Chapter 2:
Quantification of Local Kinetic and Transport Interactions in Multiphase Systems

This chapter reviews the basic concepts involved in quantification of local kinetic-transport interactions in various multiphase systems with the emphasis on gas-liquid-solid and gas-liquid systems.

Slide 1 outlines the content of the chapter while Slide 2 presents the approach to be followed. The relevance of quantifying local transport-kinetic interactions to the overall understanding of the role of a reactor in multiphase processing is discussed in Slides 2 and 3.

A. Gas-Liquid-Solid Systems
a) Intrinsic kinetic models and local reaction rates. Typical rate forms encountered in catalytic reactions are summarized in Slides 4-10. The key notions about transport effects on local rates are discussed in Slides 11-12 and the quantification of these effects is illustrated for gas-solid systems in Slide 13.
b) Interphase and c) Intraphase Effects. The notion of gas and liquid limiting reactions is introduced in Slide 14. Inter and intra phase mass transport effects for a gas limiting reaction are described in Slides 15-19. The ramifications of a controlling resistance on reactor volumetric productivity are described in Slide 20. The procedure for quantifying transport effects for liquid limiting reactions and for reactions affected by both reactants is described in Slide 21. Transport effects in dried out, vapor filled pellets are discussed in Slides 22-23 and the conditions for dryout in Slide 24.
d) Evaluation of transport effects is illustrated by the example of crotonaldehyde hydrogenation (Slide 25-28). A general procedure is outlined in Slides 29-31. An HDS example is in Slides 32-33. A aldehyde hydrogenation example is in Slides 34-37. A summary of transport effects on reactor volumetric productivity is in Slide 38.
e) Evaluation of transport parameters. Various quantities needed for quantification of transport effects are summarized in Slide 39. References and methods available for evaluation of solubility, volatility, thermodynamic properties, diffusivities and thermal conductivities are given in Slides 40-42. Order of magnitude estimates and trends with pressure and temperature are in Slide 43. The basis for theoretical evaluation of transport coefficients is summarized in Slides 43-44. Theoretical predictions for mass transfer coefficients in simple geometries and flow fields are in Slides 45-47. The options available in assessing transport effects in gas-liquid-solid systems are outlined in Slide 48.
B. Gas-Liquid Systems

a) Reaction regimes.

Slide 49 introduces the notation and quantities needed to handle gas-liquid systems. Slide 50 outlines the possible reaction regimes while Slide 51 presents the generalized chart for the evaluation of the enhancement factor. Slides 52-55 outline the criteria for identification of each regime. Slide 56 summarizes the effect of the reaction regime on the choice of the reactor-absorber. Possible nonisothermal effects are summarized in Slide 57.

b) Characteristic parameters of multiphase contactors

Slides 58-59 outline the reported transport parameters for various types of multiphase contactors. Slide 60 summarizes the energy input required to reach certain interfacial areas.

c) Experimental contactors and techniques for estimation of transport parameters

Scale-up strategies are discussed in Slide 61. Identification of kinetic regime is presented in Slide 62. Slide 63 summarizes characteristic parameters for experimental model reactors. Slide 64 lists possible laboratories models for investigation of various commercial contactors.

Measurement techniques for evaluation of gas-liquid interfacial areas are outlined in Slides 65-66. Techniques for evaluation of liquid side volumetric coefficients are summarized in Slide 67, while measurement of gas side mass transfer volumetric coefficients, liquid-solid mass transfer coefficients and gas-liquid mass transfer coefficients is covered in Slide 68.

References are listed in Slides 69-70, and Nomenclature used in Chapter 2 in Slides 71-74.

The Appendix contains:

- suggested problems
- illustration of the type of correction needed to mass transfer coefficients due to rapid fluxes (e.g. evaporation or condensation)
- illustration of the effect of volume change in the gas phase caused by reaction in the particle effectiveness factor in gas-solid reactions
- the effect of internal convection on the particle effectiveness factor. This effect is utilized to improve catalyst performance in methanol and ammonia synthesis.
- Major benefits possible in liquid systems.
- a rough draft of the text accompanying the chapter with guidelines for evaluation of effectiveness factors for reaction of any order
- a paper on the catalyst effectiveness in three phase systems.
CHAPTER 2:

QUANTIFICATION OF LOCAL KINETIC AND TRANSPORT INTERACTIONS

IN

A. GAS - LIQUID - SOLID SYSTEMS

a) Intrinsic kinetic models and local reaction rates
b) Interphase transport effects
c) Intraphase transport effects
d) Evaluation of transport effects
e) Evaluation of transport parameters

B. GAS - LIQUID SYSTEMS

a) Reaction regimes
b) Characteristic parameters of multiphase contactors
c) Experimental contactors and techniques for estimation of transport parameters
EVALUATION OF TRANSPORT EFFECTS ON LOCAL REACTION RATES IN MULTIPHASE SYSTEMS

- RELEVANCE

- BASIC NOTIONS OF KINETIC-TRANSPORT INTERACTIONS IN
  - GAS-SOLID SYSTEMS
  - GAS-LIQUID-SOLID SYSTEMS

- ESTIMATION OF TRANSPORT EFFECTS FOR EXPERIMENTALLY OBSERVED RATES

- ESTIMATION OF TRANSPORT PARAMETERS

- EVALUATION OF TRANSPORT EFFECTS IN GAS-LIQUID SYSTEMS
RELEVANCE

\[
\text{MULTIPHASE REACTOR PERFORMANCE} = f \left( \begin{array}{c}
\text{KINETICS} \\
\text{CONTACTING PATTERN} \\
\text{TRANSPORT EFFECTS} \\
\text{OPERATING AND FEED CONDITIONS}
\end{array} \right)
\]

\[
\left( \begin{array}{c}
\text{PRODUCTION RATE} \\
\text{PRODUCTION RATE}
\end{array} \right) = \left( \begin{array}{c}
\text{VOLUME AVERAGED APPARENT REACTION RATE}
\end{array} \right) \times \left( \begin{array}{c}
\text{REACTOR VOLUME}
\end{array} \right)
\]

NEED TO:

1. PREDICT TRANSPORT EFFECTS ON RATE (DESIGN)

2. UNDERSTAND THE MAGNITUDE OF TRANSPORT EFFECTS (MANUFACTURING)

3. QUANTIFY TRANSPORT EFFECT DISGUISES OF THE RATE (R&D)
REACTOR PERFORMANCE = f (INPUT AND OPERATING VARIABLES ; RATES ; MIXING PATTERN)

- CONVERSION
- SELECTIVITY
- PRODUCTION RATE

- FLOW RATES
- INLET CONC. & TEMP.
- HEAT REMOVAL

- KINETICS
- TRANSPORT

- MACRO
- MICRO

\[ \mathcal{L}(C_b) = \eta_o R (C_b, T_b) \]

\[ \mathcal{L}_h(T_b) = \sum_j (-\Delta H_{R_j}) \eta_j R_j (C_b, T_b) \]

\[ \eta_o = f (\text{KINETICS, TRANSPORT}) \]

REACTOR PERFORMANCE DETERMINES THE NUMBER OF SEPARATION UNITS AND THEIR LOAD AND HENCE PROFOUNDLY AFFECTS PROCESS ECONOMICS AND PROFITABILITY.
THREE PHASE CATALYTIC REACTIONS

A(g) + v B(l) = v E E(l).

MOST FREQUENT KINETIC FORMS

SINGLE SITE LH FORM

(1) \[ \Omega_A = \frac{k \frac{A B}{1 + K_A A + K_B B + K_E E}} \] ORDER 1 - 2

(2) \[ \Omega_A = \frac{k \frac{A B}{(1 + K_A A + K_B B + K_E E)^2}} \] ORDER 0 - 2

DUAL - SITE LH FORM

SIMILAR KINETIC FORMS PREVAIL IN SYSTEMS WITH
IMMOBILIZED ENZYMES OR IN FERMENTATIONS

\[ \Omega_A \]

\[ \ln \Omega_A \]

const B

const T

const B

const A

A

1/T

2-4
### Table 4-3. Mechanisms and Their Corresponding Rate Equations for Solid-catalyzed Reactions

| Chemical equation | Catalytic step | Rate equation *
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A + B = R</td>
<td>A + s = As</td>
<td>[ r = \frac{k(C_A - C_0(0))}{s + 1} ]</td>
</tr>
<tr>
<td></td>
<td>R + B = B</td>
<td>[ r = \frac{k(C_A - C_0(0))}{s + 1} ]</td>
</tr>
<tr>
<td>A = R + B</td>
<td>A + s = As</td>
<td>[ r = \frac{k(C_A - C_0(0))}{s + 1} ]</td>
</tr>
<tr>
<td></td>
<td>B + s = Bs</td>
<td>[ r = \frac{k(C_A - C_0(0))}{s + 1} ]</td>
</tr>
<tr>
<td>A + B = R + S</td>
<td>A + s = As</td>
<td>[ r = \frac{k(C_A - C_0(0))}{s + 1} ]</td>
</tr>
<tr>
<td></td>
<td>B + s = Bs</td>
<td>[ r = \frac{k(C_A - C_0(0))}{s + 1} ]</td>
</tr>
</tbody>
</table>

*Rate equations are simplified from [Perry, 1985].

---

**Mechanism a:**

- **Mechanism b:**

- **Mechanism c:**

- **Mechanism d:**

- **Mechanism e:**

- **Mechanism f:**

- **Mechanism g:**

- **Mechanism h:**

- **Mechanism i:**

- **Mechanism j:**

- **Mechanism k:**

- **Mechanism l:**

- **Mechanism m:**

- **Mechanism n:**

- **Mechanism o:**

- **Mechanism p:**

- **Mechanism q:**

- **Mechanism r:**

- **Mechanism s:**

- **Mechanism t:**

- **Mechanism u:**

- **Mechanism v:**

- **Mechanism w:**

- **Mechanism x:**

- **Mechanism y:**

- **Mechanism z:**

---

\[ k_\text{cat} \text{...} = \text{combined equilibrium constants} \]
\[ K_{\text{cat}} \text{...} = \text{overall equilibrium constant for the chemical equation} \]
\[ k \text{...} = \text{constant} \]
\[ r = \text{rate of product formation} \]
\[ \text{The rate equation is opposite the catalytic step assumed to be rate-controlling.} \]

---

**From Perry (1985) 2-5**
GENERAL FORM OF
LANGMUIR - H/W SHELDWOOD
HOUGEN - WATSON

RATE FORMS:

\[
\text{RATE} = \frac{(\text{KINETIC FACTOR})(\text{DRIVING FORCE GROUP})}{(\text{ADSORPTION GROUP})}
\]

FOR MODEL DISCRIMINATION NEED

- GOOD QUALITY DATA
- STATISTICAL EXPERIMENTAL DESIGN
- STATISTICAL MODEL DISCRIMINATION
Table 2.3.1-1
GROUPS IN KINETIC EQUATIONS FOR REACTIONS ON SOLID CATALYSTS

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$A \rightleftharpoons R$</th>
<th>$A + B \rightleftharpoons R + S$</th>
<th>$A + B \rightleftharpoons R + S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption of A controlling</td>
<td>$p_A \rightarrow \frac{P_A}{K}$</td>
<td>$p_A \rightarrow \frac{P_A p_an}{K}$</td>
<td>$p_A \rightarrow \frac{P_A p_an}{K}$</td>
</tr>
<tr>
<td>Adsorption of B controlling</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
</tr>
<tr>
<td>Desorption of R controlling</td>
<td>$p_A \rightarrow \frac{P_A}{K}$</td>
<td>$p_A \rightarrow \frac{P_A p_an}{K}$</td>
<td>$p_A \rightarrow \frac{P_A p_an}{K}$</td>
</tr>
<tr>
<td>Surface reaction controlling</td>
<td>$p_A \rightarrow \frac{P_A}{K}$</td>
<td>$p_A \rightarrow \frac{P_A p_an}{K}$</td>
<td>$p_A \rightarrow \frac{P_A p_an}{K}$</td>
</tr>
<tr>
<td>Impact of A controlling (A not adsorbed)</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
</tr>
<tr>
<td>Homogeneous reaction controlling</td>
<td>$p_A \rightarrow \frac{P_A}{K}$</td>
<td>$p_A \rightarrow \frac{P_A p_an}{K}$</td>
<td>$p_A \rightarrow \frac{P_A p_an}{K}$</td>
</tr>
</tbody>
</table>

Replacements in the General Adsorption Groups

$\left(1 + K_A p_A + K_B p_B + K_A p_B + K_p + K_p b\right)^n$

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$A \rightleftharpoons R$</th>
<th>$A + B \rightleftharpoons R$</th>
<th>$A + B \rightleftharpoons R + S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Where adsorption of A is rate controlling, replace $K_A p_A$ by</td>
<td>$K_A p_A$</td>
<td>$K_A p_an$</td>
<td>$K_A p_an$</td>
</tr>
<tr>
<td>Where adsorption of B is rate controlling, replace $K_B p_B$ by</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
</tr>
<tr>
<td>Where desorption of R is rate controlling, replace $K_S p_S$ by</td>
<td>$K_S p_S$</td>
<td>$K_S p_an$</td>
<td>$K_S p_an$</td>
</tr>
<tr>
<td>Where adsorption of A is rate controlling with dissociation of A, replace $K_A p_A$ by</td>
<td>$\sqrt{K_A p_A}$</td>
<td>$\sqrt{K_A p_an}$</td>
<td>$\sqrt{K_A p_an}$</td>
</tr>
<tr>
<td>Where equilibrium adsorption of A takes place with dissociation of A, replace $K_A p_A$ by (and similarly for other components adsorbed with dissociation)</td>
<td>$\sqrt{K_A p_A}$</td>
<td>$\sqrt{K_A p_an}$</td>
<td>$\sqrt{K_A p_an}$</td>
</tr>
<tr>
<td>Where A is not adsorbed, replace $K_A p_A$ by (and similarly for other components that are not adsorbed)</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
</tr>
</tbody>
</table>

ERDINGER & BISCHOFF (1991)

2-7
Table 2.3.1-1 (continued)

**Kinetic Groups**

<table>
<thead>
<tr>
<th>Adsorption of A controlling</th>
<th>( k_A )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption of B controlling</td>
<td>( k_B )</td>
</tr>
<tr>
<td>Desorption of ( R ) controlling</td>
<td>( k_r )</td>
</tr>
<tr>
<td>Adsorption of A controlling with dissociation</td>
<td>( k_A k_B )</td>
</tr>
<tr>
<td>Impact of A controlling</td>
<td>( k_A )</td>
</tr>
<tr>
<td>Homogeneous reaction controlling</td>
<td>( k )</td>
</tr>
</tbody>
</table>

**Surface Reaction Controlling**

<table>
<thead>
<tr>
<th></th>
<th>( A = R )</th>
<th>( A = R + S )</th>
<th>( A + B \Rightarrow R )</th>
<th>( A + B \Rightarrow R + S )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without dissociation</td>
<td>( k_r K_A )</td>
<td>( k_r K_A )</td>
<td>( k_r K_A K_B )</td>
<td>( k_r K_A K_B )</td>
</tr>
<tr>
<td>With dissociation of ( A )</td>
<td>( k_r K_A )</td>
<td>( k_r K_A )</td>
<td>( k_r K_A K_B )</td>
<td>( k_r K_A K_B )</td>
</tr>
<tr>
<td>( B ) not adsorbed</td>
<td>( k_r K_A )</td>
<td>( k_r K_A )</td>
<td>( k_r K_A )</td>
<td>( k_r K_A )</td>
</tr>
<tr>
<td>( B ) not adsorbed, ( A ) dissociated</td>
<td>( k_r K_A )</td>
<td>( k_r K_A )</td>
<td>( k_r K_A )</td>
<td>( k_r K_A )</td>
</tr>
</tbody>
</table>

**Exponents of Adsorption Groups**

| Adsorption of \( A \) controlling without dissociation | \( n = 1 \) |
| Desorption of \( R \) controlling | \( n = 1 \) |
| Adsorption of \( A \) controlling with dissociation | \( n = 2 \) |
| Impact of \( A \) without dissociation \( A + B \Rightarrow R \) | \( n = 1 \) |
| Impact of \( A \) without dissociation \( A + B \Rightarrow R + S \) | \( n = 2 \) |
| Homogeneous reaction | \( n = 0 \) |

**Surface Reaction Controlling**

<table>
<thead>
<tr>
<th></th>
<th>( A = R )</th>
<th>( A = R + S )</th>
<th>( A + B \Rightarrow R )</th>
<th>( A + B \Rightarrow R + S )</th>
</tr>
</thead>
<tbody>
<tr>
<td>No dissociation of ( A )</td>
<td>( 1 )</td>
<td>( 2 )</td>
<td>( 2 )</td>
<td>( 2 )</td>
</tr>
<tr>
<td>Dissociation of ( A )</td>
<td>( 2 )</td>
<td>( 2 )</td>
<td>( 3 )</td>
<td>( 3 )</td>
</tr>
<tr>
<td>Dissociation of ( A ) (( B ) not adsorbed)</td>
<td>( 2 )</td>
<td>( 2 )</td>
<td>( 2 )</td>
<td>( 2 )</td>
</tr>
<tr>
<td>No dissociation of ( A ) (( B ) not adsorbed)</td>
<td>( 1 )</td>
<td>( 2 )</td>
<td>( 1 )</td>
<td>( 2 )</td>
</tr>
</tbody>
</table>

*From Yang and Hougen (1950).*
THREE PHASE CATALYTIC REACTIONS

EXTENSIVE EXPERIMENTATION REQUIRED TO DETERMINE EXACT KINETIC KINETIC FORM. INSTEAD FACTORIAL EXPERIMENTAL DESIGN IS USED TO DETERMINE THE RANGE OF VARIABLES (T, P, CATALYST, REACTANT RATIO, ETC.) THAT MAXIMIZES RATE (OR SELECTIVITY). ONE MUST MAKE SURE THAT THESE RESULTS ARE UNMASKED BY TRANSPORT EFFECTS.

IN A NARROW RANGE OF OPERATING VARIABLES SELECTED FOR POTENTIAL COMMERCIALIZATION IT IS OFTEN POSSIBLE TO REPRESENT THE KINETIC FORM BY A POWER LAW:

\[ \Omega_A = k_0 e^{-E/RT} A^{2B} \]

OR BY A SIMPLER LH FORM:

\[ \Omega_A = \frac{k_0 e^{-E/RT} A}{1 + k_{Ao} e^{-EA/RT} A} \]

ETC.
<table>
<thead>
<tr>
<th>System</th>
<th>Catalyst used</th>
<th>Kinetic model ( \Omega_A ), mole/g/s</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogenation of ( \alpha )-methylstyrene</td>
<td>Pd–Al(_2)O(_3)</td>
<td>( k_{11}AB )</td>
<td>Satterfield et al. (1968)</td>
</tr>
<tr>
<td>Hydrogenation of crotonaldehyde</td>
<td>Pd–Al(_2)O(_3)</td>
<td>( k_1A )</td>
<td>Kenney and Sedriks (1972)</td>
</tr>
<tr>
<td>Hydrogenation of allyl-alcohol</td>
<td>Pd–Al(_2)O(_3)</td>
<td>( k_1A )</td>
<td>Ruether and Puri (1973)</td>
</tr>
<tr>
<td>Hydrogenation of acetone</td>
<td>Raney Ni</td>
<td>( k_{1/2}A^{1/2} )</td>
<td>Lemcoff and Jameson (1975b)</td>
</tr>
<tr>
<td></td>
<td>Raney Ni</td>
<td>( \frac{k_{mn}A^{1/2}B}{(1 + K_A A + K_B B + K_E E)^2} )</td>
<td>Lemcoff (1977)</td>
</tr>
<tr>
<td>Hydrogenation of glucose</td>
<td>Raney Ni</td>
<td>( k_{mn}A^{0.6}B )</td>
<td>Brahme and Doraiswamy (1976)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>or ( \frac{k_{11}AB}{1 + K_A A} )</td>
<td>Brahme (1972)</td>
</tr>
<tr>
<td>Oxidation of ( \text{SO}_2 ) (A represents ( \text{O}_2 ))</td>
<td>Activated carbon</td>
<td>( k_1A )</td>
<td>Komiyama and Smith (1975a)</td>
</tr>
<tr>
<td>Oxidation of ( \text{CO} )</td>
<td>CoO</td>
<td>( k_{11}AB )</td>
<td>Ido et al. (1976)</td>
</tr>
<tr>
<td>Ethynylation of formaldehyde</td>
<td>Cu(_2)C(_2)</td>
<td>( k_{0n}B^{0.44} )</td>
<td>Kale and Chaudhari (1978)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>or ( \frac{k_{01}B}{1 + K_B B + K_E E} )</td>
<td>Kale et al. (1981)</td>
</tr>
<tr>
<td>Oxidation of ethanol in the presence of ( \text{Na}_2\text{CO}_3 )</td>
<td>Pd–Al(_2)O(_3)</td>
<td>( k_{11}AB )</td>
<td>Hsu and Ruether (1978)</td>
</tr>
<tr>
<td>Oxidation of acetic acid</td>
<td>CuO–ZnO</td>
<td>( \frac{k_{mn}A^{1/2}B}{1 + K_B B} )</td>
<td>Levec and Smith (1976)</td>
</tr>
<tr>
<td>Hydrogenation of phenylacetylene to styrene (E)</td>
<td>Pd–Al(_2)O(_3)</td>
<td>( \frac{k_{11}AB}{(1 + K_B B + K_E E + K_A A)^3} )</td>
<td>Mochizuki and Matsui (1976)</td>
</tr>
<tr>
<td>Hydrogenation of styrene to ethyl-benzene</td>
<td>Pd–Al(_2)O(_3)</td>
<td>( \frac{kAB}{(1 + K_B B + K_A A)^3} )</td>
<td>Mochizuki and Matsui (1976)</td>
</tr>
<tr>
<td>Oxidation of formic acid</td>
<td>CuO–ZnO</td>
<td>( k_{11}AB )</td>
<td>Baldi et al. (1974)</td>
</tr>
</tbody>
</table>

*From Ramachandran and Chaudhari (1983)*
KEY IDEA

\( \text{(OBSERVED LOCAL APPARENT RATE)} = \text{(OVERALL EFFECTIVENESS FACTOR)} \times \text{(KINETIC RATE)} \)

\[ R_A = \eta_o \Omega_A (1 - \varepsilon_B) = \eta_o \Omega'_A \]

\[ \eta_o = \eta_o \left( \frac{\tau_D}{\tau_R} \right) \]

\[ \frac{\tau_D}{\tau_R} = \frac{\text{TRANSPORT RESISTANCE}}{\text{KINETIC RESISTANCE}} \]

\( \Omega_A \left( \frac{\text{mol A}}{\text{m}^3 \text{ cat. s}} \right) \quad \text{;} \quad \Omega'_A \left( \frac{\text{mol A}}{\text{m}^3 \text{ reactor s}} \right) \quad \text{EVALEUATED} \]

\( \text{AT "BULK" C, T CONDITIONS} \)

\( R_A \left( \frac{\text{mol A}}{\text{m}^3 \text{ reactor s}} \right) \quad \text{;} \quad \varepsilon_B \left( \frac{\text{m}^3 \text{ fluid}}{\text{m}^3 \text{ reactor}} \right) \quad \text{AT THE "POLE"} \)
KEY IDEA - EFFECTIVENESS FACTOR

REACTION : \( A \longrightarrow \) PRODUCTS

\[
\text{CONCENTRATION OF } A
\]

\[
\text{REACTION PHASE (CATALYST)}
\]

\[
\text{FILM MASS TRANSFER RESISTANCE}
\]

\[
\text{INTERNAL DIFFUSION AND REACTION} \rightarrow \text{PARTICLE EFFECTIVENESS FACTOR}, \; \eta_p
\]

\[
\text{(OBSERVED RATE)} = \left( \text{PARTICLE EFFECTIVENESS FACTOR} \right) \times \left( \text{KINETIC RATE AT EXT. SURFACE CONDITIONS} \right)
\]

\[
R_A = \left( \frac{\text{mol}}{\text{m}^3 \text{ react. s}} \right) = \eta_p \left( 1 - \varepsilon_B \right) k_v A_s^n
\]

\[
\text{COMBINED DIFFUSION & REACTION AND EXTERNAL TRANSPORT} \rightarrow \text{OVERALL EFFECTIVENESS FACTOR}, \; \eta_o
\]

\[
\text{(OBSERVED RATE)} = \left( \text{OVERALL EFFECTIVENESS FACTOR} \right) \times \left( \text{KINETIC RATE AT BULK CONDITIONS} \right)
\]

\[
R_A = \left( \frac{\text{mol}}{\text{m}^3 \text{ react. s}} \right) = \eta_o \left( 1 - \varepsilon_B \right) k_v A_b^n
\]

KINETIC RATE \( (\text{mol} / \text{m}^3 \text{ cat. s}) = k_v A^n = \mathcal{Q}_A \)
GAS-SOLID SINGLE REACTION

ISOTHERMAL PARTICLE WITH NO EXTERNAL TEMPERATURE GRADIENT

\[ \eta_p = \frac{\tan \beta \Lambda_p}{\Lambda_p} \]

\[ \Lambda_p = \frac{V_p}{S_p} \sqrt{\frac{k}{D_e}} \]

\[ \frac{1}{\eta_0} = \frac{1}{\eta_p} + \frac{\Lambda_p^2}{B_i m} \]

\[ B_i m = \frac{k_m V_p}{S_t D_e} \]
A. GAS LIQUID SOLID CATALYTIC SYSTEMS

\[
\text{CAT} \quad A(g) + \nu B(l) \rightarrow \nu p D
\]

REACTION CAN BE:

I. GAS REACTANT LIMITED \( A \ll B \)

II. LIQUID REACTANT LIMITED \( A >> B \)

III. AFFECTED BY BOTH REACTANTS \( A \approx B \)

PROCESS INVOLVES:

1. NONVOLATILE LIQUID REACTANT

2. VOLATILE LIQUID REACTANT

CATALYST PARTICLES ARE:

a. COMPLETELY WETTED

b. PARTIALLY EXTERNALLY WETTED

c. PARTIALLY EXTERNALLY & INTERNALLY WETTED

d. COMPLETELY DRY

b, c, d IN PACKED-BEDS ONLY
b POSSIBLE IN FINE SLURRIES OR FOAMS WHERE PARTICLES AGGLOMERATE AT THE GAS LIQUID INTERFACE
REACTION: \( A(g) + B(l) = P(l) \)

**GAS LIMITING REACTANT**
*(COMPLETELY WETTED CATALYST)*

**KINETIC RATE**
*(PER UNIT CATALYST VOLUME)*

\[ k_v A \text{ (mol/m}^3 \text{ cat. s)} \]

**RATE IN CATALYST**
*(PER UNIT REACTOR VOLUME)*

\[ k_v \eta_p (1 - \varepsilon_B) A_s \text{ (mol/m}^3 \text{ react. s)} \]

**TRANSPORT RATE**
*(mol/m}^3 \text{ react. s)} ;
*(PER UNIT REACTOR VOLUME)*

- **GAS - LIQUID**
  \[ K_1 a_B \left( \frac{A_g}{H_A} - A_l \right) \]

- **LIQUID - SOLID**
  \[ k_s a_p (A_l - A_s) \]

**OVERALL (APPARENT) RATE**
*(mol/m}^3 \text{ react. s)} :

\[ \eta_0 k_v (1 - \varepsilon_B) \frac{A_g}{H_A} = \frac{A_g}{H_A} + \frac{1}{K_1 a_B} + \frac{1}{k_s a_p} + \frac{1}{(1 - \varepsilon_B) k_v \eta_p} \]
GAS-LIMITED FIRST ORDER REACTION

COMPLETELY WETTED CATALYST

\[ \Omega_A = k A \text{ (mol/cm}^3\text{cat.s)} \]

\[ R_A = \frac{P_{Ag}/H_A}{K_{L_{AB}} + \frac{1}{k_s a_p} + \frac{1}{(w/\rho_p)k \eta_p}} \]

\[ = (1-\epsilon_0) \% \ k \frac{P_{Ag}/H_A}{A^*} \]

RESISTANCE = GAS-LIQUID + LIQUID-SOLID + PARTICLE

\[ P_{Ag} \text{ (atm)} \]

= PARTIAL PRESSURE OF A IN THE GAS

\[ H_A \text{ (atm cm}^3\text{/mol)} \]

= HENRY'S CONSTANT

\[ K_{L_{AB}} \text{ (s}^{-1}) \]

= OVERALL VOLUMETRIC GAS-LIQUID MASS TRANSFER COEFFICIENT FOR A

\[ k_s \text{ (cm/s)} \]

= LIQUID-SOLID MASS TRANSFER COEFFICIENT

\[ a_p \text{ (cm}^2/\text{cm}^3) \]

= EXTERNAL SURFACE AREA OF CATALYST PARTICLES PER UNIT VOLUME OF REACTOR

\[ a_B \text{ (cm}^2/\text{cm}^3) \]

= GAS-LIQUID INTERFACIAL AREA PER UNIT VOLUME OF REACTOR

\[ w \text{ (g/cm}^3) \]

= CATALYST MASS PER UNIT REACTOR VOLUME

\[ \rho_p \text{ (g/cm}^3) \]

= ACTUAL DENSITY OF CATALYST PARTICLES

\[ \eta_p \text{ [-]} \]

= PARTICLE (INTERNAL) EFFECTIVENESS FACTOR

\[ k \text{ (s}^{-1}) \]

= FIRST ORDER RATE CONSTANT

2-16
USEFUL RELATIONS

\[ \Lambda_p^2 = \left( \frac{V_p}{S_p} \right)^2 \frac{k}{D_{ Ae}} = \frac{\tau_D}{\tau_K} \text{ PARTICLE MODULUS} \]

\[ \eta_p = \frac{\tanh \Lambda_p}{\Lambda_p} \text{ PARTICLE EFFECTIVENESS FACTOR} \]

\[ V_p (\text{cm}^3) = \text{PARTICLE VOLUME} \]

\[ S_p (\text{cm}^2) = \text{PARTICLE EXTERNAL AREA} \]

\[ D_{ Ae} = D_A \frac{\varepsilon_p}{\tau} \text{ EFFECTIVE DIFFUSIVITY} \]

\[ D_A (\text{cm}^2/\text{s}) = \text{MOLECULAR DIFFUSIVITY} \]

\[ \varepsilon_p [-] = \text{PARTICLE POROSITY} \]

\[ \tau [-] = \text{PARTICLE TURTOUSITY} \]

\[ a_p = \frac{S_p}{V_p} \rho_p = \frac{S_R}{V_p} (1-\varepsilon_B) \]

\[ (1-\varepsilon_B) = \text{VOLUME FRACTION OF CATALYST IN THE REACTOR} = \frac{w}{S_p} \]

\[ M_A = \left( \frac{1}{K_{LaB}} + \frac{1}{k_s a_p} \right)^{-1} = \text{OVERALL TRANSPORT COEFFICIENT} \]

\[ \frac{1}{K_{LaB}} = \frac{1}{K_{LaB}}^{\text{LIQUID-SIDE}} + \frac{1}{k_{gH_A}}^{\text{GAS-SIDE}} \]
GAS-LIMITED FIRST ORDER REACTION

\[ R_A = \frac{A^*}{M_A^*} + \frac{1}{(w/\rho_p)k\eta_p} = (1-\epsilon_a)\gamma_o k A^* \quad (1) \]

ASSUMPTIONS:

1. COMPLETELY WETTED CATALYST

2. FILM THEORY FOR MASS TRANSFER

3. STEADY STATE

4. NO OVERLAP OF LIQUID FILM AND CATALYST PARTICLES

5. ISO THERMAL

\[ \frac{A_S}{A^*} = \frac{1}{w k \eta_p} \frac{1}{1 + \frac{k}{\rho_p M_A}} \rightarrow 0 \]

\[ \frac{A^* - A_S}{A^*} = R_A M_A A^* \rightarrow 1 \]

\[ A^* = \frac{P_{A^*}}{\eta_A} \]

EXTERNAL MASS TRANSFER CONTROLS THE RATE

2-18
\[ R_A = \frac{A^*}{\frac{1}{M_A} + \frac{\rho_p}{w k \eta_p}} \]

**IN PRINCIPLE VALID FOR:**

- SLURRIES (MECH. STIRRED AND BUBBLE COLUMNS)
- EBULATED BEDS
- THREE PHASE FLUIDIZED BEDS
- TRICKLE BEDS

**NOT VALID WHEN**

1. INCOMPLETELY WETTED CATALYST (TRICKLE BEDS)
2. RAPID MOVEMENT OF CATALYST PARTICLES TO REGIONS OF DIFFERENT COMPOSITION (SLURRY, FLUIDIZED BEDS)
3. DOMINANT GAS–LIQUID RESISTANCE, SMALL CATALYST IN THE LIQUID FILM AND LARGE FILM VOLUME \( i.e \)

\[ \frac{A_{\frac{L}{A}}}{A^*} = \frac{1}{1 + \frac{1}{K_{L_A}} \left[ \frac{\rho_p}{w k \eta_p} + \frac{1}{k_s a_p} \right]} \rightarrow 0 \]

\[ \frac{A^* - A_{\frac{L}{A}}}{A^*} = \frac{R_A}{K_{L_a} A^*} \rightarrow 1 \]

\[ d_p << \frac{\theta_A}{k_L} \; ; \; \frac{V_L}{V_{EF}} = \frac{H_L}{a_B \theta_A} \ll 1 \]

\[ A_{\frac{L}{A}} H_L < \frac{1}{2} (A^* + A_{\frac{L}{A}}) \frac{a_B \theta_A}{K_L} \]

\[ H_L = \text{TOTAL LIQUID HOLDUP} \]
THE FOLLOWING CONCLUSIONS CAN BE DRAWN:

KINETIC RESISTANCE DOMINATES

\[ \text{RATE} \quad \alpha \quad \left( \text{CATALYST VOLUME FRACTION} \right)^1 \]
\[ \quad \left( \text{CATALYST ACTIVITY} \right)^1 \]
\[ \quad \left( \text{CATALYST PARTICLE LOADING} \right)^1 \]
\[ \quad \left( \text{REACTANT CONCENTRATION} \right)^n \]
\[ E = E_{\text{KINETIC}} \quad ; \quad n = n_{\text{KINETIC}} \]

KINETICS + STRONG PORE DIFFUSION RESISTANCE DOMINATES

\[ \text{RATE} \quad \alpha \quad \left( \text{CATALYST VOLUME FRACTION} \right)^1 \]
\[ \quad \left( \text{CATALYST ACTIVITY} \right)^{1/2} \]
\[ \quad \left( \text{CATALYST PARTICLE LOADING} \right)^{1/2} \]
\[ \quad \left( \text{REACTANT CONCENTRATION} \right)^{(n+1)/2} \]
\[ \quad \left( \text{PARTICLE DIAMETER} \right)^{-1} \]
\[ E = E_{\text{KIN}}/2 \quad ; \quad n = \left( n_{\text{KIN}} + 1 \right)/2 \]

EXTERNAL MASS TRANSFER RESISTANCE DOMINATES

\[ \text{RATE} \quad \alpha \quad \left( \text{CATALYST VOLUME FRACTION} \right)^{0 \ to \ 1} \]
\[ \quad \left( \text{PARTICLE DIAMETER} \right)^{-2 \ to \ 0} \]
\[ \quad \left( \text{REACTANT CONCENTRATION} \right)^1 \]
\[ E_{\text{app}} = 1 \ to \ 4 \ \text{kcal} \quad ; \quad n_{\text{app}} = 1 \]

HYDRODYNAMIC REGIME, GAS AND LIQUID VELOCITIES AFFECT THE RATE

REACTOR VOLUMETRIC PRODUCTIVITY \( \alpha \) RATE

2-20
LIQUID-LIMITED REACTION

SAME PROCEDURE. JUST REPLACE $M_A$ WITH $M_B = (k_s a_p)_B$, $\Omega_{A_s}$ WITH $\Omega_{B_s} = \nu \Omega_{A_s}$, $D_{Ae}$ with $D_{B \epsilon}$ AND ALL PROPERTIES OF A WITH THAT FOR B.

BOTH REACTANTS LIMIT THE RATE ($A^* = 0 (B_L)$)

SAME PROCEDURE BUT MODIFIED. ADD EQUATIONS

$$\frac{A^* - A_S}{B_L - B_S} = \frac{M_B}{\nu M_A}$$

$$p = \frac{\nu \Omega_{Ae} A_s}{D_{B \epsilon} B_s}$$

FOR $M_B/\nu M_A > 1$ IF $p < 1$ B IS IN EXCESS

BASE EVALUATION OF ALL MODULI ON A:

$$B = B_S - \frac{\nu \Omega_{Ae} (A_S - A)}{D_{B \epsilon}}$$

EVERYWHERE IN PARTICLE AND ALL REQUIRED INTEGRATIONS CAN BE PERFORMED.

$$M_A (A^* - A_S) = \frac{w}{\rho_p} \Omega_{A_S} = \Omega_{A_g}$$

$$M_B (B_L - B_S) = \nu \frac{w}{\rho_p} \eta_p \Omega_{A_S} = \nu \eta_o \Omega_{A_g}$$
VAPOR FILLED ("DRY") PELLET

THE ABOVE PROCEDURE HOLDS EXCEPT THAT ALL PROPERTIES ARE BASED ON TRANSPORT THROUGH VAPOR PHASE. HENCE ALL TRANSPORT AND DIFFUSION COEFFICIENTS ARE INCREASED BY A FACTOR OF $10^3$ TO $10^5$.

FOR HIGHLY ENERGETIC REACTIONS WHEN $(\beta \gamma) > 2$ NONISOTHERMAL PARTICLE CONDITIONS MUST BE ACCOUNTED FOR

$$\beta = \frac{(- \Delta H_{RA}) D_A e A g s}{\lambda_e T_s} ; \quad \gamma = \frac{E}{RT_s}$$

EXTERNAL FILM TEMPERATURE DIFFERENCES ARE EVEN MORE LIKELY AND NEED TO BE ACCOUNTED FOR WHEN

$$T_s - T_g = \frac{(- \Delta H_{RA}) (R_A) V_p}{h_p S_p}$$

IS APPRECIABLE (DEPENDS ON $\gamma$)

TEMPERATURE CORRECTION IS THEN REQUIRED.
Figure 4.1. Effectiveness factor $\eta$ as a function of $\phi_1 = R \sqrt{k_i/D_{eff}}$ for $\gamma = 20$. First-order reaction in sphere. Weisz and Hicks [376].
WHETHER A TYPICAL PORE OF RADIUS $R_{pore}$ IN A CATALYST PARTICLE WILL REMAIN LIQUID FILLED OR WILL BE VAPOR FILLED CAN BE APPROXIMATELY ESTIMATED AS follows:

$$R_{pore}^* = \frac{2 \bar{V} c_L}{\Delta H_V} \frac{(1-\varepsilon_B) \ h_p S_P T_L}{(-\Delta H_{RB}) \ R_B \ V_p}$$

$$R_{pore} > R_{pore}^* \quad \text{DRY}$$

$\bar{V}$ = MOLAR VOLUME OF VOLATILE SPECIES: $\Delta H_V$ = HEAT OF VAPORIZATION
$\varepsilon_B$ = VOLUME FRACTION OF PARTICLES
$h_p$ = PARTICLE HEAT TRANSFER COEFFICIENT
$T_L$ = LIQUID BULK TEMPERATURE
$V_p/S_P$ = PARTICLE VOLUME TO EXT. SURFACE RATIO
$\Delta H_{RB}$ = HEAT OF REACTION (PER MOLE B)
$R_B$ = RATE OF REACTION OF B

GLOBALLY LIQUID VOLATILIZATION SHOULD BE EXPECTED IF

$$\frac{u_L \bar{M}_g}{u_g \bar{M}_L} < \frac{P_V(T)}{P - P_V(T)}$$

RATE ON DRY PELLET >> RATE ON VETTED PELLET
EXAMPLE 1

REACTION: \( \text{H}_2 (g) + \text{C}_3 \text{H}_5 \text{CHO}(\ell) = \text{C}_3 \text{H}_6 \text{CHOH} \)

CATALYST: 0.5% Pd ON ALUMINA

REACTOR: AGITATED SLURRY AND TBR

DATA:

\[ \begin{align*}
T & = 51^\circ \text{C} \quad ; \quad P = 1 \text{ ATM} \\
A^* & = 2.8 \times 10^{-6} \text{ (mol/cm}\^3) \\
k & = 3.69 \times 10^2 \text{ cm}^3/\text{s g Pd} \\
k_w & = 3.69 \times 10^2 \times 0.5 \times 10^{-2} = 1.84 \text{ (cm}^3/\text{g s)}
\end{align*} \]

IN TBR

\[ \begin{align*}
d_p & = 0.5 \text{ cm} \quad ; \quad \rho_p = 1.5 \text{ g/cm}^3 \\
k_{L_{AB}} & = 0.02 \text{ (s}^{-1}) \\
k_s & = 0.02 \text{ (cm/s)} \\
D_{Ae} & = 2 \times 10^{-5} \text{ (cm}^2/\text{s)} \\
1 - \varepsilon_B & = 0.6
\end{align*} \]

IN SLURRY

\[ \begin{align*}
M_A & = 0.0174 \text{ (s}^{-1}) \\
w & = 2.5 \times 10^{-2} \text{ (g/cm}^3) \\
\eta_p & = 1
\end{align*} \]

FIRST ORDER REACTION IN HYDROGEN

OBJECTIVE

- COMPARE RATES IN MECHANICALLY AGITATED SLURRY AND TBR
- DETERMINE MAGNITUDE OF TRANSPORT EFFECTS
- DETERMINE DOMINANT RESISTANCE
\[ \Lambda_p = \frac{d_p}{6} \sqrt{\frac{\rho_p \kappa_w}{D_{\text{ae}}}} = 31 \]

\[ \eta_p = \frac{\tan h \Lambda_p}{\Lambda_p} = \frac{1}{31} = 0.0322 \]

\[ M_A = \left( \frac{1}{k_L a_B} + \frac{1}{k_s a_p} \right)^{-1} = (50 + 6.9)^{-1} = 0.0176 \text{ (s}^{-1}) \]

\[ R_A = \frac{A^*}{\frac{1}{M_A} + \frac{1}{w k_w \eta_p}} = \frac{2.8 \times 10^{-6}}{56.9 + 18.7} = 0.3 \text{ g/cm}^3 \]

\[ R_A = 3.70 \times 10^{-8} \left( \frac{\text{mol}}{\text{cm}^3 \text{ s}} \right) = 0.133 \text{ (mol/L h)} \]

\[ \Omega_A' = w k_w \Lambda^* = 4.64 \times 10^{-6} \text{ (mol/cm}^3 \text{ s)} \]

\[ \eta_o = \frac{R_A}{\Omega_A'} = 0.00797 \]

WE ARE REALIZING 88% OF KINETIC RATE, EXTERNAL MASS TRANSFER RESISTANCE (GAS-LIQUID) DOMINATES.

— CAN INCREASE \( R_A \) BY INCREASING \( P \)

— CAN INCREASE \( R_A \) BY OPERATING AT INCREASED \( P \) IN LIQUID ONLY (ELIMINATES GAS-LIQUID RESISTANCE (4000 ATM))

— CAN INCREASE \( R_A \) BY OPERATING AT PARTIAL WETTING

— INCREASE IN \( T \) HELPS ONLY IF \( A^* \) INCREASES

— WATCH FOR HEAT EFFECT!
SLURRY

\[ M_A = 0.0174 \ (s^{-1}) \]

\[ \omega k_w \eta_p = 2.5 \times 10^{-2} \times 1.84 \times 1 = 0.046 \ (s^{-1}) \]

\[ R_A = \frac{1}{M_A} + \frac{1}{\omega k_w \eta_p} = \frac{2.8 \times 10^{-6}}{57.5 + 21.7} \]

\[ R_A = 3.54 \times 10^{-8} \ (\text{mol/cm}^3\text{s}) = 0.127 \ (\text{mol/L h}) \]

\[ \Omega_A' = \omega k_w A^* = 1.29 \times 10^{-7} \ (\text{mol/cm}^3\text{s}) \]

\[ \eta_o = \frac{R_A}{\Omega_A'} = 0.279 \]

27.4% OF KINETIC RATE IS REALIZED BUT RATE PER UNIT REACTOR VOLUME LOWER THAN IN TBR. INCREASE IN CATALYST LOADING WOULD HELP TO INCREASE RATE SOMEWHAT. ALSO:

— RAISE PRESSURE

— INCREASE RPM
ESTIMATION OF TRANSPORT RESISTANCES FROM DATA

\[
\frac{A^* - A_S}{A^*} = \left( \frac{\dot{R}_A}{M_A A^*} \right) = \frac{\text{OBSERVED RATE}}{\text{MAX RATE OF EXTERNAL MASS TRANSPORT}}
\]

\[
\frac{R_A}{M_A A^*} < 0.1 \quad \text{NEGLECTIBLE EXTERNAL TRANSPORT EFFECTS}
\]

\[
> 0.5 \quad \text{CONSIDERABLE EXTERNAL TRANSPORT EFFECTS}
\]

\[
\rightarrow 1 \quad \text{EXTERNAL TRANSPORT CONTROLS THE RATE}
\]

AGAIN ONE NEEDS RELIABLE ESTIMATES OF SOLUBILITY \( A^* \)

AND TRANSPORT COEFFICIENTS \( k_{L_a B}, \ k_{S_a P} \)

IF \( k_{L_a B} < k_{S_a P} \)

GAS-LIQUID RESISTANCE DOMINATES THE EXTERNAL RESISTANCE

\[
\frac{1}{M_A} = \frac{1}{k_{L_a B}} + \frac{1}{k_{S_a P}}
\]
ESTIMATION OF TRANSPORT
RESISTANCES FROM DATA

\[ \phi = \frac{\left( \frac{R_A}{1 - \epsilon_B} \right) \left( \frac{V_p}{S_p} \right)^2}{D_A e \, A_s} = \frac{\text{OBSERVED RATE}}{\text{MAX RATE OF PURE DIFFUSIONAL TRANSPORT}} \]

\[ \phi < 0.2 \quad \text{NO INTERNAL DIFFUSIONAL EFFECTS} \]

\[ \eta_p = 1 \]

\[ 0.2 < \phi < 6 \quad \text{INTERMEDIATE DIFFUSIONAL EFFECTS} \]

\[ \phi = \Lambda_p \tanh \Lambda_p \]

\[ \eta_p = \frac{\tanh \Lambda_p}{\Lambda_p} \]

\[ \phi > 6 \quad \text{STRONG PORE DIFFUSIONAL EFFECTS} \]

\[ \eta_p = \frac{1}{\phi} \]

2-29
ESTIMATION OF TRANSPORT EFFECTS FOR NONLINEAR REACTIONS IS MORE DIFFICULT

SUGGESTIONS

1. ESTIMATE SOLUBILITY AND TRANSPORT COEFFICIENTS AS ACCURATELY AS POSSIBLE.

2. DEVELOP A MODEL WITH POSSIBLE RATE FORMS.

3. EXAMINE MODEL SENSITIVITY WITH RESPECT TO OPERATING VARIABLES EG (RPM, Q_g, Q_L, w, d_p, ETC.).

4. CONDUCT EXPERIMENTS IN
   - DIFFERENTIAL REACTOR
   - CSTR

5. COLLECT DATA AND DRAW CONCLUSION FROM MODEL.

6. DO EXPERIMENTS SEQUENTIALLY.
EXAMPLE:

REACTION: HYDRODESULFURIZATION OF PETROLEUM

CATALYST: Co/Mo/Al₂O₃

REACTOR: TRICKLE-BED

DATA: 
T = 367°C ; 827 psia (56 atm)

\[ d_p = 1/8" \ (0.32 \text{ cm}) \]

\[ \varepsilon_B = 0.36 \]

\[ A^* = 4.84 \times 10^{-4} \text{ mol/cm}^3 \]

\[ D_A = 5.5 \times 10^{-5} \text{ cm}^2/\text{s} \]

Rate = 1.04 \times 10^{-6} \text{ mol/s cm}^3 \text{ pellets}

(\[ \varepsilon_p \approx 0.45 ; \tau \approx 4 \])

1% SULFUR IN FEED

OBJECTIVE

DETERMINE CONTROLLING RESISTANCE

\[ a_p = \frac{6 \left(1 - \varepsilon_B\right)}{d_p} = 12.1 \text{ (cm}^{-1}) \]

\[ V_p/S_p = d_p/6 = 0.0529 \text{ cm} \]

\[ M_A = \left(\frac{1}{k_{rA}a_B} + \frac{1}{k_{sA}a_p}\right)^{-1} \text{ UNKNOWN} \]

APPROXIMATE \[ M_A(A^* - A_S) = k_{G LS}a_p (A^* - A_S) \]

\[ R_A = (1 - \varepsilon_B) \text{ RATE} = 6.66 \times 10^{-7} \text{ (mol/cm}^3\text{s)} \]
ESTIMATE

\[ k_{\text{GLS}} \geq \frac{D_A \alpha_p}{\epsilon_B / 2} = 0.0037 \text{ (cm/s)} \]

\[ M_A > k_{\text{GLS}} \alpha_p = 0.0448 \text{ (s}^{-1}\text{)} \]

IN ABSENCE OF EXTERNAL MASS TRANSFER RESISTANCE

\[ \frac{A^* - A_S}{A^*} = \frac{R_A}{M_A A^*} < 0.1 \]

NOW

\[ \frac{R_A}{M_A A^*} = 0.031 < < 0.1 \]

EXTERNAL TRANSPORT EFFECTS UNLIKELY

IN ABSENCE OF INTERNAL TRANSPORT EFFECTS

\[ \phi = \frac{(R_A) (V_p/S_p)^2}{(1 - \epsilon_B) D_{Ae} A_s} < 0.3 \]

\[ D_{Ae} = D_A \frac{\epsilon_p/t}{5.5 \times 10^{-5} \frac{0.45}{4}} = 6.2 \times 10^{-6} \text{ (cm}^2/\text{s)} \]

\[ \phi = 0.97 = \Lambda_p \tanh \Lambda_p \]

INTERNAL DIFFUSIONAL EFFECTS MAY BE PRESENT BUT NOT PRONOUNCED.

ABOVE ESTIMATES VERY DEPENDENT ON A*, D_A, D_{Ae}
EXAMPLE 3:

REACTION: ALDEHYDE HYDROGENATION \( A(g) + 6 B(e) = P(e) \)

CATALYST: Ni

REACTOR: CSTR CONTINUOUS (AGITATED) SLURRY

DATA:
\[ T = 100^\circ C \quad ; \quad P = 500 \text{ psia} \]
\[ \rho_L = 0.8 \text{ g/cm}^3 \quad ; \quad M_B = 80 \text{ g/mol} \]
\[ B_{\infty} = 0.01 \text{ (mol/cm}^3) \quad ; \quad x_B = 0.88 \]
\[ \frac{V}{Q_L} = 600 \text{ (s)} \]
\[ d_p = 10^{-3} \text{ cm} \quad ; \quad a_p = 300 \text{ cm}^{-1} \quad ; \quad \rho_p = 2.5 \text{ (g/cm}^3) \]
\[ \varepsilon_g \approx 0.1 \]

HIGH RPM

OBJECTIVE

DOUBLE PRODUCTION CAPACITY.

CAN IT BE ACHIEVED IN THE SAME REACTOR?

ESTIMATE
\[ A^* = 5 \times 10^{-4} \text{ mol/cm}^3 \]
\[ D_A = 4 \times 10^{-5} \text{ cm}^2/\text{s} \]
\[ w = 0.125 \text{ (g/cm}^3) \]

CSTR ASSUMPTION
\[ B_L = B_{\infty} (1 - x_B) = 1.2 \times 10^{-3} \text{ (mol/cm}^3) \]

HYDROGEN IS RATE LIMITING \( (A) \)
ESTIMATE LIQUID-SOLID TRANSPORT

\[ \text{Sh} = 2 = \frac{k_s d_p}{D_A} \quad k_s = 0.08 \text{ cm/s} \]

\[ k_s a_p \geq 24 \text{ (s}^{-1}) \]

ESTIMATE GAS-LIQUID TRANSPORT

BASED ON REPORTED \( \varepsilon_g = 0.1 \), HIGH RPM, AVAILABLE CHARTS \( k_L a_B \approx 0.2 \text{ (s}^{-1}) \).

\[ \text{RA} = \frac{A^*}{ \frac{1}{k_L a_B} + \frac{1}{k_s a_p} + \frac{1}{w \eta_p k_w} } = \frac{5 \times 10^{-4}}{5 + 0.042 + PR} = 1.47 \times 10^{-5} \]

FROM DATA

\[ \text{RA} = \frac{B_l Q_X B}{V/Q_L} = 1.47 \times 10^{-5} \text{ (mol/cm}^3\text{s)} \]

\[ PR = 29.0 \text{ (s)} = \frac{1}{w \eta_p k_w} \]

IT SEEMS THAT PARTICLE DIFFUSION + KINETIC RESISTANCE DOMINATES.

TO DOUBLE THE RATE \( \text{RA} \) NEED TO REDUCE \( PR \) TO 12 (s).

THIS CAN BE ACCOMPLISHED BY INCREASING CATALYST LOADING BY A FACTOR OF 2.5.

WHEN IMPLEMENTED ONLY SLIGHT IMPROVEMENT IN \( \text{RA} \) OBSERVED!
FIGURE 9.8 Comparison of correlations for $k_{L A B}$ in an agitated reactor.
CLOSER EXAMINATION REVEALS THAT REACTOR OPERATES AT 300 rpm EXP. DETERMINED $k_{La}$ AGREES WITH CORRELATION AT 300 RPM.

$$k_{La_B} = 0.03 \text{ (s}^{-1})$$

NOW

$$R_A = \frac{5 \times 10^{-4}}{33.3 + 0.04 + PR} = 1.47 \times 10^{-5}$$

$$PR = 0.67 \text{ (s)} \quad \text{NEGLIGIBLE!}$$

GAS-LIQUID RESISTANCE CONTROLS! :!

CHOICES FOR DOUBLING THE PRODUCTION RATE:

a. MORE POWERFUL MOTOR. INCREASE RPM FROM 300 TO 2000 AT THE EXPENSE OF POWER INCREASE BY A FACTOR OF $(2000/300)^3 = 296.$

b. INCREASE PRESSURE BY A FACTOR OF TWO.

c. INCREASE GAS FLOW RATE BY A FACTOR OF TEN AND RPM BY AT LEAST TWO.

d. BUILD ANOTHER REACTOR.

NOTE: EXTREME SENSITIVITY OF CONCLUSION TO ESTIMATION OF TRANSPORT EFFECTS.
OUR TASK IN REACTOR DESIGN IS:

1. MAXIMIZE VOLUMETRIC PRODUCTIVITY \( \dot{m}_{VP} \ (kg/m^3\ h) \)

2. MAXIMIZE PRODUCT CONCENTRATION AND SELECTIVITY

\[ \begin{align*}
\dot{m}_{VP} & \quad \dot{m}_{VP\ max} \\
x & \quad x_{\max}
\end{align*} \]

\[ x \left( \frac{kg\ \text{cat.}}{m^3} \right) \quad - \text{CATALYST CONCENTRATION} \]

\[ S_a \left( \frac{kg\ P}{kg\ \text{cat}\ h} \right) \quad - \text{SPECIFIC ACTIVITY} \]

KNOWING TRANSPORT LIMITATIONS TELLS US THE POTENTIAL FOR FURTHER IMPROVEMENTS OF THE CATALYST.
FOR SUCCESSFUL INTERPRETATION OF TRANSPORT EFFECTS ON REACTIONS IN MULTIPHASE SYSTEMS ONE NEEDS ACCURATE ESTIMATE OF A NUMBER OF PROPERTIES.

- GAS REACTANT SOLUBILITY
- LIQUID REACTANT VOLATILITY
- HEAT OF REACTION
- SPECIFIC HEATS

- DIFFUSIVITIES IN LIQUIDS
- DIFFUSIVITIES IN GASES
- THERMAL CONDUCTIVITY IN LIQUIDS
  - IN GASES
  - IN PARTICLE

TRANSPORT COEFFICIENTS AND AREAS

\[ k_L \] - GAS-LIQUID (LIQUID SIDE)

\[ k_g \] - GAS-LIQUID (GAS SIDE)

\[ k_{SL} \] - LIQUID - SOLID

\[ k_{SG} \] - GAS - SOLID

\[ h_p \] - PARTICLE HEAT TRANSFER COEFF.

\[ a_B \] - GAS - LIQUID INTERFACIAL AREA

\[ a_p \] - LIQUID - SOLID INTERFACIAL AREA

2-32
FOR EVALUATION OF

- SOLUBILITY
- VOLATILITY
- HEAT OF REACTION
- EQUILIBRIA - ETC.

CONSULT CHEMICAL THERMODYNAMICS

1. PERRY'S CHEMICAL ENGINEER'S HANDBOOK

2. REID, PRAUSNITZ AND POLING
   PROPERTIES OF GASES AND LIQUIDS

3. JANAF TABLES

4. COMPANY'S OF PUBLIC DATA BASES

5. WILHELM AND BATTINO
   THERMO. FUNC. OF SOLUBILITIES ..... 
   CHEM. REVIEWS 73, 1, 1973
SOLUBILITY EVALUATION

STEADY STATE METHODS

- SATURATION
- DESORPTION

DYNAMIC METHODS

EFFECTIVE DIFFUSIVITY EVALUATION

STEADY STATE METHOD

TRANSIENT METHODS

SINGLE PELLET CELL

WICKE-KALLENBACH CELL

CSTR - BASKET

PACKED BED

BYPASS THE NEED FOR ACCURATE $D_e$ VALUES BY SCALING-UP WITH EXACTLY THE SAME CATALYST (SIZE, etc.) FOR WHICH PILOT PLANT RUNS ARE AVAILABLE.
FOR EVALUATION OF

THERMAL CONDUCTIVITY OF GASES

IN MIXTURES
TEMPERATURE AND PRESSURE EFFECT

THERMAL CONDUCTIVITY OF LIQUIDS

IN MIXTURES
TEMP. AND P EFFECT

SEE REID ET AL.

PROPERTIES OF GASES AND LIQUIDS

FOR EFFECTIVE CONDUCTIVITY

IN CATALYST PARTICLES

SEE FROMENT & BISCHOFF
ORDER OF MAGNITUDE ESTIMATES

<table>
<thead>
<tr>
<th></th>
<th>GASES</th>
<th>LIQUIDS</th>
</tr>
</thead>
<tbody>
<tr>
<td>DIFFUSIVITY (cm$^2$/s)</td>
<td>0.01 TO 1</td>
<td>10$^{-6}$ TO 10$^{-4}$</td>
</tr>
<tr>
<td>CONDUCTIVITY (w/mk)</td>
<td>5 x 10$^{-3}$ TO 10$^{-1}$</td>
<td>5 x 10$^{-2}$ TO 1</td>
</tr>
</tbody>
</table>

EXAMPLE

T = 25°C

O$_2$ - AIR

D = 0.23 cm$^2$/s

O$_2$ - WATER

D = 2.1 x 10$^{-5}$ cm$^2$/s

k$_L$ = 2.1 x 10$^{-3}$ cm$^2$/s

H$_A$ = 7.9 x 10$^5$ (atm cm$^3$/mol)

IN GASES

P / D $\leftrightarrow$ ; T / D /

IN LIQUIDS

P / D $\leftrightarrow$ ; T / D /

IN GASES

P / $\lambda$ $\rightarrow$ ; T / $\lambda$ / LOW P

P / $\lambda$ / ; T / $\lambda$ / HIGH P
THEORIES FOR PREDICTION OF

MASS TRANSFER BETWEEN TWO PHASES:

- TWO - FILM THEORY

LEWIS AND WHITMAN
IEC 16, 2215 (1924)

- PENETRATION THEORY

HIGBIE
TRANS. AM. INSTN. CHEM. ENGRS. 31, 365 (1935)

- SURFACE RENEWAL THEORY

DANCKWERTS
AICHe J. 1, 456 (1955)
MASS TRANSFER COEFFICIENTS

\( k_L \) - GAS-LIQUID (LIQUID SIDE)

\( k_g \) - GAS-LIQUID (GAS-SIDE)

\( k_s \) - LIQUID-SOLID

CAN BE EVALUATED FROM THEORY IN WELL DEFINED GEOMETRIES WITH KNOWN FLOW FIELDS.

- FILM THEORY
- PENETRATION THEORY
- SURFACE RENEWAL THEORY
- BOUNDARY LAYER THEORY
- LAMINAR FLOW THEORY (GRAETZ PROBLEM)

THE TASK IS TO FORMULATE THE DIFFUSION - CONVECTION PROBLEM AND EVALUATE THE FLUX AT THE INTERFACE. THEN:

\[- D_L \left( \frac{dA}{dn} \right) \bigg|_{\text{INTERFACE}} = k_L \frac{(A^* - A_L)}{A_L} \]

- REPRESENTS TIME AVERAGING
- DEPENDENCE OF \( k_L \) ON \( D_L \) AND \( u_L \) VARIES FROM MODEL TO MODEL
- CORRECTION NEEDED FOR HIGH FLUXES
ACCURATE PREDICTION OF TRANSPORT COEFFICIENTS BASED ON THEORY IS MOST FREQUENTLY NOT POSSIBLE.

- WHEN GEOMETRY AND FLOW FIELD IS KNOWN
  - FILM FLOW OVER FLAT SURFACE
  - FLOW IN SLITS
  ETC.

OFTEN THEORETICAL ASSUMPTIONS ARE NOT SATISFIED e.g., NON-FLAT SURFACE DUE TO RIPPLING, HIGHLY NON-EXOTHERMIC EFFECTS, TURBULENCE, LARGE FLUXES, ETC.

- WHEN GEOMETRY AND FLOW FIELD ARE NOT KNOWN A PURELY THEORETICAL APPROACH IS NOT POSSIBLE. DIMENSIONAL ANALYSIS YIELDS GROUPS TO USE IN CORRELATIONS, e.g.,

    Re, Sc, etc.

THESE CORRELATIONS ARE REACTOR TYPE AND OFTEN PROCESS DEPENDENT. THEY ARE LIMITED TO SMALL FLUXES.
### Theories for mass transfer coefficients

<table>
<thead>
<tr>
<th>Method</th>
<th>Basic form</th>
<th>$f(\text{flow})$</th>
<th>$f(D)$</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Film theory</td>
<td>$k = \frac{D}{l}$</td>
<td>—</td>
<td>1.0</td>
<td>Simple; often good base for ideas</td>
<td>Film thickness $l$ is unknown</td>
</tr>
<tr>
<td>Penetration theory</td>
<td>$k = 2\sqrt{Dv^0/\pi L}$</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{4}$</td>
<td>Simplest including flow</td>
<td>Contact time $(L/v^0)$ often unknown</td>
</tr>
<tr>
<td>Surface-renewal theory</td>
<td>$k = \sqrt{D/\tau}$</td>
<td>—</td>
<td>$\frac{1}{2}$</td>
<td>Similar math to penetration theory, but better physical picture</td>
<td>Surface-renewal rate $(\tau)$ is unknown</td>
</tr>
<tr>
<td>Boundary layer theory</td>
<td>$k = 0.626 \frac{D}{L} \left( \frac{Lv^0}{v} \right)^{1/2} \left( \frac{v}{D} \right)^{1/3}$</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{3}$</td>
<td>Much better physical picture</td>
<td>Laminar flow past flat plate of length $L$ only; math hard.</td>
</tr>
<tr>
<td>Graetz-Nusselt theory</td>
<td>$k = \left( \frac{2}{3\Gamma(\frac{4}{3})} \right) \frac{D}{L} \left( \frac{L^2v^0}{DR} \right)^{1/3}$</td>
<td>$\frac{1}{3}$</td>
<td>$\frac{1}{3}$</td>
<td>Exact result for short tubes</td>
<td>Valid only in laminar flow</td>
</tr>
</tbody>
</table>
Table 9.3-2. A selection of mass transfer correlations\textsuperscript{a} \hspace{1cm} (FROM COSSLER (1984))

<table>
<thead>
<tr>
<th>Physical situation</th>
<th>Basic equation\textsuperscript{b}</th>
<th>Key variables</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid interfaces</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Membrane</td>
<td>$\frac{kD}{D} = 1$</td>
<td>$l =$ membrane thickness</td>
<td>Often applied even where membrane is hypothetical</td>
</tr>
<tr>
<td>Laminar flow along flat plate</td>
<td>$\frac{kD}{D} = 0.323 \left( \frac{u_D^0}{\nu} \right)^{1/2} \left( \frac{\nu}{D} \right)^{1/3}$</td>
<td>$z =$ distance from start of plate</td>
<td>Solid theoretical foundation, which is unusual</td>
</tr>
<tr>
<td>Turbulent flow through horizontal slit</td>
<td>$\frac{kD}{D} = 0.026 \left( \frac{d u_D^0}{\nu} \right)^{0.8} \left( \frac{\nu}{D} \right)^{1/3}$</td>
<td>$u_D^0 =$ average velocity in slit $d =$ (2/$\pi$) (slit width)</td>
<td>Mass transfer here is identical with that in a pipe of equal wetted perimeter</td>
</tr>
<tr>
<td>Turbulent flow through circular pipe</td>
<td>$\frac{kD}{D} = 0.026 \left( \frac{d u_D^0}{\nu} \right)^{0.8} \left( \frac{\nu}{D} \right)^{1/3}$</td>
<td>$u_D^0 =$ average velocity in pipe $d =$ pipe diameter</td>
<td>Same as slit, because only wall region is involved</td>
</tr>
<tr>
<td>Laminar flow through circular pipe\textsuperscript{c}</td>
<td>$\frac{kD}{D} = 1.86 \left( \frac{d u_D^0}{D} \right)^{0.8}$</td>
<td>$d =$ pipe diameter</td>
<td>Not reliable when ($du/D)$ &lt; 10 because of free convection</td>
</tr>
<tr>
<td>Forced convection around a solid sphere</td>
<td>$\frac{kD}{D} = 2.0 + 0.6 \left( \frac{d u_D^0}{\nu} \right)^{1/2} \left( \frac{\nu}{D} \right)^{1/3}$</td>
<td>$d =$ sphere diameter</td>
<td>Very difficult to reach ($kd/\nu$) = 2 experimentally; no sudden laminar–turbulent transition</td>
</tr>
<tr>
<td>Free convection around a solid sphere</td>
<td>$\frac{kD}{D} = 2.0 + 0.6 \left( \frac{d^3 [\Delta \rho] g}{\rho \nu^2} \right)^{1/4} \left( \frac{\nu}{D} \right)^{1/3}$</td>
<td>$d =$ sphere diameter</td>
<td>For a 1-cm sphere in water, free convection is important when $\Delta \rho = 10^{-9}$ $g/cm^3$</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Source: COSSLER (1984)

\textsuperscript{b} $u_D^0$ is the bulk velocity in the flow.

\textsuperscript{c} The flow through a circular pipe is assumed laminar.
<table>
<thead>
<tr>
<th>Category</th>
<th>Equation</th>
<th>Explanation</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spinning disc</td>
<td>( \frac{kd}{D} = 0.62 \left( \frac{d^2 \omega}{\nu} \right)^{1/2} \left( \frac{\nu}{D} \right)^{1/3} )</td>
<td>( d = ) disc diameter, ( \omega = ) disc rotation (radians/time)</td>
<td>Valid for Reynolds numbers between 100 and 20,000</td>
</tr>
<tr>
<td>Flow normal to capillary</td>
<td>( \frac{kd}{D} = f \left( \frac{d^\beta}{\nu}, \frac{\nu}{D} \right) )</td>
<td>( d = ) tube diameter, ( \nu^\beta = ) average velocity</td>
<td>Large number of correlations with different exponents found by analogy with heat transfer</td>
</tr>
<tr>
<td>Packed beds</td>
<td>( \frac{k}{\nu^\beta} = 1.17 \left( \frac{d\nu^\beta}{\nu} \right)^{-0.42} \left( \frac{\nu}{D} \right)^{-0.67} )</td>
<td>( d = ) particle diameter, ( \nu^\beta = ) superficial velocity</td>
<td>The superficial velocity is that which would exist without packing</td>
</tr>
<tr>
<td>Fluid-fluid interfaces</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Drops or bubbles in</td>
<td>( \frac{kL}{D} = 0.13 \left( \frac{L^4(P/V)}{\rho^3} \right)^{1/4} \left( \frac{\nu}{D} \right)^{1/3} )</td>
<td>( L = ) stirrer length, ( P/V = ) power per volume</td>
<td>Correlations versus power per volume are common for dispersions</td>
</tr>
<tr>
<td>stirred solution</td>
<td></td>
<td></td>
<td>&quot;Large&quot; is defined as ( \sim 0.3 \text{-cm diameter} )</td>
</tr>
<tr>
<td>Large drops in unstirred</td>
<td>( \frac{kd}{D} = 0.42 \left( \frac{d^3 \Delta \rho g}{\rho \nu^2} \right)^{1/3} \left( \frac{\nu}{D} \right)^{1/2} )</td>
<td>( d = ) bubble diameter, ( \Delta \rho = ) density difference</td>
<td>These behave like rigid spheres</td>
</tr>
<tr>
<td>solution</td>
<td></td>
<td>between bubble and surrounding fluid</td>
<td></td>
</tr>
<tr>
<td>Small drops of pure</td>
<td>( \frac{kd}{D} = 1.13 \left( \frac{d\nu^\beta}{\nu} \right)^{0.8} )</td>
<td>( d = ) bubble diameter, ( \nu^\beta = ) bubble velocity</td>
<td></td>
</tr>
<tr>
<td>solute in unstirred</td>
<td></td>
<td></td>
<td>These behave like rigid spheres</td>
</tr>
<tr>
<td>solution</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Falling films</td>
<td>( \frac{kz}{D} = 0.69 \left( \frac{z\nu^\beta}{D} \right)^{1/2} )</td>
<td>( z = ) position along film, ( \nu^\beta = ) average film velocity</td>
<td>Frequently embroidered and embellished</td>
</tr>
</tbody>
</table>

- The symbols used include the following: \( \rho \) is the fluid density; \( \nu \) is the kinematic viscosity; \( D \) is the diffusion coefficient of the material being transferred; \( k \) is the local mass transfer coefficient. Other symbols are defined for the specific situation.
- The dimensionless groups are defined as follows: \( (d\nu) \) and \( (d^2 \omega \nu) \) are the Reynolds number; \( \nu/D \) is the Schmidt number; \( (d^3 \Delta \rho g/\rho \nu^2) \) is the Grashof number; \( kd/D \) is the Sherwood number; \( k/\nu \) is the Stanton number.
- The mass transfer coefficient given here is the value averaged over the length.

Source: Data from Calderbank (1967), McCabe and Smith (1975), Schlichting (1979), Sherwood et al. (1975), and Treybal (1980).
GAS - LIQUID - SOLID SYSTEMS

- TRANSPORT PARAMETERS (E.G. MASS TRANSFER COEFFICIENTS) DIFFICULT TO ESTIMATE WITH ACCURACY FOR VARIOUS REACTOR TYPES AND CONFIGURATIONS, OPERATING CONDITIONS AND CHEMICAL SYSTEMS OF INTEREST.

- CORRELATIONS FOR TRANSPORT COEFFICIENTS ARE REACTOR TYPE (AND OFTEN SIZE) AND FLOW REGIME DEPENDENT.

- AN ALTERNATIVE TO ESTIMATING TRANSPORT PARAMETERS IN LARGE REACTORS IS SCALE-UP
  - SELECT REACTOR TYPE AND CONTACTING PATTERN
  - ON SMALL SCALE REACTOR DETERMINE RATES AND MAGNITUDE OF TRANSPORT EFFECTS
  - ON SMALL SCALE REACTOR STUDY EFFECT OF FLOW CONDITIONS CHARACTERISTIC OF LARGE UNITS ON TRANSPORT EFFECTS
  - BUILD TO SCALE COLD MODEL OF LARGE UNIT AND ASSESS CRITICAL PARAMETERS
  - SCALE UP BASED ON SAME LHSV, USE SAME CATALYST SIZE AS IN SMALL REACTORS