A First Course on Kinetics and Reaction Engineering
Unit 8. Rate-Determining Step

Definitions

rate-determining step - kinetically demanding step representing the bottleneck in the mechanism; the free energy change is equivalent to the free energy change for the overall macroscopically observed reaction

quasi-equilibrated step - in mechanisms with a rate determining step, reaction other than the rate determining step for which the free energy change is nearly equal to zero and an equilibrium expression can be written

Nomenclature

[ ]	symbols indicating the concentration or, if a gas, partial pressure of the species within the brackets
ΔG_j	free energy change for reaction j; rds indicates the rate determining step
$\nu_{i,j}$	stoichiometric coefficient of species i in reaction j; rds indicates the rate determining step
$K_{eq,s}$	equilibrium constant for step s
b_j	coefficient multiplying reaction j in the linear combination of reactions that equals the overall reaction; rds indicates the rate determining step
k_j	rate coefficient for reaction j, an additional subscripted "f" indicates rate coefficient for the absolute rate in the forward direction; rds indicates the rate determining step
r_j	generalized net rate of reaction j; rds indicates the rate determining step

Equations

$$r_j = r_{rds} \tag{8.1}$$

$$\Delta G_j = b_1 \Delta G_1 + b_2 \Delta G_2 + \cdots b_{rds} \Delta G_{rds} + \cdots \tag{8.2}$$

$$\Delta G_j \approx b_{rds} \Delta G_{rds} \tag{8.3}$$

$$\Delta G_k \approx 0 \qquad k \neq rds \tag{8.4}$$

$$r_j = r_{rds} = k_{rds,f} \left(\prod_{\substack{m=\text{all} \\ \text{reactants}}} \left[m \right]^{-\nu_{m,rds}} \right) \tag{8.5}$$

$$K_{eq,s} = \prod_{\substack{i=\text{all} \\ \text{species}}} \left[i \right]^{\nu_{i,s}} \qquad s \neq rds \tag{8.6}$$