canonical rate constant

The rate constant for a system in which the reactants are in thermal equilibrium at a given temperature. In statistical mechanics the expression 'canonical ensemble' is used to refer to a closed system in thermal equilibrium, the species being present in a statistical distribution. By contrast, a microcanonical ensemble is composed of systems all having the same energy: a canonical ensemble therefore consists of a statistical distribution of microcanonical ensembles. The canonical or thermal rate constant can be obtained from the microcanonical rate constant by summing over the energy, taking into account the statistical distribution.

Source:
PAC, 1996, 68, 149 (A glossary of terms used in chemical kinetics, including reaction dynamics (IUPAC Recommendations 1996)) on page 155