This Page Intentionally Left Blank
R. J. Wijngaarden
A. Kronberg
K. R. Westerterp

Industrial Catalysis

Optimizing Catalysts and Processes
This Page Intentionally Left Blank
Catalysis is the acceleration of a chemical reaction by a small quantity of a substance, which may take part in the reaction, but in the end is not changed by the reaction. This alien substance can be dissolved in the reaction mixture or one of its components, which is referred to as homogeneous catalysis. It can also form its own separate phase, yielding heterogeneous catalysis. Homogeneous and heterogeneous catalysis are equally important from an industrial point of view. Homogeneous catalysis will not be the subject of this book. We will focus on heterogeneous catalysis, where the catalyst is a porous material itself or is impregnated in such material.

In heterogeneous catalysis reactants have to be transported to the catalyst and (if the catalyst is a porous, solid particle) also through the pores of the particle to the active material. In this case all kinds of transport resistances may play a role, which prevent the catalyst from being fully effective in its industrial application. Furthermore, because appreciable heat effects accompany most reactions, heat has to be removed from the particle or supplied to it in order to keep it in the appropriate temperature range (where the catalyst is really fully effective). Furthermore, heterogeneous catalysis is one of the most complex branches of chemical kinetics. Rarely do we know the compositions, properties or concentrations of the reaction intermediates that exist on the surfaces covered with the catalytically effective material. The chemical factors that govern reaction rates under these conditions are less well known than in homogeneous catalysis. Yet solid catalysts display specificities for particular reactions, and selectivity's for desired products, that in most practical cases cannot be equaled in other ways. Thus use of solid catalysts and the proper (mathematical) tools to describe their performance are essential.

The selection of a solid catalyst for a given reaction is often still empirical and based on prior experience or analogy. However, at the same time there are many aspects of this complex situation which are really well understood. For example we know how the true chemical kinetics, which are an intrinsic property of the catalyst, and all the many aspects of transport of material and heat around the catalytic particles interact. The chemist searching for new and better catalysts should always consider these physical factors, for they can be brought under control, and often in this way definite gains can usually be made both in activity and in selectivity.

Considerations based on the known physical phenomena can guide the choice of catalyst porosity and porous structure, catalyst size and shape and reactor type and size. These considerations apply both to laboratory as well as to large-scale operations. Many comprehensive reviews and good books on the problem of reactor design are available in the literature. The purpose of this book is to teach the reader the mathematical tools that are available for calculating interaction between the transport phenomena and true chemical kinetics, allowing optimization of catalyst performance. The discussed theories are elucidated with examples to provide training for application of the mathematics.

RJW, AEK, KRW
# Contents

## 1 Introduction
1.1 Introduction ................................................... 1  
1.2 Catalysis in an Industrial Reactor ............................ 2  
1.3 Catalytic Reactors ............................................ 4  
  1.3.1 Large Particle Catalyst .................................... 4  
  1.3.2 Small Particle Catalyst .................................... 5  
1.4 Characteristics of Reactor Performance ........................ 6  
References ...................................................................... 8

## 2 Kinetics
2.1 General ............................................................ 9  
2.2 Heterogeneous Catalytic Reactions .............................. 13  
2.3 Catalyst Performance ........................................... 18  
  2.3.1 Deactivation .................................................. 18  
  2.3.2 Selectivity .................................................... 19  
2.4 Kinetics in Practice ............................................. 21  
References ...................................................................... 24

## 3 Production and Physical Characteristics of Solid Catalysts
3.1 Introduction ....................................................... 25  
3.2 Catalyst Manufacture .......................................... 28  
  3.2.1 Materials and Methods ....................................... 28  
  3.2.2 Precipitated Catalysts ....................................... 30  
  3.2.3 Impregnated Catalysts ....................................... 31  
  3.2.4 Skeletal Catalysts ............................................ 32  
  3.2.5 Fused and Molten Catalysts ................................. 33  
  3.2.6 Calcination .................................................... 33  
  3.2.7 Reduction ..................................................... 33  
  3.2.8 Shape Formation of the Catalyst Particles ............... 33  
3.3 Physical Characterization of Catalysts ......................... 35  
  3.3.1 Void Fraction .................................................. 35  
  3.3.2 Surface Area .................................................. 35  
  3.3.3 Pore-size Distribution ...................................... 39  
3.4 Mass and Heat Transfer in Porous Catalysts .................. 41  
  3.4.1 Introduction .................................................. 41  
  3.4.2 Ordinary Diffusion in Multicomponent Gases ............. 43  
  3.4.3 Models of Mass Transport in Porous Media ............... 48  
  3.4.4 Heat Transfer in Porous Catalysts ......................... 56
### Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.3 Intraparticle Pressure Gradients</td>
<td>158</td>
</tr>
<tr>
<td>7.3.1 Pressure Gradients</td>
<td>159</td>
</tr>
<tr>
<td>7.3.2 Effective Diffusion Coefficient</td>
<td>162</td>
</tr>
<tr>
<td>7.3.3 Aris Numbers</td>
<td>163</td>
</tr>
<tr>
<td>7.3.4 Negligibility Criteria</td>
<td>165</td>
</tr>
<tr>
<td>7.3.5 Bimolecular Reactions</td>
<td>166</td>
</tr>
<tr>
<td>7.4 Anisotropic Catalyst Pellets</td>
<td>171</td>
</tr>
<tr>
<td>7.5 Summary Complex Situations</td>
<td>174</td>
</tr>
<tr>
<td>References</td>
<td>176</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>8 Design of Catalyst Pellets</td>
<td>177</td>
</tr>
<tr>
<td>8.1 Porous Structure and Observed Reaction Rate</td>
<td>177</td>
</tr>
<tr>
<td>8.1.1 Porous Structure and Catalyst Activity</td>
<td>177</td>
</tr>
<tr>
<td>8.1.2 Influence of Mass Transport on Selectivity</td>
<td>184</td>
</tr>
<tr>
<td>8.2 Optimal Particle Shape and Size</td>
<td>189</td>
</tr>
<tr>
<td>8.2.1 Pressure Drop</td>
<td>189</td>
</tr>
<tr>
<td>8.2.2 Diffusion Limitations</td>
<td>193</td>
</tr>
<tr>
<td>8.3 Distribution of Catalytic Material in Pellets</td>
<td>198</td>
</tr>
<tr>
<td>8.3.1 Dehydrogenation of Butene</td>
<td>198</td>
</tr>
<tr>
<td>8.3.2 Poison-resistant Catalyst for Automotive Emission Control</td>
<td>199</td>
</tr>
<tr>
<td>References</td>
<td>201</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>9 Examples</td>
<td>203</td>
</tr>
<tr>
<td>9.1 Analysis of Rate Equations</td>
<td>203</td>
</tr>
<tr>
<td>9.2 Comparison of Published Rate Equations</td>
<td>206</td>
</tr>
<tr>
<td>9.3 Permeation of Gases through a Porous Slug</td>
<td>209</td>
</tr>
<tr>
<td>9.4 Gaseous Counter-diffusion in a Capillary</td>
<td>212</td>
</tr>
<tr>
<td>9.5 Estimation of Diffusion Coefficients in Gases</td>
<td>214</td>
</tr>
<tr>
<td>9.6 Estimation of Diffusion Coefficients in Liquids</td>
<td>215</td>
</tr>
<tr>
<td>9.7 Measurement of Reaction Kinetics and Effective Pellet</td>
<td>215</td>
</tr>
<tr>
<td>Diffusivity in a Single-pellet Reactor</td>
<td>215</td>
</tr>
<tr>
<td>9.8 Langmuir-Hinshelwood Kinetics in a Ring-shaped Catalyst</td>
<td>216</td>
</tr>
<tr>
<td>9.9 Nonisothermal Catalyst Pellets and First-order Reactions</td>
<td>217</td>
</tr>
<tr>
<td>9.10 Effectiveness Factor for Nonisothermal Catalyst Pellets</td>
<td>217</td>
</tr>
<tr>
<td>9.11 Exothermic, Zeroth-order Reaction in a Ring-shaped Catalyst</td>
<td>219</td>
</tr>
<tr>
<td>9.12 Negligibility of Intraparticle Temperature Gradients</td>
<td>221</td>
</tr>
<tr>
<td>9.13 Effectiveness Factors Larger than one for</td>
<td>221</td>
</tr>
<tr>
<td>Langmuir-Hinshelwood Kinetics</td>
<td>221</td>
</tr>
<tr>
<td>9.15 Langmuir-Hinshelwood Kinetics and Intraparticle Temperature Gradients</td>
<td>223</td>
</tr>
<tr>
<td>9.16 Approximation of the Effectiveness Factor for Bimolecular Reactions</td>
<td>225</td>
</tr>
<tr>
<td>9.18 Calculation of ( K_{D} ) at ( x = 0 )</td>
<td>227</td>
</tr>
<tr>
<td>9.19 Maximum Pressure Difference in a Porous Pellet</td>
<td>227</td>
</tr>
<tr>
<td>9.20 Can a Gas be Regarded as Being Diluted</td>
<td>228</td>
</tr>
<tr>
<td>9.21 Are Gases Diluted for the Oxidation of Ethylene</td>
<td>228</td>
</tr>
<tr>
<td>9.22 Anisotropy of a Ringshaped Catalyst Pellet</td>
<td>229</td>
</tr>
<tr>
<td>References</td>
<td>230</td>
</tr>
</tbody>
</table>
Appendix A ........................................................... 233
Derivation of a Formula for the Zeroth Aris Number $A_n_0$
for Simple Reactions .............................................. 233

Appendix B ............................................................ 237
Derivation of a Formula for the First Aris Number $A_n_1$, for Simple Reactions... 237

Appendix C ............................................................ 241
Calculation of the Effectiveness Factor for a First-order Reaction
and the Geometry Factor for a Ring-shaped Catalyst ................. 241
References .......................................................... 244

Appendix D ............................................................ 245
Intraparticle Pressure Gradients for Nondiluted Gases and Simple Reactions . 245
References .......................................................... 254

Appendix E ............................................................ 255
Effective Diffusion Coefficient as a Function of the Gas Composition
for Nondiluted Gases and Simple Reactions .......................... 255

Appendix F ............................................................ 259
First Aris Number $A_n_1$, for Concentration-dependent Effective
Diffusion Coefficients and Simple Reactions. ......................... 259

Subject Index ......................................................... 263

Author Index ......................................................... 267
### Symbols and Abbreviations

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>amount of gas adsorbed</td>
<td>mol</td>
</tr>
<tr>
<td>a</td>
<td>specific contact area between reaction and nonreaction phase per unit reactor volume</td>
<td>m² m⁻³</td>
</tr>
<tr>
<td>aᵢ</td>
<td>chemical activity of component i</td>
<td>mol m⁻³</td>
</tr>
<tr>
<td>aᵣ</td>
<td>amount of gas adsorbed in monolayer</td>
<td>mol</td>
</tr>
<tr>
<td>A, B, P, Q, ...</td>
<td>component A, B, P, Q, ...</td>
<td></td>
</tr>
<tr>
<td>An</td>
<td>modified Arrhenius number</td>
<td>m²</td>
</tr>
<tr>
<td>An₀</td>
<td>zeroth Aris number (becomes equivalent to 1/η² for low values of η)</td>
<td>m²</td>
</tr>
<tr>
<td>An₁</td>
<td>first Aris number (becomes equivalent to 1-η² for values of η close to one)</td>
<td>m²</td>
</tr>
<tr>
<td>Aᵣ</td>
<td>external surface area catalyst pellet</td>
<td>m²</td>
</tr>
<tr>
<td>cᵣ</td>
<td>heat capacity at constant pressure, per unit mass</td>
<td>J kg⁻¹ K⁻¹</td>
</tr>
<tr>
<td>C</td>
<td>total molar concentration</td>
<td>mol m⁻³</td>
</tr>
<tr>
<td>Cᵣ</td>
<td>molar concentration of species A</td>
<td>mol m⁻³</td>
</tr>
<tr>
<td>Cᵣ</td>
<td>concentration of component A in well-mixed fluid bulk</td>
<td>mol m⁻³</td>
</tr>
<tr>
<td>Dᵣᵣ, Dᵣᵣᵣ, ...</td>
<td>binary diffusivities for system A-P, A-D, ...</td>
<td>m² s⁻¹</td>
</tr>
<tr>
<td>Dᵣᵣ</td>
<td>effective binary diffusivity for system i-j m² s⁻¹</td>
<td>m² s⁻¹</td>
</tr>
<tr>
<td>Dᵣᵣ</td>
<td>Knudsen diffusivity of component A</td>
<td>m² s⁻¹</td>
</tr>
<tr>
<td>Dᵣᵣ</td>
<td>surface diffusivity of component A</td>
<td>m² s⁻¹</td>
</tr>
<tr>
<td>Dᵣᵣ</td>
<td>effective diffusion coefficient</td>
<td>m² s⁻¹</td>
</tr>
<tr>
<td>d</td>
<td>molecular diameter</td>
<td>m</td>
</tr>
<tr>
<td>dᵣ</td>
<td>equivalent pore diameter</td>
<td>m</td>
</tr>
<tr>
<td>dᵣ</td>
<td>pellet diameter</td>
<td>m</td>
</tr>
<tr>
<td>Eₐ</td>
<td>energy of activation</td>
<td>J mol⁻¹</td>
</tr>
<tr>
<td>h</td>
<td>longitudinal coordinate</td>
<td>m</td>
</tr>
<tr>
<td>H</td>
<td>height of the catalyst pellet</td>
<td>m</td>
</tr>
<tr>
<td>(ΔHₑₑ)</td>
<td>adsorption enthalpy (exothermic reactions (ΔH) &gt; 0; endothermic reactions (ΔH) &lt; 0)</td>
<td>J mol⁻¹</td>
</tr>
<tr>
<td>J</td>
<td>mole flux through the cross-sectional area of the catalyst pellet (see Appendix E)</td>
<td>mol m² s⁻¹</td>
</tr>
<tr>
<td>Jᵢ</td>
<td>mole flux of species i through the cross-sectional area of the catalyst pellet</td>
<td>mol m² s⁻¹</td>
</tr>
<tr>
<td>Jᵢ</td>
<td>mole flux through the cross-sectional area of the catalyst pores (see Appendix E)</td>
<td>mol m² s⁻¹</td>
</tr>
<tr>
<td>k</td>
<td>reaction rate constant (dimensions depend on kinetic expression)</td>
<td>m² s⁻¹</td>
</tr>
<tr>
<td>kᵣ</td>
<td>reaction rate constant per unit outer surface of the pellet (dimensions depend on kinetic expression)</td>
<td>m² s⁻¹</td>
</tr>
<tr>
<td>kᵣ</td>
<td>mass transfer coefficient</td>
<td>m s⁻¹</td>
</tr>
<tr>
<td>K</td>
<td>adsorption constant for Langmuir-Hinshelwood kinetics</td>
<td>m³ mol⁻¹</td>
</tr>
<tr>
<td>Kn</td>
<td>Knudsen number</td>
<td>m</td>
</tr>
<tr>
<td>Kn</td>
<td>Knudsen number, modified for multicomponent systems</td>
<td>m</td>
</tr>
<tr>
<td>L</td>
<td>length (thickness) of a catalyst pellet</td>
<td>m</td>
</tr>
<tr>
<td>L</td>
<td>reactor length</td>
<td>m</td>
</tr>
<tr>
<td>m</td>
<td>reaction order for the component in excess in bimolecular reactions</td>
<td></td>
</tr>
</tbody>
</table>
XI1 Symbols and Abbreviations

\[ m \] mass \hspace{1cm} \text{kg}
\[ m \] distribution coefficient
\[ M \] molar mass \hspace{1cm} \text{kg mol}^{-1}
\[ \langle M \rangle \] average molar mass of the gas mixture \hspace{1cm} \text{kg mol}^{-1}
\[ n \] reaction order of reactant not in excess for bimolecular reactions
\[ n \] number of moles
\[ N \] conversion rate \hspace{1cm} \text{mol s}^{-1}
\[ N_e \] molar flux at pellet external surface \hspace{1cm} \text{mol m}^{-2} s^{-1}
\[ N_A \] Avogadro number \((6.02 \times 10^{23} \text{ molecules/mole})\)
\[ P \] total pressure \hspace{1cm} \text{Pa}
\[ P_A \] partial pressure of species \( A \) \hspace{1cm} \text{Pa}
\[ P_g \] adsorbent saturation pressure \hspace{1cm} \text{Pa}
\[ P \] mean pressure across the porous particle \hspace{1cm} \text{Pa}
\[ r \] radial coordinate \hspace{1cm} \text{m}
\[ r_e \] equivalent pore radius \hspace{1cm} \text{m}
\[ R \] gas constant \hspace{1cm} \text{J mol}^{-1} \text{ K}^{-1}
\[ R \] conversion rate per cubic metre catalyst volume \hspace{1cm} \text{mol m}^{-3} \text{ s}^{-1}
\[ R \] distance between centre and outer surface of the catalyst pellet for an infinite slab, infinite cylinder or sphere \hspace{1cm} \text{m}
\[ R_{ad} \] adsorption rate \hspace{1cm} \text{mol m}^{-2} \text{ s}^{-1}
\[ R_{ds} \] desorption rate \hspace{1cm} \text{mol m}^{-2} \text{ s}^{-1}
\[ R_i \] inner radius of a ring-shaped catalyst pellet \hspace{1cm} \text{m}
\[ R_o \] outer radius of a ring-shaped catalyst pellet \hspace{1cm} \text{m}
\[ R_e = \Omega r/\Phi \] recycle ratio
\[ [R] \] conversion rate per cubic metre catalyst volume \hspace{1cm} \text{mol m}^{-3} \text{ s}^{-1}
\[ \bar{R} \] reaction rate per unit pore surface \hspace{1cm} \text{mol m}^{-2} \text{ s}^{-1}
\[ R \] reaction rate per unit external pellet surface \hspace{1cm} \text{mol m}^{-2} \text{ s}^{-1}
\[ \langle R \rangle \] average reaction rate per unit pellet volume \hspace{1cm} \text{mol m}^{-3} \text{ s}^{-1}
\[ s_i \] surface area occupied by a molecule of an adsorbed species \hspace{1cm} \text{m}^2
\[ S \] internal surface area per unit catalyst volume \hspace{1cm} \text{m}^2 \text{ m}^{-3}
\[ S_i \] internal surface area per unit gram of catalyst \hspace{1cm} \text{cm}^2 \text{ g}^{-1}
\[ S_{cx} \] reactor cross-section \hspace{1cm} \text{m}^2
\[ S_{ix} \] total internal surface area of the catalyst \hspace{1cm} \text{m}^2
\[ Sc^* \] Schmidt number, modified for multicomponent systems
\[ T \] temperature \hspace{1cm} \text{K}
\[ \bar{v} \] mean molecular speed \hspace{1cm} \text{m s}^{-1}
\[ v_i \] velocity of species \( i \) \hspace{1cm} \text{m s}^{-1}
\[ V \] characteristic number for viscous flow inside catalyst pores
\[ V_A = \frac{r_p^2}{8\eta_s} \frac{P}{D_{st}} \frac{\nabla P}{\nabla (\kappa A P)} \] (Equation A.105)
\[ V_s \] pore volume per unit gram of catalyst \hspace{1cm} \text{cm}^3 \text{ g}^{-1}
\[ V_r \] volume of the catalyst pellet \hspace{1cm} \text{m}^3
\[ W \] width of a catalyst pellet \hspace{1cm} \text{m}
\[ x \] rectangular coordinate \hspace{1cm} \text{m}
\[ x_A \] mole fraction of species \( A \) \hspace{1cm} \text{m}
\[ X_A = V/A_p \] characteristic, shape-generalized dimension \hspace{1cm} \text{m}
\[ y \] rectangular coordinate \hspace{1cm} \text{m}
\[ Y_p \] yield \hspace{1cm} \text{m}
\[ z \] rectangular coordinate \hspace{1cm} \text{m}
Greek symbols

$\alpha$  

dimensionless adiabatic temperature rise inside a catalyst pellet  

$$\alpha = \frac{T_{m} - T_{x}}{T_{x}} = \frac{(- \Delta H) D_{e,A} C_{A, i}}{\gamma_{t} T_{x}} \quad \text{(Equations 6.15 and 7.1)}$$

$\beta$  

measure for the influence of the component in excess for bimolecular reactions  

$$\beta = v \frac{D_{e,A}}{D_{e,B}} \frac{C_{A,i}}{C_{B,i}} \quad \text{(Equation 7.30)}$$

$\gamma$  

measure for the dependence of the effective diffusion coefficient on the gas composition and pressure  

$$\gamma = \frac{\sqrt[4]{V_{p}} + 1 - \psi}{1 + K \tilde{t}_{e} + \psi \sqrt[4]{V_{p}} - 1} \cdot \left(\sqrt[4]{V_{p}} - 1\right) \kappa_{A,i} \quad \text{(Equation 7.78)}$$

$\gamma_{1}$  

activity coefficient or fugacity coefficient of component $J$

$\gamma_{p}$  

tortuosity of the catalyst pores

$\gamma(\rho, \omega)$  

dimensionless concentration  

$$\gamma(\rho, \omega) = \frac{C_{A}(\rho, \omega)}{C_{A,i}} \quad \text{(Equation A.37)}$$

$\Gamma$  

geometry factor

$\delta_{\alpha, 0}, \delta_{\alpha, 1}$  

relative error in $\eta$ and $1-\eta$ respectively, introduced if for a bimolecular reaction the concentration of the component in excess is taken as constant

$\delta_{\gamma, 0}, \delta_{\gamma, 1}$  

relative error in $\eta$ and $1-\eta$ respectively, introduced if the dependence of the effective diffusion coefficient on the gas composition and pressure is neglected

$\delta_{\lambda, 0}, \delta_{\lambda, 1}$  

relative error in $\eta$ and $1-\eta$, respectively, introduced if intraparticle temperature gradients are neglected

$\delta^{2-3}$  

relative error, introduced if instead of the three-parameter model the two-parameter model is used (see Equation 7.7)

$\delta^{2-3}_{\text{max}}$  

maximum value of $\delta^{2-3}$; i.e. the value of $\delta^{2-3}$ for $C_{A} = 0$

$\Delta$  

relative deviation between $\eta$ and the approximation $\eta$ for $\eta < \frac{1}{2}$ and $1-\eta$ for $\eta > \frac{1}{2}$

$\Delta_{\text{max}}$  

maximum value of $\Delta$ for the interval $\eta \in [0,1]$

$\Delta_{\sigma}$  

relative deviation between $\sigma$ and the approximation $\tilde{\sigma}$

$\varepsilon = E_{a}/RT$, dimensionless energy of activation or Arrhenius number

$\varepsilon_{\rho}$  

porosity of the catalyst pellet

$\eta$  

effectiveness factor

$\eta$  

approximation for $\eta$

$\tilde{\eta}$  

approximation for $\eta$

$\zeta$  

relative degree of conversion
XIV  Symbols and Abbreviations

\[ \eta_i \] effectiveness factor for first order kinetics and arbitrary catalyst geometries

\[ \eta_e \] dynamic viscosity of the gas mixture \( \text{Pa s} \)

\[ \eta_m \] modified effectiveness factor for ring-shaped pellets

\[ \theta \] degree of occupation of the surface

\[ \theta_m \] = \[\sqrt{\lambda \eta_b}\] the generalized modified Thiele modulus

\[ \iota = R/R_e \] dimensionless inner radius of a ring-shaped catalyst pellet

\[ \lambda = H/R_e \] dimensionless height of a ring-shaped catalyst pellet

\[ \lambda \] molecular mean free path \( \text{m} \)

\[ \lambda_p \] heat conductivity of the catalyst pellet \( \text{W m}^{-1}\text{K}^{-1} \)

\[ \mu \] viscosity \( \text{Pa s} \)

\[ \mu \] first moment of the response curve

\[ \nu_b \] stoichiometric coefficient, moles of component \( B \) per \( \nu_A \) moles of key reactant \( A \)

\[ \nu_t \] kinematic viscosity of the gas mixture \( \text{m}^2\text{s}^{-1} \)

\[ \Delta \nu \] net yield of molecules per molecule of key reactant converted (for bimolecular reactions \( \Delta \nu = \nu_r + \nu_q - \nu_b - 1 \))

\[ \xi = \alpha \varepsilon \] measure for the importance of intraparticle temperature gradients

\[ \xi \] parameter according to Karanth, Koh and Hughes

\[ \xi = \frac{1}{\nu_b} \frac{D_{r,B}}{D_{r,A}} \frac{C_{r,t}}{C_{t,A}} - 1 = \frac{1 - \beta}{\beta} \] (Equation 6.20)

\[ \rho = \frac{n}{R_e} \] dimensionless radial coordinate

\[ \rho_e \] density of the gas mixture \( \text{kg m}^{-3} \)

\[ \rho \] density of the reaction mixture \( \text{kg m}^{-3} \)

\[ \sigma = \frac{(P - P_J)}{P_J} \] dimensionless intraparticle pressure

\[ \sigma \] approximation for \( \sigma \)

\[ \sigma_r \] selectivity

\[ \sigma_r' \] differential selectivity or selectivity of the catalyst

\[ \sigma^2 \] second central moment of the response curve \( \text{s}^2 \)

\[ \tau \] average residence time \( \text{s} \)

\[ \phi = \frac{H}{(R_e - R)} \] measure for the geometry of a ring-shaped catalyst pellet

\[ \phi_1 \] shape-generalized Thiele modulus for first-order kinetics of Aris

\[ \phi_1 = X_o \sqrt{\frac{k}{D_e}} \] (Equation 6.2)

\[ \phi_{hc} \] Thiele modulus for a hollow cylinder

\[ \phi_{hc} = R_u \sqrt{\frac{k}{D_h}} \] (Equation A.40)

\[ \phi_r \] modified Thiele modulus for a plate or an infinite slab

\[ \phi_r = \frac{1}{\eta} \] for low \( \eta \) (Equation 6.6)
modified Thiele modulus for a sphere

\[ \phi_s = \frac{3}{\eta} \text{ for low } \eta \text{ (Equation 6.5)} \]

Thiele modulus according to Thiele

\[ \phi_r = R \sqrt{\frac{R(C_{A,s})}{D_{e,t}C_{A,s}}} \text{ (Equation 6.1)} \]

volume flow rate \( \Phi_s \) recycle volume flow rate \( \Phi_{\text{r}} \)

\[ \chi = \frac{\eta|\beta - \eta|_{|\beta=0}}{\eta|\beta=1 - \eta|_{|\beta=0}} \text{ defined by Equation 7.37} \]

\[ \psi = \frac{(Kn^*)^2}{(Kn^*)^2 + \left( (v_p - 1)K_{A,s} + \sqrt{v_p + 2}K_n^* + 1/2 \right) \left( \sqrt{v_p} + 1 \right)} \text{ defined by Equation 7.99} \]

\[ \omega = h/H \text{, dimensionless longitudinal coordinate} \]

\[ \omega \text{ mass fraction} \]

Subscript

\( A, B, P, Q, \ldots \) for component \( A, B, P, Q, \ldots \)

g gas

l liquid

m at the centre of the catalyst pellet

p for the catalyst pellet

s solid

s at the outer surface of the catalyst pellet

\( \beta \) modified for bimolecular reactions

0 initial or inlet condition

+ forward reaction

– reverse reaction
Superscripts

\( H \) in the longitudinal direction
\( R \) in the radial direction
\(*\) modified for non-diluted gases
\(+\) modified for anisotropy

Mathematical functions and symbols

\( \text{erf}(x) \) error function
\[
\text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-y^2} dy
\]

\( F(\phi,K) \) elliptic integral of the first kind
\[
F(\phi,k) = \int_0^\phi \frac{1}{\sqrt{1-k^2 \sin^2 \theta}} d\theta
\]

\( I_0(x), I_1(x) \) modified Bessel functions of the first kind of zeroth and first order, respectively
\[
I_n(x) = (x/2)^n \sum_{i=0}^\infty \frac{(x/2)^i}{i!(n+i)!}
\]

\( K_0(x), K_1(x) \) modified Weber functions (Bessel functions of the second kind of zeroth and first order, respectively)
\[
K_n(x) = 1/2 \cdot (x/2)^n \sum_{i=0}^\infty \frac{(n+i-1)!}{i!} \cdot \left( -x^2/4 \right) + \\
(-1)^{n+1} \ln \left( x/2 \right) I_n(x) + \\
(-1)^n \cdot 1/2 \cdot (x/2)^n \sum_{i=0}^\infty \psi(i+1) - \psi(n+i+1)) \cdot \\
\frac{(x/2)^i}{i!(n+i)!}
\]

with the Psi or digamma function
\[
\psi(m) = -\gamma + \sum_{i=1}^m \frac{1}{i}
\]
and $\gamma$ Euler's constant

$$\gamma = \lim_{m \to \infty} \left( \sum_{i=1}^{m} \frac{1}{i} \right) - \ln(m) = 0.5772156649$$

is approximately equal to

is equivalent to

approaches

approaches from above

approaches from below

universal kwantor

is an element of

gradient of a parameter field, or divergence of a gradient field

Laplacian operator
1 Introduction

1.1 Introduction

Catalysis is the acceleration of a chemical reaction by a small quantity of a substance, which may take part in the reaction, but in the end is not changed by the reaction. This alien substance can either be mixed with or dissolved in the reaction mixture or one of its components and forms one single phase with it (we speak of homogeneous catalysis in this case), or it can form its own separate phase. In the last case we speak of heterogeneous catalysis. Both methods of homogeneous as well as heterogeneous catalysis are equally important from an industrial point of view. Homogeneous catalysis is not the subject of this book; we focus on heterogeneous catalysis, where the catalyst is a porous material itself or is impregnated in such material.

In heterogeneous catalysis the reactants first have to be transported to the catalyst and – if the catalyst is a porous, solid particle – also through the pores of the particle to the active material, that truly enhances the reaction rate. In this case all kinds of transport resistance’s may play a role, which prevent the catalyst from being fully effective in its industrial application. Reactants have to transported to the catalyst particle and the products away from it. Furthermore, because appreciable heat effects accompany most reactions, heat has to be removed from the particle or supplied to it in order to keep it in the appropriate temperature range (where the catalyst is really fully effective). Heterogeneous catalysis, in which gases and liquids are contacted with solids so the reactions are accelerated, is one of the most complex branches of chemical kinetics. Rarely do we know the compositions, properties or concentrations of the reaction intermediates that exist on the surfaces covered with the catalytically effective material. The chemical factors that govern reaction rates under these conditions are less well known than in homogeneous catalysis. Yet solid catalysts display specificities for particular reactions, and selectivities for desired products that, in most practical cases, cannot be equaled in any other way. Thus use of solid catalysts is essential.

The selection of a solid catalyst for a given reaction is to a large extent still empirical and based on prior experience or analogy. However, there are now many aspects of this complex situation that are quite well understood. For example we know how the true chemical kinetics, which are an intrinsic property of the catalyst, and all the many aspects of transport of material and heat around the catalytic particles, interact. In other words, the physical characteristics around the catalyst system and their effects on catalyst performance are well known today. The chemist searching for new and better catalysts should always consider these physical factors, for they can be brought under control, and often in this way definite gains can usually be made both in activity and in selectivity. Further, this knowledge enables us to avoid
some common errors of interpretation of apparent reaction rates, as observed in experiments.

Considerations based on the known physical phenomena can guide the choice of catalyst porosity and porous structure, catalyst size and shape and reactor type and size. These considerations apply both to the laboratory as well as to large-scale operations. Many comprehensive reviews and good books on the problem of reactor design are available in the literature. The basic theory for porous catalysts is summarized in this book and simple rules are set forth to aid in making optimum choices to obtain fully effective catalyst particles, which give the best performance from an economic point of view.

1.2 Catalysis in an Industrial Reactor

Consider a long, slender cylinder filled with catalyst pellets and a flow of reactants entering at one end. The reactant stream may be a gas, a liquid or a mixture of them. The flow occurs in the interstices between the catalyst granules. The rate of flow, relative to the catalyst particle, is the prime factor, together with temperature and catalyst properties, in determining the amount of conversion. The velocity and turbulence of the flow determine how rapidly molecules are carried from the fluid phase to the exterior surfaces of catalyst pellets. Rapid transfer from fluid to solid outer surface is obtained with highly turbulent flow, which means a highly irregular flow pattern with momentary velocities strongly deviating from the main flow direction. High turbulence is obtained with high flow velocities, large particles and low viscosities. The amount of turbulence also has a strong influence on the rate of heat transfer between the catalyst pellet and the fluid, and also to the wall of the cylinder.

Flow conditions may cause a more or less broad distribution of residence times for individual fluid packets or molecules. Effects of variable residence times have to be taken into account in the design and operation of large industrial reactors: with adequate precautions the chemical engineer can prevent the undesirable effects of a residence time distribution, or utilize them.

Once a molecule has arrived at the exterior boundary of a catalyst pellet it has a chance to react. Most of the active surface, however, will be inside the pellet and will only be reached after diffusion for an appreciable distance. Usually we need a much larger active surface than is available on the exterior surface of a pellet. For practical particle sizes of porous catalysts, the interior surface greatly exceeds the exterior. For example, with 3 mm diameter pellets of an interior surface area of 100 m² g⁻¹, the interior total surface area is 100 000 times larger than the exterior surface of the pellets. There are, however, some catalysts so active that reaction on the outer surface of a nonporous catalyst of a convenient size suffices for obtaining useful rates. The platinum gauze used for the ammonia oxidation is an example. Such nonporous catalysts are ideal if they can be used, for in this case we are free from the usually harmful diffusion effects.

When the reaction mixture diffuses into a porous catalyst, simultaneous reaction and diffusion have to be considered when obtaining an expression for the overall conversion rate. The pore system is normally some kind of complex maze and must be approximated to allow mathematical description of mass transport inside the particles, such as a sys-
tem of uniform pores. It is important to note that catalyst pellets can be of many structural types, which all have an influence on the degree of diffusion limitation of the overall conversion rates. An extreme type is the gel catalyst with tiny pores, which have quite low effective diffusion coefficients: silica, alumina and zeolites are examples of this structure. Another extreme type of pellet is an aggregate of quite large particles cemented together at points of contact. The channels in the ultimate particles may be as big as 100 μm in diameter. A third type is an aggregate of aggregates, where there are large pores leading into the interior and smaller pores leading to the major portion of the active surface. Such a structure is close to ideal from the standpoint of low diffusion resistance and high internal surface area.

If diffusion is fast relative to the rate of reaction, then all the interior surfaces of a catalyst pellet are bathed in fluid of the same composition. This composition will depend on the position of the pellet in the reactor; that is, on the distance from the inlet. But if the diffusion rate is of the same order of magnitude as the reaction rate, or slower, the concentration of the reactants and product will vary within the pores: we then speak of a diffusion limitation of the transport of reactants, generally resulting in a lower conversion rate. Diffusion limitation can have quite profound effects. Some of these are listed below:

- the apparent activity of the catalyst is generally lowered;
- the apparent order of the reaction may be changed;
- the selectivity may be altered markedly;
- the temperature gradient within a pellet may become large;
- inner portions of pellets may be more or less rapidly deactivated than outer portions, or vice versa.

All these effects are significant in our interpretation of a catalytic experiment or the behavior of an industrial reactor. If we do not recognize the role of diffusion, we may be badly misled in our interpretations. However, with the aid of knowledge about diffusion, we can sometimes improve our results over what they otherwise would have been.

Temperature differences between catalyst and fluid will exist even without a diffusion limitation. For an exothermic reaction the entire catalyst pellet must be somewhat hotter than the surrounding, flowing fluid, as only this temperature difference serves as the driving force for removal of the heat of reaction. This excess temperature is usually only some tenths of a degree to a few degrees centigrade. When reaction rates are extremely high compared to the heat removal capabilities, the temperature difference between pellet and fluid may become very large and can be around the local adiabatic temperature rise of the reaction. This adiabatic temperature rise ΔT_{ad} is an extremely important property of a reaction and is given by

\[
\Delta T_{ad} = (-\Delta H)_A C_A / \rho c_p
\] (1.1)

Where \((\Delta H)_A\) is the heat of reaction evolved, \(C_A\) the inlet concentration of the reactant in the fluid and \(\rho c_p\) the sensible heat per unit of volume of the reaction mixture. The value of ΔT_{ad} should always be determined first, before studying a reaction. When it is low, heat effects are relative unimportant, for high values heat removal is a must in catalyst utilization.
1.3 Catalytic Reactors

Industrial catalytic reactors exhibit a great variety of shapes, types and sizes. It is not our aim here to discuss all possibilities; a survey of the most important reactor types is given by Ullmann [1]. In general, heterogeneous catalytic reactors can be divided in two categories, depending on the size of the catalyst particles, large and small.

1.3.1 Large Particle Catalyst

Large particle catalysts can be kept stationary, so that packed in a bed they can be kept in the reactor and the reaction mixture passes through the bed of particles. Of course, the aim is to keep the catalyst charge as long as possible in the reactor, say for many years. This method avoids all the trouble of eliminating the catalyst from the product stream coming out of the reactor. Whatever the shape of the particles, their size in industrial reactors is usually larger than 2 mm. In Figure 1.1 some examples are given of reactors with catalyst beds. In Figure 1.1(a) the common adiabatic packed bed reactor is shown. This reactor is used for single-phase reaction mixtures, either gases or liquids with moderate heat effects. Also, systems with multiple beds with cooling in between the beds are frequently used, such as for NH₃ and CH₃OH production. For reactions with high heat effects the cooled tubular reactor is used (Figure 1.1(b)). Here the reactor consists of a large number of parallel tubes, which are cooled with a coolant flowing around the outside of the tubes. To maintain the catalyst bed in the tubes as isothermal as possible, only a small number of particles across a tube diameter is permitted, say between 3 and 20 particles. Depending on the required reactor capacity the number of tubes varies between from 30 to 30000. Adiabatic packed bed and cooled tubular reactors can be used both for gaseous and liquid reactor feeds.

![Figure 1.1](Image)

**Figure 1.1** Examples of reactors with fixed catalyst beds: (a) adiabatic packed bed; (b) cooled tubular reactor; (c) cocurrent trickle bed reactor; (d) packed bubble column.

When a mixture of gas and liquid is to be fed to a packed bed reactor then, depending on the required residence times in the reactor, two reactor types are commonly
used. In Figure 1.1(c) the trickle flow reactor is shown, in which the gas and the liquid streams are fed cocurrently at the top of the reactor. The liquid wets the catalyst particles and slowly trickles to the bottom through the bed. The gas dissolves in the liquid and is transported to the catalyst surface, where reaction takes place with reactants coming from the liquid phase. A counter current flow of gas and liquid can also be applied. Residence times for the liquid phase in industrial trickle flow reactors can be as high as 10-15 min. If much larger residence times are required for the liquid phase, the packed bed bubble column reactor in Figure 1.1(d) is often used. Here gas and liquid are both fed to the bottom of the reactor. The reactor is filled with liquid through which the gas bubbles slowly upwards. In these reactors liquid residence times of the order of hours can easily be achieved; the catalyst is fully wetted with the liquid phase.

1.3.2 Small Particle Catalyst

For small catalyst particles completely different reactor types are used. The catalyst is now suspended in the flowing reaction mixture and has to be separated at the reactor exit or is carried along with the fluid. Particle sizes are now from 10 μm up to 1 mm. In Figure 1.2 some of the common reactor types are shown. Figure 1.2(a) shows the fluid bed reactor, where the gaseous feed keeps the small catalyst particle in suspension. Catalyst carried over in the exit stream is separated, for example, in cyclones. For even shorter contact times, riser reactors are used in which the solid catalyst is transported in the gas stream. Fluid bed reactors are also used for feed mixtures of a liquid and a gas.

In cases when the feed stream is a liquid, which requires rather long residence times, the suspension bubble column or an agitated tank reactor is used (Figures 1.2(b) and 1.2(c)). Here, in the reactor exit, quite elaborate filtering systems are required to remove the catalyst from the liquid stream. In these reactors a gas generally is supplied, because these suspension reactors are mostly used for hydrogenations and oxidations.

![Figure 1.2](image-url) Common reactor types with moving catalyst beds: (a) fluid-bed reactor; (b) bubble column with suspended catalyst; (c) sparged stirred tank with suspended catalyst.
1.4 Characteristics of Reactor Performance

For the quantitative description of a reactor and the individual catalyst particles in it, an expression must be available for the chemical production rate [2]. The production \( R_A \) rate of component \( A \), is defined as the number of moles of \( A \) produced per unit time and unit volume. If \( A \) is consumed in a chemical reaction, \( R_A \) is negative; if \( A \) is produced then \( R_A \) is positive. The production rate in mass units is found by multiplying \( R_A \) by the molar mass \( M_A \).

For convenience, the concept of the chemical conversion rate \( |R| \) is often used. \( |R| \) is always positive when a reaction proceeds in the direction of the arrow in the reaction equation. The conversion rate is expressed in moles of **key reactant** consumed or produced per unit time and unit volume. When a reaction proceeds according to

\[
\nu_A A + \nu_B B \rightarrow \nu_P P + \nu_Q Q
\]

and \( A \) is chosen as key reactant, then

\[
|R| = -R_A = -\frac{\nu_A}{\nu_B} \frac{\nu_A}{\nu_P} = \frac{\nu_A}{\nu_P} \frac{\nu_A}{\nu_Q} = \frac{\nu_A}{\nu_Q} (1.2)
\]

The coefficients \( \nu_A, \nu_B, \nu_P, \) and \( \nu_Q \) are called the stoichiometric coefficients. Often, and also in this text, the value of \( \nu_A \) for the key reactant is taken equal to one, so that \( \nu_A/\nu_B \) (etc.) can be taken as \( 1/\nu_B \) (etc.).

In this text, the conversion rate is used in relevant equations to avoid difficulties in applying the correct sign to the reaction rate in material balances. Note that the chemical conversion rate is not identical to the chemical reaction rate. The chemical reaction rate only reflects the chemical kinetics of the system, that is, the conversion rate measured under such conditions that it is not influenced by physical transport (diffusion and convective mass transfer) of reactants toward the reaction site or of product away from it. The reaction rate generally depends only on the composition of the reaction mixture, its temperature and pressure, and the properties of the catalyst. The conversion rate, in addition, can be influenced by the conditions of flow, mixing, and mass and heat transfer in the reaction system. For homogeneous reactions that proceed slowly with respect to potential physical transport, the conversion rate approximates the reaction rate. In contrast, for homogeneous reactions in poorly mixed fluids and for relatively rapid heterogeneous reactions, physical transport phenomena may reduce the conversion rate. In this case, the conversion rate is lower than the reaction rate.

For a single reaction as given above, the mass fractions of the reactants, \( \omega_A \) and \( \omega_B \), decrease and those of the products, \( \omega_P \) and \( \omega_Q \), increase as the reaction proceeds from left to right. For a closed system (no material added or withdrawn),

\[
\omega_A + \omega_B + \omega_P + \omega_Q = \text{constant} = \omega_{\text{tot}}
\]

For such a system the **relative degree of conversion** \( \zeta \) can be introduced, which is a measure of the extent to which the reaction has proceeded. It can be defined quite generally as the fraction of the amount of a reactant, fed prior to and during reaction
that has been converted. For a closed system, \( \zeta_i \), can be expressed in terms of mass fractions as

\[
\zeta_i = \frac{\omega_{i,0} - \omega_i}{\omega_{i,0}}
\]

(1.3)

with \( J = A, B \), respectively. Since, by definition, the total mass within a closed system \( m \) is constant, the relative degree of conversion can also be expressed in terms of the number of moles:

\[
\zeta_i = \frac{\omega_{i,0}m_A - \omega_i m_B}{M_j} = \frac{n_{i,0} - n_j}{n_{i,0}}
\]

(1.4)

Here \( M_j \) is the molar mass of either \( A \) or \( B \). If the total volume of the reaction mixture does not depend on the relative degree of conversion, the latter can be expressed relatively easily in terms of concentrations:

\[
\zeta_i = \frac{n_{i,0} - n_j}{V} = \frac{C_{i,0} - C_j}{C_{i,0}}
\]

where \( V \) is the volume of the reaction mixture. If this volume changes during the reaction, the equation becomes

\[
\zeta_i = \frac{C_{i,0} \frac{m}{\rho_0} - C_{i,0} \frac{m}{\rho}}{C_{i,0} \frac{m}{\rho_0}} = \frac{C_{i,0} - \rho \frac{C_j}{\rho}}{C_{i,0}}
\]

(1.5)

with \( \rho_0 \) being the density of the reaction mixture for zero conversion and \( \rho \) the density for a conversion \( \zeta_i \).

The chemical reaction rate is usually dependent on the molar concentrations of the reactants and not on their mass fractions, because it depends on the chance of collision of molecules. However, here the definition of \( \zeta \) in terms of mass fractions is preferred, because it can readily be incorporated into mass balances. A definition in terms of moles or molar concentrations might invite the use of mole balances instead of mass balances. Since, contrary to conservation of mass, there is no such thing as conservation of moles (because one molecule might divide into several molecules, or several might condense into one), the use of mole balances is strongly dissuaded. More information concerning the definition of conversion can be found elsewhere [2].

In industrial chemical operations, a reactant \( A \) or reactants \( A \) and \( B \) very often react to form not only desired products, but also undesirable ones. Therefore, in chemical reactor technology the concepts of selectivity and yield are often used.
The **selectivity** $\sigma_p$ is the ratio between the amount of desired product $P$ obtained and the amount of key reactant $A$ converted; both quantities are usually expressed such that $\sigma_p$ ranges between 0 (no $P$ formed) and 1 (all $A$ converted to $P$). This definition leads to

$$\sigma_p = \frac{(\omega_p - \omega_{p,0})M_A}{(\omega_{A,0} - \omega_A)M_P\nu_p}$$  \hspace{1cm} (1.6)

For constant density of the reaction mixture, this can be written as

$$\sigma_p = \frac{(C_p - C_{p,0})}{(C_{A,0} - C_A)\nu_p}$$  \hspace{1cm} (1.7)

The yield $\eta_p$ is the ratio between the amount of desired product $P$ obtained and the amount that could be obtained if all of key reactant $A$ were converted to $P$ with 100% selectivity. Therefore, $Y_p$ can be calculated from

$$Y_p = \sigma_p \phi_A$$  \hspace{1cm} (1.8)

Like $\sigma_p$, the yield $Y_p$ usually varies between 0 and 1. It is high when both the selectivity and the relative degree of conversion are high; it is low when either of them is low.

If in the product separation section of the reactor, the key reactant $A$ can be removed and recycled to the reactor, selectivity is the key factor in economical operation of the plant. However, if $A$ cannot be recycled, then yield is the key factor.

**References**

2 Kinetics

2.1 General

Elementary reactions are individual reaction steps that are caused by collisions of molecules. The collision can occur in a more or less homogeneous reaction medium or at the reaction sites on a catalyst surface. Only three elementary kinetic processes exist: mono-, bi-, and trimolecular processes. Of these, trimolecular processes are rarely found, because the chance of three molecules colliding at the same time is very small. Each elementary reaction consists of an activation of the reactants, followed by a transition state and decomposition of the latter into reaction products:

\[
A(+) + B \xleftrightarrow{Activation} \{Energized\} \xrightarrow{Deactivation} \{Transition\} \rightarrow \text{products}
\]

Energized and transition state molecules are unstable, and as such cannot be isolated.

For elementary reactions, the influence of the temperature and composition of the reaction mixture can be represented separately. The influence of temperature is accounted for by the reaction rate constant \(k\), referred to as a constant because it does not depend on the composition of the reaction mixture. The temperature dependence of \(k\) is

\[
k = k_\infty \exp\left\{\frac{-E_a}{RT}\right\}
\]  

(2.1)

Where \(E_a\) is called the activation energy of the reaction. Equation 2.1 is illustrated in Figure 2.1, where the reaction rate constant is plotted as a function of temperature (both

\[\begin{align*}
\text{Figure 2.1 A) Temperature dependence of the reaction rate constant} \\
&\text{(note that as } E/R \text{ ranges from 5000 K} \\
&\text{to 35 000 K; in practice only the region } RT/E_a < 1 \text{ is of interest). B) Enlarge-}
\end{align*}\]
quantities in dimensionless form). The term $E/R$ is sometimes referred to as the activation temperature. For most reactions the activation energy lies in the range 40-300 kJ mol$^{-1}$; hence the activation temperature $E/R$ ranges from 5000 K to 35 000 K.

Therefore, for industrial purposes, only the range $RT/E_a < 1$ is of interest. This region is shown enlarged in Figure 2.1(b). As can be seen from Figure 2.1(a), although at extreme temperature $k$ approaches $k_0$, in practice it is several orders of magnitude lower.

The temperature increase required for doubling a reaction rate constant ($\Delta T_{\text{double}}$) as a function of the temperature of the reaction mixture and activation energy is given in Figure 2.2. The higher the activation energy, the more temperature sensitive are the reactions. To double the reaction rate at $T = 100$ °C, for example, a temperature increase of 3 °C ($E_a = 300$ kJ mol$^{-1}$) to 20 °C ($E_a = 50$ kJ mol$^{-1}$) is required. Also note that in the higher temperature range much larger temperature changes are necessary to double the reaction rate at constant activation energy.

![Figure 2.2](image)

The influence of the composition of the reaction mixture on the chemical reaction rate is determined by the chemical activity (liquids) or fugacity (gases) of the reactants. These quantities can be expressed in relation to each other as

$$a_J = \frac{\gamma_J P_J}{RT}$$

where $a_J$ is the chemical activity, $\gamma_J$ the activity coefficient or fugacity coefficient, and $P_J$ the partial pressure of component $J$. The product $\gamma_J P_J$ is called the fugacity. For ideal reaction mixtures, $\gamma_J = 1$ and the reaction rate is determined by the molar concentration or partial pressure of the reactants.

For elementary reactions and ideal reaction mixtures, the reaction rate is proportional to the concentration of each of the reactants, since the number of molecular collisions per unit time is proportional to it. For example, for a bimolecular elementary reaction:

$$A + B \rightarrow \text{products}$$

$$|R| = \frac{dC_A}{dt} = \frac{dC_B}{dt} = kC_A C_B$$