

Relaxation Kinetics

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

Diffusion Controlled Reactions in Solution



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

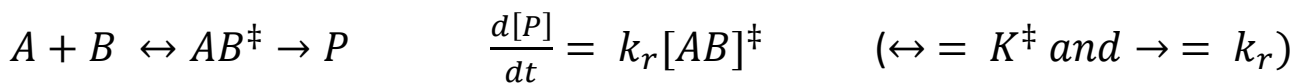
$$k_D = \frac{8RT}{3\eta}$$

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

$$k_D^I = 4\pi L D_{AB} d_{eff} \quad d_{eff} = d_{AB} \left(\frac{\delta}{e^{\delta} - 1} \right) \quad \delta = \frac{Z_A Z_B e^2}{4\pi \epsilon_0 \epsilon_r d_{AB} k_B T}$$

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

Activation Controlled Reactions and Transition State Theory



$$K^\ddagger = \frac{k_D}{k_{-D}} \quad K^\ddagger = \frac{k_B T}{h} \quad \text{so} \quad k_{TST} = \kappa \frac{k_B T}{h C_0} K^\ddagger$$

$$k_{TST} = \kappa \frac{k_B T}{h C_0} e^{\left(\frac{\Delta S^\ddagger}{R}\right)} e^{-\left(\frac{\Delta H^\ddagger}{RT}\right)}$$

$$A = e \kappa \frac{k_B T}{h C_0} e^{\left(\frac{\Delta S^\ddagger}{R}\right)} \quad \Delta G_{ES}^\ddagger = \frac{Z_A Z_B e^2 L}{4\pi \epsilon_0 \epsilon_r d_{AB}} \quad \ln k_{TST}^I = \ln k_{TST} - \frac{Z_A Z_B e^2}{4\pi \epsilon_0 d_{AB} k_B T} \left(\frac{1}{\epsilon_r}\right)$$

$$\Delta S_{ES}^\ddagger = -\frac{C_s Z_A Z_B e^2 L}{4\pi \epsilon_0 \epsilon_r d_{AB}}$$

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