A First Course on Kinetics and Reaction Engineering
Unit 5. Empirical and Theoretical Rate Expressions

Definitions

empirical rate expression - a rate expression, as defined in Unit 4, that is chosen on the basis of its ability to accurately predict experimental results, and not on some theoretical basis

reaction order with respect to a given species - the power to which the species concentration is raised in a power-law type of rate expression

overall reaction order - the sum of the reaction orders of all the species in a system

elementary reaction - a reaction where the reaction equation is an exact description of the molecular event taking place

collision cross section - projected area around a molecule that will result in a collision if another molecule enters the area

molecularity - the number of reactants participating in an elementary reaction

steric limitation - requirement that reactants must be in a particular orientation relative to each other in order to react

steric factor - ratio of the number of collisions that satisfy the steric limitation to the total number of collisions

potential energy surface - a plot of the potential energy of a system as a function of the spatial coordinates of all of the atoms in that system

activated complex - the species that exists at the point on the reaction coordinate with the greatest potential energy; it is said to be in the transition state and has a geometry somewhere between that of reactants and that of products

transition state - the thermodynamic state of an activated complex; the thermodynamic state corresponding to the point on the reaction coordinate with the greatest potential energy

saddle point - a point on a surface where the curvature is uphill in all directions but one

activation energy - the maximum energy along the reaction coordinate

reaction coordinate - the sequence of atomic positions a system will display as reactants are converted to products while maintaining the lowest energy possible at all times in the process

transmission coefficient - correction factor introduced into a transition state rate expression to account for quantum mechanical tunneling through the activation barrier

Nomenclature

[ ] symbols indicating the concentration or, if a gas, partial pressure of the species within the brackets

‡ symbol, when superscripted, indicating a species to be an activated complex or a quantity to be associated with the transition state; when subscripted it indicates a quantity to be associated with the transition state after the partition function for the critical vibrational mode has been factored out

$|_{\text{equilibrium}}$ symbol indicating that the preceding quantity is evaluated at equilibrium

ΔE^0_0 difference in the ground state electronic energy at absolute zero

ε_0 minimum relative translational energy necessary for a collision to result in chemical reaction

μ specific cell growth rate or reduced mass; when the subscript "max" is present it indicates the maximum specific cell growth rate, a parameter in the Monod equation

ν stoichiometric coefficient (in which case the first subscript denotes the species and the second subscript denotes the reaction) or frequency (in which case a subscript may indicate the event the frequency is for); a subscripted c denotes the critical vibrational mode corresponding to motion along the reaction coordinate

σ_{ij} cross section for a collision between species i and j

C concentration; a subscripted "S" indicates the mass concentration of substrate during cell growth, otherwise the subscript indicates the chemical species and that it is a molar concentration

D distance between molecules i and j

E activation energy; a subscript j denotes the associated reaction and an additional subscripted "f" indicates as measured in the forward direction

K equilibrium constant; a subscript j denotes the associated reaction; (T) may follow to indicate it is a function of temperature; when followed by a subscripted "s" it represents the saturation constant in the Monod equation

L average distance traveled by a molecule between collisions

N_{Av} Avogadro's number

N_i number of molecules of species i

N^*_i number of molecules of species i per unit volume

P pressure, a subscript "i" indicates the partial pressure of species i

R ideal gas constant, or, when written with a subscript "i," collision radius of species i

T temperature

V volume; a superscripted * and subscripted "i" denotes the average volume per molecule of i

Z collision number; a prime denotes the total collision number and the absence of a prime denotes a collision number for collisions involving energy greater than some threshold energy; subscripts indicate the colliding species

a parameter in a power-law rate expression

h Planck's constant

k_B Boltzmann's constant

k_j rate coefficient for the generalized net rate of reaction j, an additional subscripted "f" indicates rate coefficient for the absolute rate in the forward direction and "r" denotes the reverse direction

$k_{0,j}$ pre-exponential term (not necessarily equal to the Arrhenius pre-exponential factor) in the 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

l termolecular collision distance; when three molecules are within this distance of each other, they are taken to have collided

m_i reaction order of species i or mass of species i

q_i partition function for species i; additional subscripts may indicate a partition function for a particular type of motion

r_j generalized net rate of reaction j; an "f" as a second subscript denotes the absolute rate in the forward direction and an "r" as a second subscript denotes the absolute rate in the reverse direction

t time; a subscript may indicate the time required for a particular event to occur

u velocity

Equations

$$r_j = k_j \prod_{\substack{i=\text{all}\\ \text{species}}} \left[i\right]^{m_i} \tag{5.1}$$

$$\left\{ 1 - \frac{\prod\limits_{\substack{i=\text{all}\\ \text{species}}} \left[i\right]^{\nu_{i,j}}}{K_{eq,j}\left(T\right)} \right\}^{a} \tag{5.2}$$

$$r_j = k_{0,j} \exp\left(\frac{-E_j}{RT}\right) \prod_{\substack{i=\text{all}\\ \text{species}}} \left[i\right]^{m_i} \left\{ 1 - \frac{\prod\limits_{\substack{i=\text{all}\\ \text{species}}} \left[i\right]^{\nu_{i,j}}}{K_{eq,j}\left(T\right)} \right\}^{a} \tag{5.3}$$

$$\mu = \frac{\mu_{\max} C_S}{K_s + C_S} \tag{5.4}$$

H_2 + Br_2 2 HBr (5.5)

$$dN_A = \left(4\pi N_A^* u^2\right)\left(\frac{\mu}{2\pi k_B T}\right)^{3/2} \exp\left(\frac{-\mu u^2}{2k_B T}\right) du \tag{5.6}$$

$$\mu = \frac{m_A m_B}{m_A + m_B} \tag{5.7}$$

$$\sigma_{AB} = \pi\left(R_A + R_B\right)^2 \tag{5.8}$$

$$V_B^* = \frac{1}{N_B^*} \tag{5.9}$$

$$L = \frac{V_B^*}{\sigma_{AB}} \tag{5.10}$$

$$t = \frac{L}{u} \tag{5.11}$$

$$t_{\text{one collision}} = \frac{V_B^*}{u\sigma_{AB}} \tag{5.12}$$

$$\nu_{\substack{\text{collisions of single A}\\ \text{molecule with velocity u}}} = \frac{u\sigma_{AB}}{V_B^*} \tag{5.13}$$

$$\nu_{\substack{\text{collisions of all A}\\ \text{molecules with velocity u}}} = \frac{u\sigma_{AB}}{V_B^*} dN_A^* \tag{5.14}$$

$$Z'_{AB} = N_A^* N_B^* \sigma_{AB} \sqrt{\frac{8k_BT}{\pi\mu}} \tag{5.15}$$

$$Z_{AB} = N_A^* N_B^* \sigma_{AB} \sqrt{\frac{8k_BT}{\pi\mu}} \exp\left(\frac{-\varepsilon_0}{k_BT}\right) \tag{5.16}$$

$$Z_{AA} = \left(N_A^*\right)^2 \sigma_{AA} \sqrt{\frac{2k_BT}{\pi\mu}} \exp\left(\frac{-\varepsilon_0}{k_BT}\right) \tag{5.17}$$

$$Z_{ABC} = 8N_A^* N_B^* N_C^* \sigma_{AB} \sigma_{BC} l \sqrt{\frac{2k_BT}{\pi}} \left(\frac{1}{\mu_{AB}} + \frac{1}{\mu_{BC}}\right) \exp\left(\frac{-\varepsilon_0}{k_BT}\right) \tag{5.18}$$

$$\varepsilon_0 = \frac{E}{N_{Av}} \tag{5.19}$$

$$k_B = \frac{R}{N_{Av}} \tag{5.20}$$

$$N_i^* = N_{Av} C_i \tag{5.21}$$

$$Z_{AB} = N_{Av} r_{j,f} \tag{5.22}$$

$$r_{AB,f} = N_{Av}\sigma_{AB}C_AC_B\sqrt{\frac{8k_BT}{\pi\mu}}\exp\left(\frac{-E_j}{RT}\right) \tag{5.23}$$

$$r_{AA,f} = N_{Av}\sigma_{AA}C_A^2\sqrt{\frac{2k_BT}{\pi\mu}}\exp\left(\frac{-E_j}{RT}\right) \tag{5.24}$$

$$r_{ABC,f} = 8N_{Av}\sigma_{AB}\sigma_{BC}lC_AC_BC_C\sqrt{\frac{2k_BT}{\pi}\left(\frac{1}{\mu_{AB}}+\frac{1}{\mu_{BC}}\right)}\exp\left(\frac{-E_j}{RT}\right) \tag{5.25}$$

$$r_{j,f} = k_{0,j,f}\sqrt{T}\exp\left(\frac{-E_{j,f}}{RT}\right)\prod_{\substack{i=\text{all}\\ \text{reactants}}} C_i^{-\nu_{i,j}} \tag{5.26}$$

$$r_{j,r} = k_{0,j,r}\sqrt{T}\exp\left(\frac{-E_{j,r}}{RT}\right)\prod_{\substack{i=\text{all}\\ \text{products}}} C_i^{\nu_{ij}} \tag{5.26}$$

$$\frac{k_{0,j,f}\sqrt{T}\exp\left(\frac{-E_{j,f}}{RT}\right)}{k_{0,j,r}\sqrt{T}\exp\left(\frac{-E_{j,r}}{RT}\right)} = K_{j,eq_c} \tag{5.27}$$

$$r_j = k_{0,j,f}\sqrt{T}\exp\left(\frac{-E_{j,f}}{RT}\right)\prod_{\substack{i=\text{all}\\ \text{reactants}}} C_i^{-\nu_{i,j}} - k_{0,j,r}\sqrt{T}\exp\left(\frac{-E_{j,r}}{RT}\right)\prod_{\substack{i=\text{all}\\ \text{products}}} C_i^{\nu_{ij}} \tag{5.28}$$

$$r_j = k_{0,j,f}\sqrt{T}\exp\left(\frac{-E_{j,f}}{RT}\right)\left(\prod_{\substack{i=\text{all}\\ \text{reactants}}} C_i^{-\nu_{ij}}\right)\left(1-\frac{\prod_{\substack{i=\text{all}\\ \text{species}}} C_i^{\nu_{ij}}}{K_{j,eq_c}}\right) \tag{5.29}$$

$$C_i = \frac{n_i}{V} = \frac{P_i}{RT} \tag{5.30}$$

AB + C → A + BC (5.31)

AB + C ⇄ ABC‡ (5.32)

$$K^{\ddagger} = \frac{\left[ABC^{\ddagger}\right]}{\left[AB\right]\left[C\right]} \tag{5.33}$$

$$\left[ABC^{\ddagger}\right] = K^{\ddagger}\left[AB\right]\left[C\right] \tag{5.34}$$

$$K^{\ddagger} = \frac{N_{Av} q_{ABC^{\ddagger}}}{q_{AB} q_C} \exp\left(\frac{-\Delta E_0^0}{k_B T} \right) \tag{5.35}$$

$$q_i = q_{tr-i} q_{rot-i} q_{vib-i} \tag{5.36}$$

$$q_{vib-i} = q_{v_1-i} q_{v_2-i} q_{v_3-i} q_{v_4-i} \tag{5.37}$$

$$q_{v-i} = \frac{1}{1 - \exp\left(\frac{-h\nu_n}{k_B T} \right)} \tag{5.38}$$

$$q_{ABC^{\ddagger}} = q_{tr-ABC^{\ddagger}} q_{rot-ABC^{\ddagger}} \left\{ \prod_{n=1}^{N_{\text{vib}}} q_{v_n-ABC^{\ddagger}} \right\} \tag{5.39}$$

$$\lim_{\nu_c \to 0} \frac{1}{1 - \exp\left(\frac{-h\nu_c}{k_B T} \right)} = \frac{k_B T}{h\nu_c} \tag{5.40}$$

$$q_{ABC^{\ddagger}} = q_{tr-ABC^{\ddagger}} q_{rot-ABC^{\ddagger}} \left\{ \prod_{\substack{n=1 \\ n \neq \text{critical} \\ \text{mode}}}^{N_{\substack{\text{vibrational} \\ \text{modes}}}} q_{v_n-ABC^{\ddagger}} \right\} \left\{ \frac{k_B T}{h\nu_c} \right\} \tag{5.41}$$

$$q_{\ddagger} = \frac{q_{ABC^{\ddagger}}}{\left\{ \frac{k_B T}{h\nu_c} \right\}} = q_{tr-ABC^{\ddagger}} q_{rot-ABC^{\ddagger}} \left\{ \prod_{\substack{n=1 \\ n \neq \text{critical} \\ \text{mode}}}^{N_{\substack{\text{vibrational} \\ \text{modes}}}} q_{v_n-ABC^{\ddagger}} \right\} \tag{5.42}$$

$$q_{ABC^{\ddagger}} = q_{\ddagger} \left\{ \frac{k_B T}{h\nu_c} \right\} \tag{5.43}$$

$$K^{\ddagger} = \frac{N_{Av} q_{\ddagger} \left\{ \frac{k_B T}{h\nu_c} \right\}}{q_{AB} q_C} \exp\left(\frac{-\Delta E_0^0}{k_B T} \right) \tag{5.44}$$

$$\nu_c = \frac{N_{Av} q_{\ddagger}}{K^{\ddagger} q_{AB} q_C} \left\{ \frac{k_B T}{h} \right\} \exp\left(\frac{-\Delta E_0^0}{k_B T} \right) \tag{5.45}$$

$$r_{j,f} = \left[ABC^{\ddagger} \right] \nu_c \tag{5.46}$$

$$r_{j,f} = \left(K^{\ddagger}\left[AB\right]\left[C\right]\right)\frac{N_{Av}q_{\ddagger}}{K^{\ddagger}q_{AB}q_{C}}\left\{\frac{k_BT}{h}\right\}\exp\left(\frac{-\Delta E_0^0}{k_BT}\right)$$

$$r_{j,f} = \frac{N_{Av}q_{\ddagger}}{q_{AB}q_{C}}\left\{\frac{k_BT}{h}\right\}\exp\left(\frac{-\Delta E_0^0}{k_BT}\right)\left[AB\right]\left[C\right] \tag{5.47}$$

$$k_{j,f} = \frac{N_{Av}q_{\ddagger}}{q_{AB}q_{C}}\left\{\frac{k_BT}{h}\right\}\exp\left(\frac{-\Delta E_0^0}{k_BT}\right) \tag{5.48}$$

$$r_j = k_{0,j,f}T\exp\left(\frac{-E_{j,f}}{RT}\right)\left(\prod_{\substack{i=\text{all}\\ \text{reactants}}} C_i^{-\nu_{ij}}\right)\left(1-\frac{\prod\limits_{\substack{i=\text{all}\\ \text{species}}} C_i^{\nu_{ij}}}{K_{j,eq_c}}\right) \tag{5.49}$$

$$k_{0,j,f} = \left(\frac{q_{\ddagger}}{N_{Av}}\right)\left(\prod_{\substack{i=\text{all}\\ \text{reactants}}}\left(\frac{q_i}{N_{Av}}\right)^{\nu_{ij}}\right)\left(\frac{k_B}{h}\right) \tag{5.50}$$

$$r_j = k_{0,j,f}\exp\left(\frac{-E_{j,f}}{RT}\right)\prod_{\substack{i=\text{all}\\ \text{reactants}}} C_i^{-\nu_{i,j}} - k_{0,j,r}\exp\left(\frac{-E_{j,r}}{RT}\right)\prod_{\substack{i=\text{all}\\ \text{products}}} C_i^{\nu_{ij}} \tag{5.51}$$

$$r_j = k_{0,j,f}\exp\left(\frac{-E_{j,f}}{RT}\right)\left(\prod_{\substack{i=\text{all}\\ \text{reactants}}} C_i^{-\nu_{ij}}\right)\left(1-\frac{\prod\limits_{\substack{i=\text{all}\\ \text{species}}} C_i^{\nu_{ij}}}{K_{j,eq_c}}\right) \tag{5.52}$$

$$C_i = \frac{P_i}{RT} \tag{5.53}$$

$$r_j = k_{0,j,f}\exp\left(\frac{-E_{j,f}}{RT}\right)\prod_{\substack{i=\text{all}\\ \text{reactants}}}\left[i\right]^{-\nu_{i,j}} - k_{0,j,r}\exp\left(\frac{-E_{j,r}}{RT}\right)\prod_{\substack{i=\text{all}\\ \text{products}}}\left[i\right]^{\nu_{i,j}} \tag{5.54}$$

$$r_j = k_{0,j,f}\exp\left(\frac{-E_{j,f}}{RT}\right)\left(\prod_{\substack{i=\text{all}\\ \text{reactants}}}\left[i\right]^{-\nu_{i,j}}\right)\left(1-\frac{\prod\limits_{\substack{i=\text{all}\\ \text{species}}}\left[i\right]^{\nu_{i,j}}}{K_{j,eq}}\right) \tag{5.55}$$