A First Course on Kinetics and Reaction Engineering
Unit 6. Reaction Mechanisms

Definitions

reaction mechanism - a sequence of elementary reactions that occur at the molecular level, giving the impression, at the macroscopic level, that a single non-elementary reaction is occurring

reactive intermediate - a chemical species that appears in a reaction mechanism, but not in the macroscopically observed, non-elementary reaction to which it corresponds

stoichiometric number - the number of times a mechanistic step must occur each time the macroscopically observed, non-elementary reaction occurs once, as written

initiation step - an elementary reaction in a chain reaction mechanism that has no reactive intermediates as reactants and one or more reactive intermediates as products

termination step - an elementary reaction in a chain reaction mechanism that has one or more reactive intermediates as reactants and no reactive intermediates as products

propagation step - an elementary reaction in a chain reaction mechanism that involves one reactive intermediate as a reactant and a different reactive intermediate as a product and that can be combined with other propagation steps to give the macroscopically observed, non-elementary reaction to which the mechanism corresponds

chain branching step - an elementary reaction in a chain reaction mechanism that includes one reactive intermediate as a reactant and two reactive intermediates as products

chain transfer step - an elementary reaction in a chain reaction mechanism that terminates one closed sequence of steps while initiating a new closed sequence of steps

Nomenclature

[ ]	symbols indicating the concentration or, if a gas, partial pressure of the species within the brackets
$\nu_{i,j}$	stoichiometric coefficient of species i in reaction j
K	equilibrium constant; a subscript j denotes the associated reaction; (T) may follow to indicate iti s a function of temperature
k_j	rate coefficient for reaction j, an additional subscripted "f" indicates rate coefficient for the absolute rate in the forward direction and "r" denotes the reverse direction
$r_{i,j}$	rate of generation of species i via reaction j, or, equivalently, the rate of reaction j with respect to species i
r_j	generalized net rate of reaction j

Equations

$$r_j = k_{j,f} \prod_{\substack{i=\text{all}\\ \text{reactants}}} \left[i \right]^{-\nu_{i,j}} - k_{j,r} \prod_{\substack{i=\text{all}\\ \text{products}}} \left[i \right]^{\nu_{i,j}} \tag{6.1}$$

$$r_j = k_{j,f} \left(\prod_{\substack{i=\text{all}\\ \text{reactants}}} \left[i \right]^{-\nu_{i,j}} \right) \left(1 - \frac{\prod_{\substack{i=\text{all}\\ \text{species}}} \left[i \right]^{\nu_{i,j}}}{K_{j,eq}} \right) \tag{6.2}$$

$H_2 + Br_2 \rightarrow 2\ HBr$ (6.3)

$Br_2 \rightleftarrows 2\ Br\cdot$ (6.4)

$Br\cdot + H_2 \rightleftarrows HBr + H\cdot$ (6.5)

$H\cdot + Br_2 \rightleftarrows HBr + Br\cdot$ (6.6)

$2\ H\cdot \rightleftarrows H_2$ (6.7)

$$r_{i,j} = \sum_{\substack{s=\text{ all}\\ \text{steps}}} \nu_{i,s} r_s \tag{6.8}$$

$$r_{i,j} = \sum_{\substack{s=\text{ all}\\ \text{steps}}} \nu_{i,s} \left(k_{s,f} \prod_{\substack{m=\text{all}\\ \text{reactants}}} \left[m \right]^{-\nu_{m,s}} - k_{s,r} \prod_{\substack{n=\text{all}\\ \text{products}}} \left[n \right]^{\nu_{n,s}} \right) \tag{6.9}$$