A First Course on Kinetics and Reaction Engineering
Unit 4. Reaction Rates and Temperature Effects

Definitions

normalization factor - quantity used to convert extensive reaction rates to intensive variables; the best quantity to use is the size (area or volume) of the location where the reaction actually takes place

catalyst - substance that is not consumed or generated in the reaction environment, but whose presence causes the rate of one or more reactions to increase

heterogeneous catalyst - a catalyst, as defined above, that exists in a separate phase from the reacting mixture

homogeneous catalyst - a catalyst, as defined above, that exists in the same phase as the reacting mixture

rate expression - a mathematical model for the dependence of a reaction rate on the environmental variables (temperature, pressure and composition)

Nomenclature

ΔG_j Gibbs free energy change for reaction j

ΔH_j heat (enthalpy) of reaction j

ΔS_j entropy change for reaction j

Δm_{cells} change in the cell mass

$\Delta n_{i,j}$ change in the number of moles of species i due to its participation in reaction j

Δt interval of time

ξ_j extent of reaction j

μ specific cell growth rate

$\nu_{i,j}$ stoichiometric coefficient of species i in reaction j; value is positive for products and negative for reactants

A_j pre-exponential factor in the Arrhenius expression for the temperature dependence of the rate coefficient for reaction j; the symbol $k_{0,j}$ is sometimes used to represent the same quantity

C_{cells} mass concentration of cells

C_i molar concentration of species i

E_j activation energy in the Arrhenius expression for the temperature dependence of the rate coefficient for reaction j

K an equilibrium constant, a subscript may be used to indicate the reaction it pertains to or to otherwise distinguish it

$K_{0,j}$ pre-exponential term for the equilibrium constant of reaction j when the enthalpy change and entropy change are treated as constants that are independent of T

P pressure; a subscript may be used to indicate partial pressure of the subscripted species

R	ideal gas constant
T	temperature
V	volume
$f()$	unspecified function of the variables that appear within the parentheses
k	a rate coefficient, a subscript may be used to indicate the reaction it pertains to or to otherwise distinguish it
$k_{0,j}$	pre-exponential factor in the Arrhenius expression for the temperature dependence of the rate coefficient for reaction j; the symbol A_j is sometimes used to represent the same quantity
m_{cells}	cell mass
n_i	number of moles of species i
r_g	rate of growth of cell mass
$r_{i,j}$	the rate of reaction j with respect to species i, or equivalently, the rate of production of species i due to reaction j
r_j	the generalized rate of reaction j
t	time
$\underline{x}$	vector notation for a set of composition variables (e. g. concentrations or partial pressures) of a reacting system

Equations

$$r_{i,j} = \frac{1}{V}\lim_{\Delta t \to 0}\frac{\Delta n_{i,j}}{\Delta t} = \frac{1}{V}\frac{dn_{i,j}}{dt} \tag{4.1}$$

$$r_j = \frac{r_{i,j}}{\nu_{i,j}} = \frac{1}{V}\frac{d\xi_j}{dt} \tag{4.2}$$

$$r_j = \frac{r_{i,j}}{\nu_{i,j}} = \frac{r_{k,j}}{\nu_{k,j}} \tag{4.3}$$

$$r_g = \frac{1}{V}\lim_{\Delta t \to 0}\frac{\Delta m_{cells}}{\Delta t} = \frac{1}{V}\frac{dm_{cells}}{dt} \tag{4.4}$$

$$\mu = \frac{r_g}{C_{cells}} \tag{4.5}$$

$$r_j = f\left(T, P, \underline{x}\right) \tag{4.6}$$

$$H_2 + Br_2 \rightarrow 2\ HBr \tag{4.7}$$

$$r_{4.7} = \frac{k_A P_{H_2}}{K_B + \frac{P_{Br_2}}{P_{HBr}}} \tag{4.8}$$

$$P_i = \frac{n_i RT}{V} \tag{4.9}$$

$$C_i = \frac{n_i}{V} = \frac{P_i}{RT} \tag{4.10}$$

$$K_j = \exp\left\{\frac{-\Delta G_j}{RT}\right\} = \exp\left\{\frac{\Delta S_j}{R}\right\}\exp\left\{\frac{-\Delta H_j}{RT}\right\} = K_{0,j}\exp\left\{\frac{-\Delta H_j}{RT}\right\} \tag{4.11}$$

$$k_j = k_{0,j}\exp\left(\frac{-E_j}{RT}\right) \tag{4.12}$$

$$\ln k_j = \left(\frac{-E_j}{R}\right)\frac{1}{T} + \ln k_{0,j} \tag{4.13}$$