microscopic diffusion control (encounter control)

The observable consequence of the limitation that the rate of a bimolecular chemical reaction in a homogeneous medium cannot exceed the rate of encounter of the reacting molecular entities. If (hypothetically) a bimolecular reaction in a homogeneous medium occurred instantaneously when two reactant molecular entities made an encounter, the rate of reaction would be an encounter-controlled rate, determined solely by rates of diffusion of reactants. Such a hypothetical 'fully diffusion controlled rate' is also said to correspond to 'total microscopic diffusion control', and represents the asymptotic limit of the rate of reaction as the rate constant for the chemical conversion of the encounter pair into product (or products) becomes large relative to the rate constant for separation (or dissociation) of the encounter pair. 'Partial microscopic diffusion control' is said to operate in a homogeneous reaction when the rates of chemical conversion and of separation are comparable. (The degree of microscopic diffusion control cannot usually be determined with any precision.)
See also: mixing control

Source:
PAC, 1994, *66*, 1077 *(Glossary of terms used in physical organic chemistry (IUPAC Recommendations 1994))* on page 1140

See also:
PAC, 1996, *68*, 149 *(A glossary of terms used in chemical kinetics, including reaction dynamics (IUPAC Recommendations 1996))* on page 173