Relaxation Kinetics

$$\tau_{pert} << \frac{1}{k_{fast}}$$

Diffusion Controlled Reactions in Solution

$A + B \rightarrow C$ $\qquad -\frac{d[A]}{dt} = k_D[A][B]$

$$k_D = 4\pi L D_{AB} d_{AD}$$

$$k_D = \frac{8RT}{3\eta}$$

$$k_{OBS} = \frac{k_D k_r}{k_D + k_r}$$

$k_D^I = 4\pi L D_{AB} d_{eff}$ $\qquad d_{eff} = d_{AB}\left(\frac{\delta}{e^{\delta-1}}\right)$ $\qquad \delta = \frac{Z_A Z_B e^2}{4\pi\varepsilon_0\varepsilon_r d_{AB} k_B T}$

$$\tau_E \approx \frac{d_{AB}^2}{6D_{AB}}$$

Activation Controlled Reactions and Transition State Theory

$A + B \leftrightarrow AB^{\ddagger} \rightarrow P$ $\qquad \frac{d[P]}{dt} = k_r[AB]^{\ddagger}$ $\qquad (\leftrightarrow = K^{\ddagger} \; and \rightarrow = k_r)$

$K^{\ddagger} = \frac{k_D}{k_{-D}}$ $\qquad K^{\ddagger} = \frac{k_B T}{h}$ so $k_{TST} = \kappa \frac{k_B T}{hC_0} K^{\ddagger}$

$$k_{TST} = \kappa \frac{k_B T}{hC_0} e^{\left(\frac{\Delta S^{\ddagger}}{R}\right)} e^{-\left(\frac{\Delta H^{\ddagger}}{RT}\right)}$$

$A = e\kappa \frac{k_B T}{hC_0} e^{\left(\frac{\Delta S^{\ddagger}}{R}\right)}$ $\qquad \Delta G_{ES}^{\ddagger} = \frac{Z_A Z_B e^2 L}{4\pi\varepsilon_0\varepsilon_r d_{AB}}$ $\qquad ln k_{TST}^I = ln k_{TST} - \frac{Z_A Z_B e^2}{4\pi\varepsilon_0 d_{AB} k_B T}\left(\frac{1}{\varepsilon_r}\right)$

$$\Delta S_{ES}^{\ddagger} = -\frac{C_s Z_A Z_B e^2 L}{4\pi\varepsilon_0\varepsilon_r d_{AB}}$$

$$log\left(\frac{k_{TST}^{I(DH)}}{k_{TST}^I}\right) = 2AZ_A Z_B\sqrt{I}$$