

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

$v_{i,j}$ stoichiometric coefficient of species i in reaction j

K equilibrium constant; a subscript j denotes the associated reaction; (T) may follow to indicate it is 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

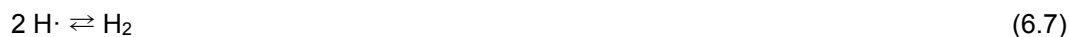
Equations

$$r_j = k_{j,f} \prod_{i=\text{all}} [\textit{i}]^{-v_{i,j}} - k_{j,r} \prod_{i=\text{all}} [\textit{i}]^{v_{i,j}} \quad (6.1)$$

reactants
products

$$r_j = k_{j,f} \left(\prod_{i=\text{all}} [\textit{i}]^{-v_{i,j}} \right) \left(1 - \frac{\prod_{i=\text{all}} [\textit{i}]^{v_{i,j}}}{K_{j,eq}} \right) \quad (6.2)$$

reactants
species



$$r_{i,j} = \sum_{s=\text{all}} v_{i,s} r_s \quad (6.8)$$

steps

$$r_{i,j} = \sum_{s=\text{all}} v_{i,s} \left(k_{s,f} \prod_{m=\text{all}} [\textit{m}]^{-v_{m,s}} - k_{s,r} \prod_{n=\text{all}} [\textit{n}]^{v_{n,s}} \right) \quad (6.9)$$

reactants
products