(p + \Delta p)$ is from one equilibrium state where $A = 0$ to another equilibrium state where $A$ is also zero. Such an equilibrium transformation is, in thermodynamic terms, reversible. All changes under the constraint that $A$ remains at zero are reversible.