

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) Intrapphase 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 laboratory 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

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

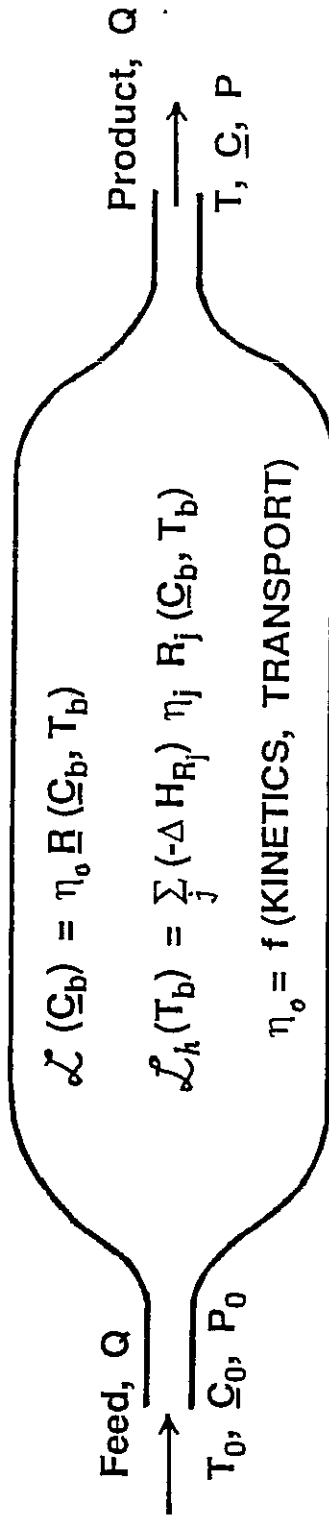
$$\left( \begin{array}{l} \text{PRODUCTION} \\ \text{RATE} \end{array} \right) = \left( \begin{array}{l} \text{VOLUME AVERAGED} \\ \text{APPARENT} \\ \text{REACTION RATE} \end{array} \right) \times \left( \begin{array}{l} \text{REACTOR} \\ \text{VOLUME} \end{array} \right)$$

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 — FLOW RATES — KINETICS — MACRO
- SELECTIVITY — INLET CONC. & TEMP. — TRANSPORT — MICRO
- PRODUCTION RATE — HEAT REMOVAL



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

## THREE PHASE CATALYTIC REACTIONS



MOST FREQUENT KINETIC FORMS

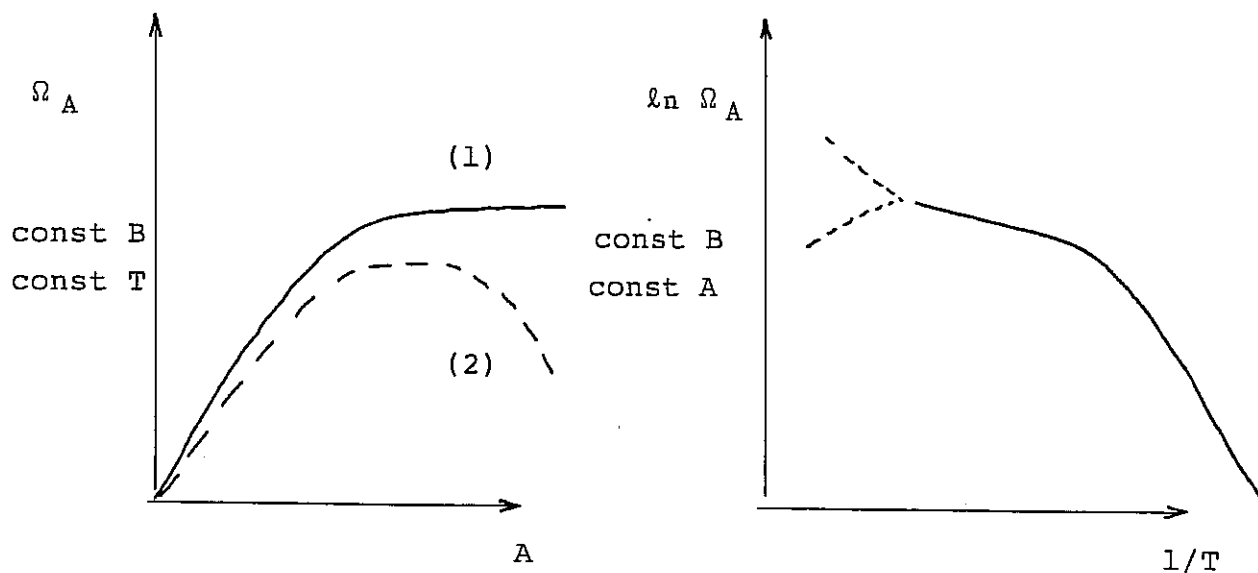
SINGLE SITE LH FORM

$$(1) \quad \Omega_A = \frac{k_A B}{1 + K_A A + K_B B + K_E E} \quad \text{ORDER 1 - 2}$$

$$(2) \quad \Omega_A = \frac{k_A B}{(1 + K_A A + K_B B + K_E E)^2} \quad \text{ORDER 0 - 2}$$

DUAL - SITE LH FORM

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



# RATE FORMS FOR CATALYTIC REACTIONS BASED ON THE RLS ASSUMPTION.

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

Chemical equation	Catalytic steps	Rate equation*
$A = R$	$A + s = A_s$	$r = \frac{k(C_A - C_R/K)}{1 + K_R C_R}$
	$A_s = R_s$	$r = \frac{k(C_A - C_R/K)}{1 + K_A C_A + K_R C_R}$
	$R_s = R + s$	$r = \frac{k(C_A - C_R/K)}{1 + K_A C_A}$
$A = R$	$2A + s = A_{2s}$	$r = \frac{k(C_A^2 - C_R^2/K^2)}{1 + K_R C_R + K_A^2 C_A^2}$
	$A_{2s} + s = 2A_s$	$r = \frac{k(C_A^2 - C_R^2/K^2)}{(1 + K_R C_R + K_A C_A^2)^2}$
	$A_s = R_s$	$r = \frac{k(C_A - C_R/K)}{1 + K_A C_A^2 + K_A' C_A + K_R C_R}$
	$R_s = R + s$	$r = \frac{k(C_A - C_R/K)}{1 + K_A C_A^2 + K_A' C_A}$
		$r = \frac{k(C_A - C_R/K)}{(1 + \sqrt{K_R C_R} + K_R' C_R)^2}$
$A = R$	$A + 2s = 2A_{1/2s}$	$r = \frac{k(C_A - C_R/K)}{(1 + \sqrt{K_A C_A} + K_R C_R)^2}$
	$2A_{1/2s} = R_s + s$	$r = \frac{k(C_A - C_R/K)}{(1 + \sqrt{K_A C_A} + K_R C_R)^2}$
	$R_s = R + S$	$r = \frac{k(C_A - C_R/K)}{1 + \sqrt{K_A C_A} + K_A' C_A}$
$A = R + S$	$A + s = A_s$	$r = \frac{k(C_A - C_R C_S/K)}{1 + K_{RS} C_R C_S + K_R C_R + K_S C_S}$
	$A_s + s = R_s + S_s$	$r = \frac{k(C_A - C_R C_S/K)}{(1 + K_A C_A + K_R C_R + K_S C_S)^2}$
	$R_s = R + s$	$r = \frac{k(C_A - C_R C_S/K)}{C_S(1 + K_A C_A + (K_{RS} C_R / C_S) + K_R C_R)}$
	$S_s = S + s$	$r = \frac{k(C_A - C_R C_S/K)}{1 + K_R C_R + K_{RS} C_R C_S}$
$A = R + S$	$A + s = A_s$	$r = \frac{k(C_A - C_R C_S/K)}{1 + K_A C_A + K_R C_R}$
	$A_s = R_s + S$	$r = \frac{k(C_A - C_R C_S/K)}{C_S(1 + K_A C_A + K_{RS} C_R / C_S)}$
	$R_s = R + s$	$r = \frac{k(C_A - C_R C_S/K)}{1 + (K_{RS} C_R / C_S) + K_R C_R + K_S C_S}$
		$r = \frac{k(C_A C_S - C_R / K)}{(1 + K_A C_A + K_R C_R + K_S C_S)^2}$
$A + B = R$	$A + s = A_s$	$r = \frac{k(C_A - C_R / K C_B)}{1 + (K_{RB} C_R / C_B) + K_R C_R + K_S C_S}$
	$B + s = B_s$	$r = \frac{k(C_B - C_R / K C_A)}{1 + K_A C_A + (K_{RB} C_R / C_A) + K_R C_R}$
	$A_s + B_s = R_s + s$	$r = \frac{k(C_A C_B - C_R / K)}{(1 + K_A C_A + K_R C_R + K_S C_S)^2}$
	$R_s = R + s$	$r = \frac{k(C_A C_B - C_R / K)}{1 + K_A C_A + K_R C_R + K_{AB} C_A C_B / C_S}$
$A + B = R + S$	$A + s = A_s$	$r = \frac{k(C_A - C_R C_S / K C_B)}{1 + (K_{RS} C_R C_S / C_B)^2 + K_R C_R + K_S C_S + K_B C_B}$
	$B + s = B_s$	$r = \frac{k(C_B - C_R C_S / K C_A)}{1 + (K_{RS} C_R C_S / C_A) + K_A C_A + K_R C_R + K_S C_S}$
	$A_s + B_s = R_s + S_s$	$r = \frac{k(C_A C_B - C_R C_S / K)}{(1 + K_A C_A + K_R C_R + K_S C_S)^2}$
	$R_s = R + s$	$r = \frac{k(C_A C_B / C_S) - C_R / K}{1 + K_A C_A + K_R C_R + K_S C_S + K_{AB} C_A C_B / C_S}$
	$S_s = S + s$	$r = \frac{k(C_A - C_R C_S / K C_B)}{[1 + (K_{RS} C_R C_S / C_B)^2 + K_R C_R + K_S C_S]^2}$
		$r = \frac{k(C_A C_B - C_R C_S / K)}{1 + \sqrt{K_A C_A} + (K_{RS} C_R C_S / C_A) + K_R C_R + K_S C_S}$
$A + B = R + S$	$A + 2s = 2A_{1/2s}$	$r = \frac{k(C_A C_B - C_R / K)}{(1 + \sqrt{K_A C_A} + K_R C_R + K_S C_S)^2}$
	$2A_{1/2s} + B_s = R_s + S_s + s$	$r = \frac{k(C_A C_B / C_S) - C_R / K}{1 + \sqrt{K_A C_A} + K_R C_R + K_S C_S}$
	$R_s = R + s$	$r = \frac{k(C_A C_B / C_S) + K_R C_R + K_S C_S}{1 + K_A \sqrt{C_A} + K_R C_R + (K_{AB} C_A C_B / C_S) + K_S C_S}$
	$S_s = S + s$	$r = \frac{k(C_A C_B / C_S - C_R / K)}{1 + \sqrt{K_A C_A} + K_R C_R + K_S C_S + K_{AB} C_A C_B / C_S}$
		$r = \frac{k(C_B - C_R C_S / K C_A)}{1 + K_R C_R + K_{RS} C_R C_S / C_A}$
		$r = \frac{k(C_A C_B - C_R / K)}{1 + K_R C_R + K_S C_S}$
$A + B = R + S$	$B + s = B_s$	$r = \frac{k(C_B - C_R C_S / K C_A)}{1 + (K_{AB} C_A C_B / C_B) + K_R C_R}$
	$A + B_s = R_s + S$	$r = \frac{k(C_A C_B / C_S) - C_R / K}{1 + K_{AB} C_A C_B / C_S + K_R C_R}$

$K_{AB...}$  = combined equilibrium constants.  
 $K$  = over-all equilibrium constant for the chemical equation.  
 $k$  = constant.  
 $r$  = rate of product formation  
 \*The rate equation is opposite the catalytic step assumed to be rate-controlling.

FROM PERRY (1985)

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GENERAL FORM OF  
LANGMUIR - HINSHELWOOD  
(HOUSEN - 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<sup>a</sup>

Reaction	Driving-Force Groups			
	$A = R$	$A = R + S$	$A + B = R$	$A + B = R + S$
Adsorption of A controlling	$p_A - \frac{p_R}{K}$	$p_A - \frac{p_R p_S}{K}$	$p_A - \frac{p_R}{K p_B}$	$p_A - \frac{p_R p_S}{K p_B}$
Adsorption of B controlling	0	0	$p_B - \frac{p_R}{K p_A}$	$p_B - \frac{p_R p_S}{K p_A}$
Desorption of R controlling	$p_A - \frac{p_R}{K}$	$\frac{p_A}{p_S} - \frac{p_R}{K}$	$p_A p_B - \frac{p_R}{K}$	$\frac{p_A p_B}{p_S} - \frac{p_R}{K}$
Surface reaction controlling	$p_A - \frac{p_R}{K}$	$p_A - \frac{p_R p_S}{K}$	$p_A p_B - \frac{p_R}{K}$	$p_A p_B - \frac{p_R p_S}{K}$
Impact of A controlling (A not adsorbed)	0	0	$p_A p_B - \frac{p_R}{K}$	$p_A p_B - \frac{p_R p_S}{K}$
Homogeneous reaction controlling	$p_A - \frac{p_R}{K}$	$p_A - \frac{p_R p_S}{K}$	$p_A p_B - \frac{p_R}{K}$	$p_A p_B - \frac{p_R p_S}{K}$

*Replacements in the General Adsorption Groups*  
 $(1 + K_A p_A + K_B p_B + K_R p_R + K_S p_S + K_i p_i)^n$

Reaction	$A = R$	$A = R + S$	$A + B = R$	$A + B = R + S$
Where adsorption of A is rate controlling, replace $K_A p_A$ by	$\frac{K_A p_R}{K}$	$\frac{K_A p_R p_S}{K}$	$\frac{K_A p_R}{K p_B}$	$\frac{K_A p_R p_S}{K p_B}$
Where adsorption of B is rate controlling, replace $K_B p_B$ by	0	0	$\frac{K_B p_R}{K p_A}$	$\frac{K_B p_R p_S}{K p_A}$
Where desorption of R is rate controlling, replace $K_R p_R$ by	$K K_R p_A$	$K K_R \frac{p_A}{p_S}$	$K K_R p_A p_B$	$K K_R \frac{p_A p_B}{p_S}$
Where adsorption of A is rate controlling with dissociation of A, replace $K_A p_A$ by	$\sqrt{\frac{K_A p_R}{K}}$	$\sqrt{\frac{K_A p_R p_S}{K}}$	$\sqrt{\frac{K_A p_R}{K p_B}}$	$\sqrt{\frac{K_A p_R p_S}{K p_B}}$
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)	$\sqrt{K_A p_A}$	$\sqrt{K_A p_A}$	$\sqrt{K_A p_A}$	$\sqrt{K_A p_A}$
Where A is not adsorbed, replace $K_A p_A$ by (and similarly for other components that are not adsorbed)	0	0	0	0

FROHNT & BISCIOFF (1991)

Table 2.3.1-1 (continued)

<i>Kinetic Groups</i>				
Adsorption of A controlling				$k_A$
Adsorption of B controlling				$k_B$
Desorption of R controlling				$k_r K$
Adsorption of A controlling with dissociation				$k_A$
Impact of A controlling				$k_A K_B$
Homogeneous reaction controlling				$k$

	<i>Surface Reaction Controlling</i>			
	$A = R$	$A = R + S$	$A + B = R$	$A + B = R + S$
Without dissociation	$k_s K_A$	$k_{sr} K_A$	$k_s K_A K_B$	$k_s K_A K_B$
With dissociation of A	$k_s K_A$	$k_{sr} K_A$	$k_{sr} K_A K_B$	$k_{sr} K_A K_B$
B not adsorbed	$k_s K_A$	$k_{sr} K_A$	$k_{sr} K_A$	$k_{sr} K_A$
B not adsorbed, A dissociated	$k_{sr} K_A$	$k_{sr} K_A$	$k_{sr} K_A$	$k_{sr} K_A$

<i>Exponents of Adsorption Groups</i>	
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 $A + B = R$	$n = 1$
Impact of A without dissociation $A + B = R + S$	$n = 2$
Homogeneous reaction	$n = 0$

	<i>Surface Reaction Controlling</i>			
	$A = R$	$A = R + S$	$A + B = R$	$A + B = R + S$
No dissociation of A	1	2	2	2
Dissociation of A	2	2	3	3
Dissociation of A (B not adsorbed)	2	2	2	2
No dissociation of A (B not adsorbed)	1	2	1	2

\*From Yang and Hougen (1950).

FROMENT & BISCHOFF (1991)

### THREE PHASE CATALYTIC REACTIONS

EXTENSIVE EXPERIMENTATION REQUIRED TO DETERMINE EXACT 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:

$$\Omega_A = k_0 e^{-E/RT} A^2 B^r$$

OR BY A SIMPLER LH FORM:

$$\Omega_A = \frac{k_0 e^{-E/RT} A}{1 + K_{A0} e^{-E_A/RT} A}$$

ETC.

TABLE 2.1  
Kinetic models used to represent three-phase catalytic reactions.

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

FROM RAMACHANDRAN AND CHAUDHARI (1983)

KEY IDEA

(OBSERVED LOCAL APPARENT RATE) = (OVERALL EFFECTIVENESS FACTOR) (KINETIC RATE)

$$R_A = \eta_O \Omega_A (1 - \epsilon_B) = \eta_O \Omega_A'$$

$$\eta_O = \eta_O \left( \frac{\tau_D}{\tau_R} \right)$$

$$\frac{\tau_D}{\tau_R} = \frac{\text{TRANSPORT RESISTANCE}}{\text{KINETIC RESISTANCE}}$$

$$\Omega_A \left( \frac{\text{mol A}}{\text{m}^3 \text{ cat. s}} \right)$$

$$; \quad \Omega_A' \left( \frac{\text{mol A}}{\text{m}^3 \text{ reactor s}} \right)$$

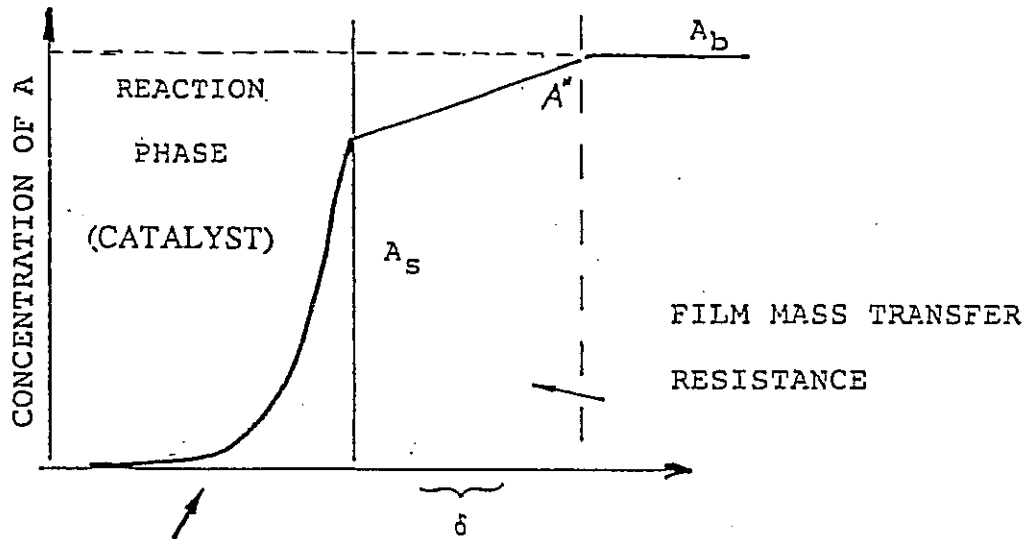
- EVALUATED AT "BULK" C, T CONDITIONS AT THE "POINT"

$$R_A \left( \frac{\text{mol A}}{\text{m}^3 \text{ reactor s}} \right)$$

$$; \quad \epsilon_B \left( \frac{\text{m}^3 \text{ Fluid}}{\text{m}^3 \text{ reactor}} \right)$$

## KEY IDEA - EFFECTIVENESS FACTOR

REACTION : A  $\longrightarrow$  PRODUCTS



INTERNAL DIFFUSION AND REACTION  $\longrightarrow$  PARTICLE EFFECTIVENESS FACTOR,  $\eta_p$

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

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

COMBINED DIFFUSION & REACTION AND EXTERNAL TRANSPORT  $\longrightarrow$  OVERALL EFFECTIVENESS FACTOR,  $\eta_o$

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

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

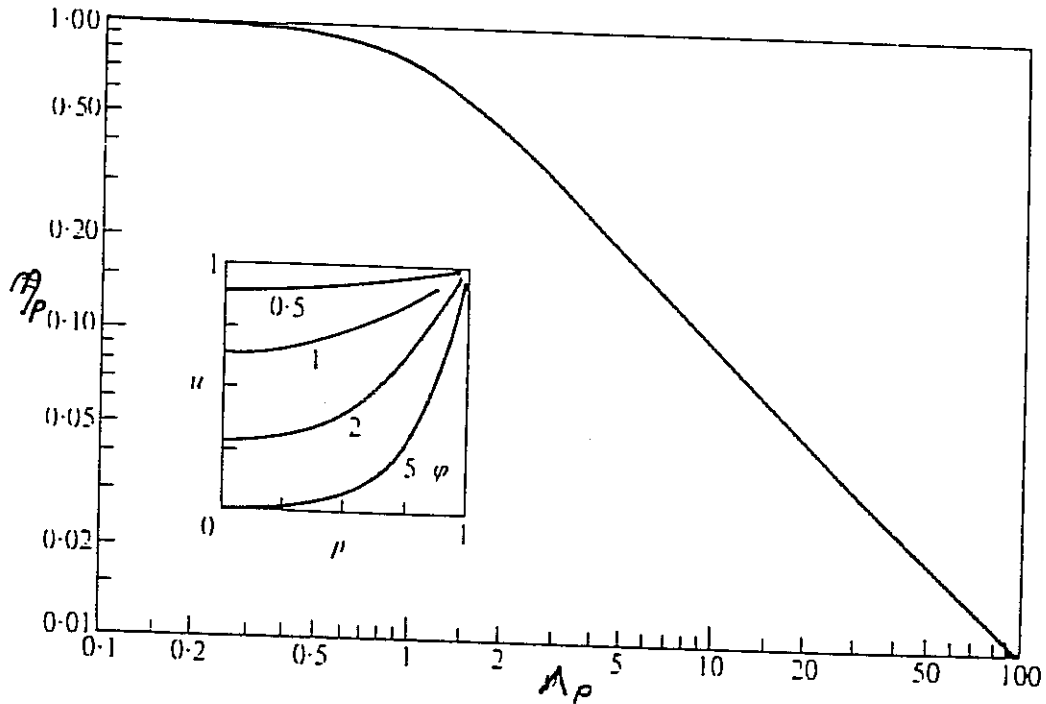
$$\text{KINETIC RATE (mol / m}^3 \text{ cat. s)} = k_v A^n = \mathcal{R}_A$$

# GAS-SOLID SINGLE REACTION

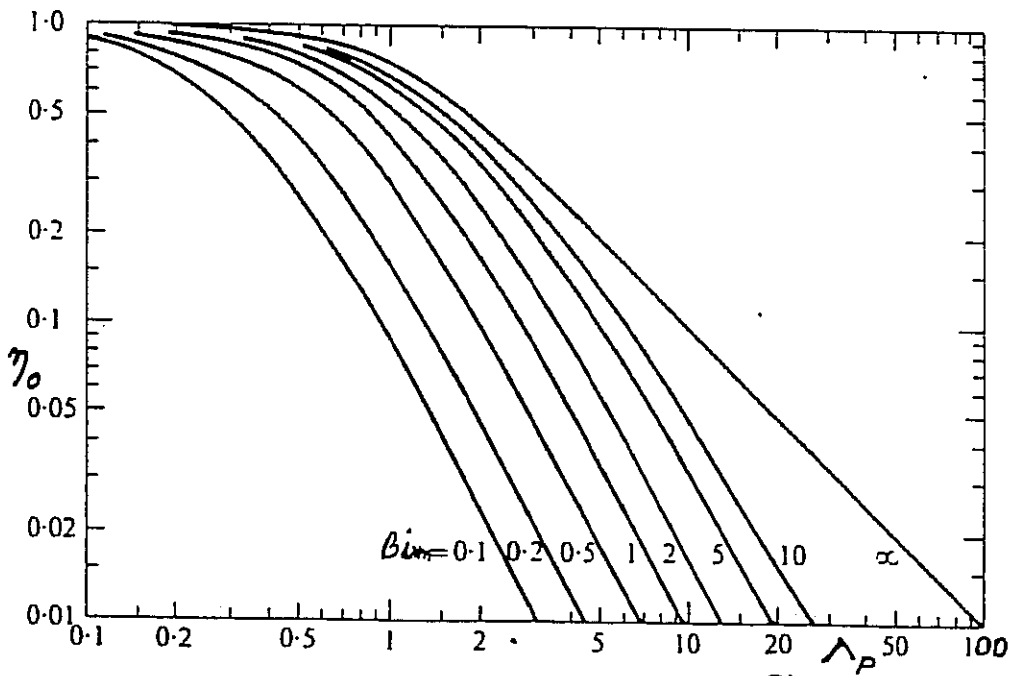
ISOTHERMAL PARTICLE WITH  
NO EXTERNAL TEMPERATURE GRADIENT

$$\eta_p = \frac{\tanh \Lambda_p}{\Lambda_p}$$

$$\Lambda_p = \frac{V_p}{S_p} \sqrt{\frac{k}{D_e}}$$



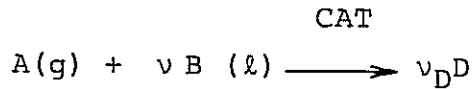
$$\frac{1}{\eta_0} = \frac{1}{\eta_p} + \frac{\Lambda_p^2}{Bi_m}$$



$$Bi_m = \frac{k_m V_p / S_p}{D_e}$$



## A. GAS-LIQUID-SOLID CATALYTIC SYSTEMS



### REACTION CAN BE:

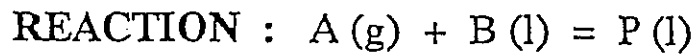
- |                                 |                   |
|---------------------------------|-------------------|
| I. GAS REACTANT LIMITED         | $A_l < < B_l$     |
| II. LIQUID REACTANT LIMITED     | $A_l > > B_l$     |
| III. AFFECTED BY BOTH REACTANTS | $A_l \approx B_l$ |

### 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



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

**KINETIC RATE** :  $k_v A$  (mol/m<sup>3</sup> cat. s)  
( PER UNIT CATALYST VOLUME )

**RATE IN CATALYST** :  $k_v \eta_p (1 - \epsilon_B) A_s$  (mol/m<sup>3</sup> react. s)  
( PER UNIT REACTOR VOLUME )

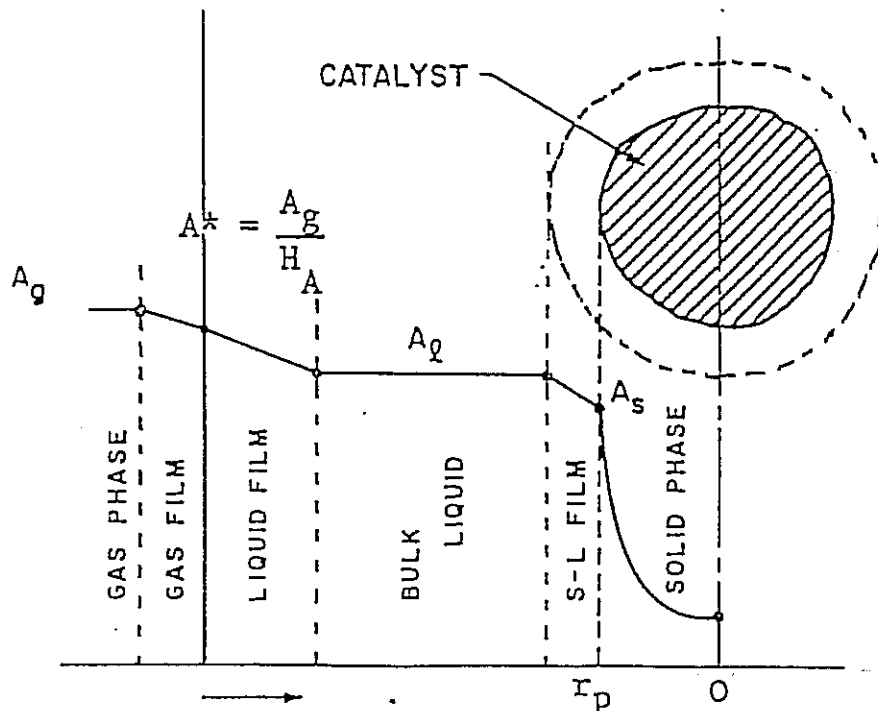
**TRANSPORT RATE** (mol/m<sup>3</sup> react. s) ;  
( PER UNIT REACTOR VOLUME )

- GAS - LIQUID :  $K_l a_B \left( \frac{A_g}{H_A} - A_l \right)$

- LIQUID - SOLID :  $k_s a_p (A_l - A_s)$

**OVERALL ( APPARENT ) RATE** (mol/m<sup>3</sup> react. s) :

$$\eta_o k_v (1 - \epsilon_B) \frac{A_g}{H_A} = \frac{\frac{A_g}{H_A}}{\frac{1}{K_l a_B} + \frac{1}{k_s a_p} + \frac{1}{(1 - \epsilon_B) k_v \eta_p}}$$



GAS-LIMITED FIRST ORDER REACTION  
COMPLETELY WETTED CATALYST

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

$$R_A = \frac{P_{Ag}/H_A}{\frac{1}{K_L a_B} + \frac{1}{k_s a_p} + \frac{1}{(w/\rho_p) k \eta_p}} = (1-\epsilon_B) \eta_o k \overbrace{P_{Ag}/H_A}^{A^*} \quad (1)$$

RESISTANCE = GAS-LIQUID + LIQUID-SOLID + PARTICLE

- $P_{Ag}$  (atm) = PARTIAL PRESSURE OF A IN THE GAS
- $H_A$  (atm cm<sup>3</sup>/mol) = HENRY'S CONSTANT
- $K_L a_B$  (s<sup>-1</sup>) = OVERALL VOLUMETRIC GAS-LIQUID MASS TRANSFER COEFFICIENT FOR A
- $k_s$  (cm/s) = LIQUID-SOLID MASS TRANSFER COEFFICIENT
- $a_p$  (cm<sup>2</sup>/cm<sup>3</sup>) = EXTERNAL SURFACE AREA OF CATALYST PARTICLES PER UNIT VOLUME OF REACTOR
- $a_B$  (cm<sup>2</sup>/cm<sup>3</sup>) = GAS-LIQUID INTERFACIAL AREA PER UNIT VOLUME OF REACTOR
- $w$  (g/cm<sup>3</sup>) = CATALYST MASS PER UNIT REACTOR VOLUME
- $\rho_p$  (g/cm<sup>3</sup>) = ACTUAL DENSITY OF CATALYST PARTICLES
- $\eta_p$  [-] = PARTICLE (INTERNAL) EFFECTIVENESS FACTOR
- $k$  (s<sup>-1</sup>) = FIRST ORDER RATE CONSTANT

USEFUL RELATIONS

$$(2) \quad \Lambda_p^2 = \left( \frac{V_p}{S_p} \right)^2 \frac{k}{D_{Ae}} = \frac{\tau_{Dp}}{\tau_k} \quad \text{PARTICLE MODULUS}$$

$$(3) \quad \eta_p = \frac{\tanh \Lambda_p}{\Lambda_p} \quad \text{PARTICLE EFFECTIVENESS FACTOR}$$

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

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

$$D_{Ae} = D_A \frac{\epsilon_p}{\tau} \quad \text{EFFECTIVE DIFFUSIVITY}$$

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

$$\epsilon_p [-] = \text{PARTICLE POROSITY}$$

$$\tau [-] = \text{PARTICLE TORTUOSITY}$$

$$a_p = \frac{S_p w}{V_p \rho_p} = \frac{S_R}{V_p} (1 - \epsilon_B)$$

$$(1 - \epsilon_B) = \text{VOLUME FRACTION OF CATALYST IN THE REACTOR} = \frac{w}{\rho_p}$$

$$M_A = \left( \frac{1}{K_L a_B} + \frac{1}{k_s a_p} \right)^{-1} = \text{OVERALL TRANSPORT COEFFICIENT}$$

$$\frac{1}{K_L a_B} = \underbrace{\frac{1}{k_L a_B}}_{\text{LIQUID-SIDE}} + \underbrace{\frac{1}{k_g H_A}}_{\text{GAS-SIDE}}$$

GAS-LIMITED FIRST ORDER REACTION

$$R_A = \frac{A^*}{\frac{1}{M_A} + \frac{1}{(w/\rho_p)k\eta_p}} = (1-\epsilon_b)\eta_o k A^* \quad (1)$$

ASSUMPTIONS:

1. COMPLETELY WETTED CATALYST
2. FILM THEORY FOR MASS TRANSFER
3. STEADY STATE
4. NO OVERLAP OF LIQUID FILM AND CATALYST PARTICLES
5. ISOTHERMAL

$$\frac{A_S}{A^*} = \frac{1}{1 + \frac{w k \eta_p}{\rho_p M_A}} \longrightarrow 0$$

$$\frac{A^* - A_S}{A^*} = \frac{R_A}{M_A A^*} \longrightarrow 1$$

} EXTERNAL MASS  
TRANSFER CONTROLS  
THE RATE

$$A^* = P_{A_2} / H_A$$

$$R_A = \frac{A^*}{\frac{1}{M_A} + \frac{\rho_p}{w k \eta_p}}$$

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

$$\frac{A_l}{A^*} = \frac{1}{1 + \frac{1}{K_L a_B} \left[ \frac{\rho_p}{w k \eta_p} + \frac{1}{k_s a_p} \right]} \rightarrow 0$$

$$\frac{A^* - A_l}{A^*} = \frac{R_A}{K_L a_B A^*} \rightarrow 1$$

$$d_p \ll \frac{\mathcal{D}_A}{k_L} ; \quad \frac{V_L}{V_{EF}} = \frac{H_L K_L}{a_B \mathcal{D}_A} \ll 1$$

$$A_l H_L < \frac{1}{2} (A^* + A_l) \frac{a_B \mathcal{D}_A}{K_L}$$

$H_L$  = TOTAL LIQUID HOLDUP

THE FOLLOWING CONCLUSIONS CAN BE DRAWN:

KINETIC RESISTANCE DOMINATES

$$\begin{aligned} \text{RATE} & \propto (\text{CATALYST VOLUME FRACTION})^1 \\ & (\text{CATALYST ACTIVITY})^1 \\ & (\text{CATALYST PARTICLE LOADING})^1 \\ & (\text{REACTANT CONCENTRATION})^n \\ E & = E_{\text{KINETIC}} ; n = n_{\text{KINETIC}} \end{aligned}$$

KINETICS + STRONG PORE DIFFUSION RESISTANCE DOMINATES

$$\begin{aligned} \text{RATE} & \propto (\text{CATALYST VOLUME FRACTION})^1 \\ & (\text{CATALYST ACTIVITY})^{1/2} \\ & (\text{CATALYST PARTICLE LOADING})^{1/2} \\ & (\text{REACTANT CONCENTRATION})^{(n+1)/2} \\ & (\text{PARTICLE DIAMETER})^{-1} \\ E & = E_{\text{KIN}/2} ; n = (n_{\text{KIN}} + 1)/2 \end{aligned}$$

EXTERNAL MASS TRANSFER RESISTANCE DOMINATES

$$\begin{aligned} \text{RATE} & \propto (\text{CATALYST VOLUME FRACTION})^{0 \text{ to } 1} \\ & (\text{PARTICLE DIAMETER})^{-2 \text{ to } 0} \\ & (\text{REACTANT CONCENTRATION})^1 \\ E_{\text{app}} & = 1 \text{ to } 4 \text{ kcal} ; n_{\text{app}} = 1 \\ & \text{HYDRODYNAMIC REGIME, GAS AND LIQUID} \\ & \text{VELOCITIES AFFECT THE RATE} \end{aligned}$$

REACTOR VOLUMETRIC PRODUCTIVITY  $\propto$  RATE

## 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  $D_{Be}$  AND ALL  
PROPERTIES OF A WITH THAT FOR B.

BOTH REACTANTS LIMIT THE RATE ( $A^* \approx 0$  ( $B_l$ ))

SAME PROCEDURE BUT MODIFIED. ADD EQUATIONS

$$\frac{A^* - A_s}{B_l - B_s} = \frac{M_B}{\nu M_A}$$

$$p = \frac{\nu D_{Ae} A_s}{D_{Be} B_s}$$

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

BASE EVALUATION OF ALL MODULI ON A:

$$B = B_s - \frac{\nu D_{Ae} (A_s - A)}{D_{Be}}$$

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") PELLETT

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

$$\beta = \frac{(-\Delta H_{RA}) D_{Ae} A_{gs}}{\lambda_e T_s} \quad ; \quad \gamma = \frac{E}{RT_s}$$

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.

FRON SATTEN FIELD <sup>(1974)</sup> TEMPERATURE GRADIENTS

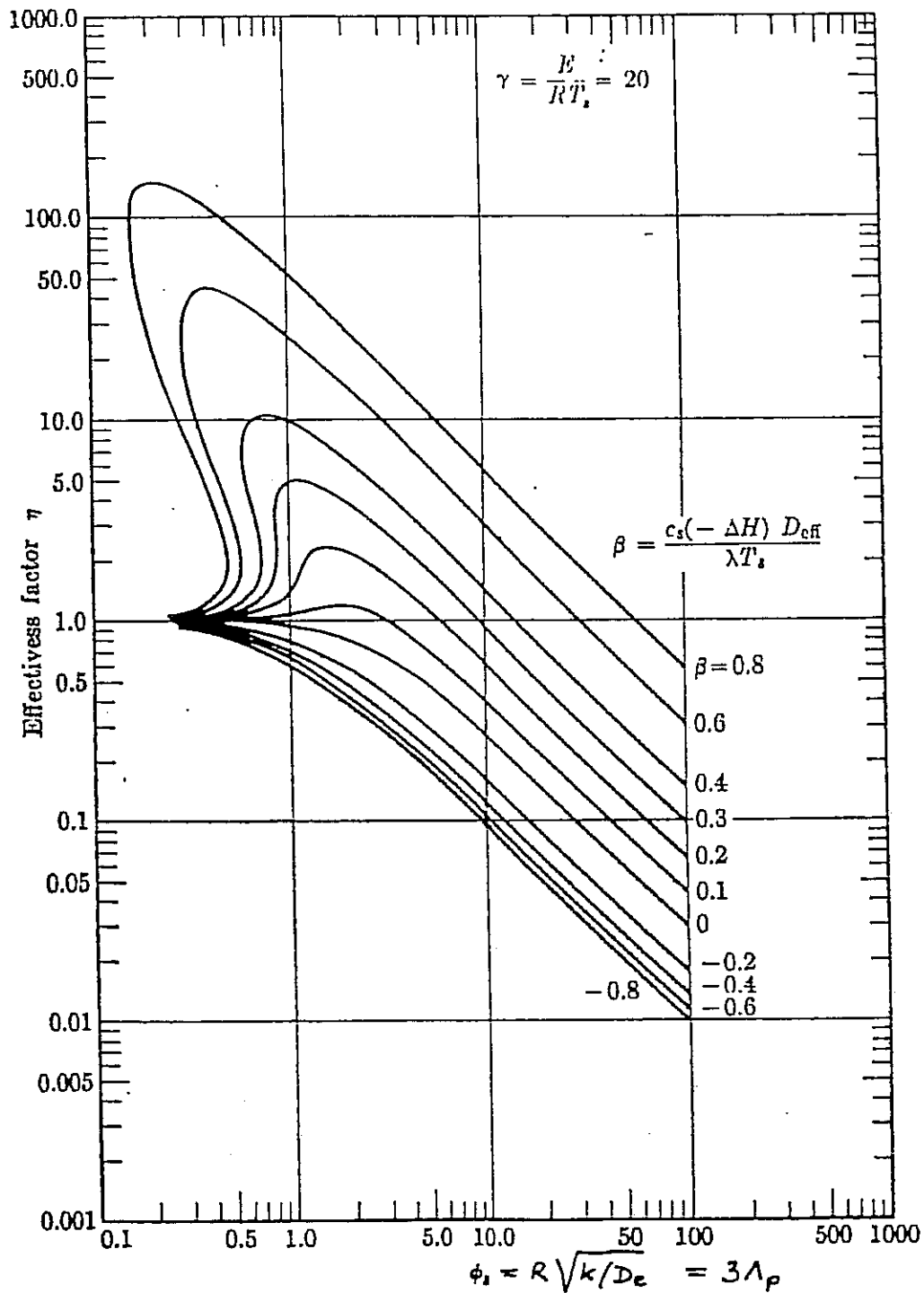


Figure 4.1. Effectiveness factor  $\eta$  as a function of  $\phi_s = R\sqrt{k/D_{eff}}$  for  $\gamma = 20$ . First-order reaction in sphere. Weisz and Hicks [376].

WHETHER A TYPICAL PORE OF RADIUS  $R_{\text{pore}}$  IN A CATALYST PARTICLE WILL REMAIN LIQUID FILLED OR WILL BE VAPOR FILLED CAN BE APPROXIMATELY ESTIMATED AS FOLLOWS:

$$R_{\text{pore}}^* = \frac{2 \bar{V} \sigma_L}{\Delta H_V} \frac{(1 - \epsilon_B) h_p S_p T_L}{(-\Delta H_{rB}) R_B V_p}$$

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

$\bar{V}$  = MOLAR VOLUME OF VOLATILE SPECIES:  $\Delta H_V$  - HEAT OF VAPORIZATION :  $G_L$  - SURFACE TENSION

$\epsilon_B$  = 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

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

*RATE ON DRY PELLETS  $\gg$  RATE ON WETTED PELLETS*

EXAMPLE 1

REACTION:  $H_2(g) + C_3H_5CHO(l) = C_3H_5CHOH$

CATALYST: 0.5% Pd ON ALUMINA

REACTOR: AGITATED SLURRY AND TBR

DATA:

$$T = 51^\circ C \quad ; \quad P = 1 \text{ ATM}$$

$$A^* = 2.8 \times 10^{-6} \text{ (mol/cm}^3\text{)}$$

$$k = 3.69 \times 10^2 \text{ cm}^3/\text{s g Pd}$$

$$k_w = 3.69 \times 10^2 \times 0.5 \times 10^{-2} = 1.84 \text{ (cm}^3/\text{g s)}$$

IN TBR

$$d_p = 0.5 \text{ cm} \quad ; \quad \rho_p = 1.5 \text{ g/cm}^3$$

$$k_L a_B = 0.02 \text{ (s}^{-1}\text{)}$$

$$k_s = 0.02 \text{ (cm/s)}$$

$$D_{Ae} = 2 \times 10^{-5} \text{ (cm}^2/\text{s)}$$

$$1 - \epsilon_B = 0.6$$

IN SLURRY

$$M_A = 0.0174 \text{ (s}^{-1}\text{)}$$

$$w = 2.5 \times 10^{-2} \text{ (g/cm}^3\text{)}$$

$$\eta_p = 1$$

FIRST ORDER REACTION IN HYDROGEN

OBJECTIVE

- COMPARE RATES IN MECHANICALLY AGITATED SLURRY AND TBR
- DETERMINE MAGNITUDE OF TRANSPORT EFFECTS
- DETERMINE DOMINANT RESISTANCE

TBR

$$\Lambda_p = \frac{d_p}{6} \sqrt{\frac{\rho_p k_w}{D_{Ae}}} = 31 \quad ; \quad a_p = \frac{6(1-\epsilon_B)}{d_p} = 7.2 \text{ cm}^{-1}$$

$$\eta_p = \frac{\tanh \Lambda_p}{\Lambda_p} = \frac{1}{31} = 0.0322$$

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

$$R_A = \frac{A^*}{\frac{1}{M_A} + \frac{1}{w k_w \eta_p}} = \frac{2.8 \times 10^{-6}}{56.9 + 18.7} \quad ; \quad w = \rho_p (1-\epsilon_B) = 0.9 \text{ g/cm}^3$$

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

$$\Omega'_A = w k_w A^* = 4.64 \times 10^{-6} \text{ (mol/cm}^3 \text{ s)}$$

$$\eta_o = \frac{R_A}{\Omega'_A} = 0.00797$$

WE ARE REALIZING 0.8% 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

$$M_A = 0.0174 \text{ (s}^{-1}\text{)}$$

$$w k_w \eta_p = 2.5 \times 10^{-2} \times 1.84 \times 1 = 0.046 \text{ (s}^{-1}\text{)}$$

$$R_A = \frac{A^*}{\frac{1}{M_A} + \frac{1}{w k_w \eta_p}} = \frac{2.8 \times 10^{-6}}{57.5 + 21.7}$$

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

$$\Omega'_A = w k_w A^* = 1.29 \times 10^{-7} \text{ (mol/cm}^3\text{s)}$$

$$\eta_o = \frac{R_A}{\Omega'_A} = 0.279$$

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

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

$$\frac{R_A}{M_A A^*} < 0.1 \quad \text{NEGLIGIBLE EXTERNAL TRANSPORT EFFECTS}$$

$$> 0.5 \quad \text{CONSIDERABLE EXTERNAL TRANSPORT EFFECTS}$$

$$\longrightarrow 1 \quad \text{EXTERNAL TRANSPORT CONTROLS THE RATE}$$

AGAIN ONE NEEDS RELIABLE ESTIMATES OF SOLUBILITY  $A^*$   
AND TRANSPORT COEFFICIENTS  $K_L a_B$ ,  $k_S a_p$

$$\text{IF } K_L a_B \ll k_S a_p$$

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

$$\phi = \frac{(R_A) (V_P/S_P)^2}{(1 - \epsilon_B) D_{Ae} A_S} = \frac{\text{OBSERVED RATE}}{\text{MAX RATE OF PURE DIFFUSIONAL TRANSPORT}}$$

$\phi < 0.2$                       NO INTERNAL DIFFUSIONAL EFFECTS

$$\eta_P = 1$$

$0.2 < \phi < 6$                 INTERMEDIATE DIFFUSIONAL EFFECTS

$$\phi = \Lambda_P \tanh \Lambda_P$$

$$\eta_P = \frac{\tanh \Lambda_P}{\Lambda_P}$$

$\phi > 6$                               STRONG PORE DIFFUSIONAL EFFECTS

$$\eta_P = \frac{1}{\phi}$$



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 2:

REACTION: HYDRODESULFURIZATION OF PETROLEUM

CATALYST: Co/Mo/Al<sub>2</sub>O<sub>3</sub>

REACTOR: TRICKLE-BED

DATA: T = 367°C ; 827 psia (56 atm)

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

$$\epsilon_B = 0.36$$

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

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

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

$$(\epsilon_p \approx 0.45 ; \tau \approx 4)$$

1% SULFUR IN FEED

OBJECTIVE

DETERMINE CONTROLLING RESISTANCE

$$a_p = \frac{6(1 - \epsilon_B)}{d_p} = 12.1 \text{ (cm}^{-1}\text{)}$$

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

$$M_A = \left( \frac{1}{k_L a_B} + \frac{1}{k_S a_p} \right)^{-1} \quad \text{UNKNOWN}$$

$$\text{APPROXIMATE } M_A (A^* - A_S) = k_{GLS} a_p (A^* - A_S)$$

$$R_A = (1 - \epsilon_B) \text{ RATE} = 6.66 \times 10^{-7} \text{ (mol/cm}^3\text{s)}$$

ESTIMATE

$$k_{GLS} \geq \frac{D_A a_p}{\epsilon_B/2} = 0.0037 \text{ (cm/s)}$$

$$M_A > k_{GLS} a_p = 0.0448 \text{ (s}^{-1}\text{)}$$

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

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

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

$$\phi = 0.97 = \Lambda_p \tanh \Lambda_p$$

INTERNAL DIFFUSIONAL EFFECTS MAY BE PRESENT BUT NOT  
PRONOUNCED.

ABOVE ESTIMATES VERY DEPENDENT ON  $A^*$ ,  $D_A$ ,  $D_{Ae}$

EXAMPLE 3:

REACTION: ALDEHYDE HYDROGENATION  $A(g) + b B(l) = P(l)$

CATALYST: Ni

REACTOR: CSTR CONTINUOUS (AGITATED) SLURRY

DATA:  $T = 100^{\circ}\text{C}$  ;  $P = 500$  psia

$$\rho_L = 0.8 \text{ g/cm}^3 \quad ; \quad M_B = 80 \text{ g/mol}$$

$$B_{l0} = 0.01 \text{ (mol/cm}^3\text{)} \quad ; \quad x_B = 0.88$$

$$V/Q_L = 600 \text{ (s)}$$

$$d_p = 10^{-3} \text{ cm} \quad ; \quad a_p = 300 \text{ cm}^{-1} \quad ; \quad \rho_p = 2.5 \text{ (g/cm}^3\text{)}$$

$$\varepsilon_g \approx 0.1$$

HIGH RPM

OBJECTIVE

DOUBLE PRODUCTION CAPACITY.

CAN IT BE ACHIEVED IN THE SAME REACTOR?

ESTIMATE

$$A^* = 5 \times 10^{-4} \text{ mol/cm}^3$$

$$D_A = 4 \times 10^{-5} \text{ cm}^2/\text{s}$$

$$w = 0.125 \text{ (g/cm}^3\text{)}$$

CSTR ASSUMPTION

$$B_l = B_{l0} (1 - x_B) = 1.2 \times 10^{-3} \text{ (mol/cm}^3\text{)}$$

HYDROGEN IS RATE LIMITING

(A)

ESTIMATE LIQUID-SOLID TRANSPORT

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

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

ESTIMATE GAS-LIQUID TRANSPORT

BASED ON REPORTED  $\epsilon_g = 0.1$ , HIGH RPM, AVAILABLE

CHARTS  $K_L a_B \approx 0.2 \text{ (s}^{-1}\text{)}$ .

$$R_A = \frac{A^*}{\frac{1}{K_L a_B} + \frac{1}{k_s a_p} + \frac{1}{w \eta_p k_w}} = \frac{5 \times 10^{-4}}{5 + 0.042 + PR} = 1.47 \times 10^{-5}$$

FROM DATA

$$R_A = \frac{B \rho^x_B}{V/Q_L} = 1.47 \times 10^{-5} \text{ (mol/cm}^3\text{s)}$$

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

IT SEEMS THAT PARTICLE DIFFUSION + KINETIC RESISTANCE  
DOMINATES.

TO DOUBLE THE RATE  $R_A$  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  $R_A$  OBSERVED!

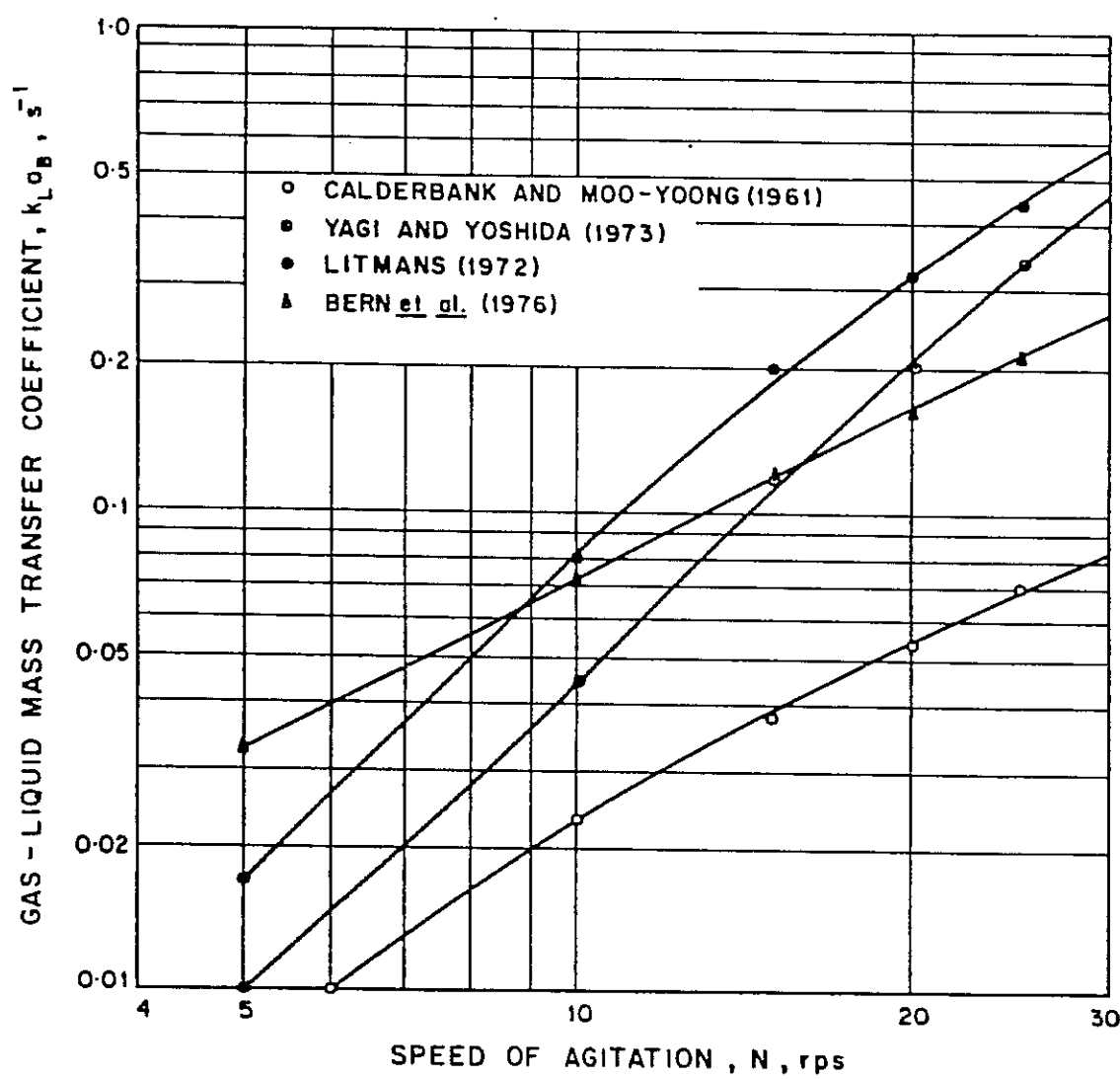


FIGURE 9.8 Comparison of correlations for  $k_L a_B$  in an agitated reactor.

CLOSER EXAMINATION REVEALS THAT REACTOR OPERATES AT 300 rpm EXP. DETERMINED  $k_L a$  AGREES WITH CORRELATION AT 300 RPM.

$$K_L a_B \approx 0.03 \text{ (s}^{-1}\text{)}$$

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! !

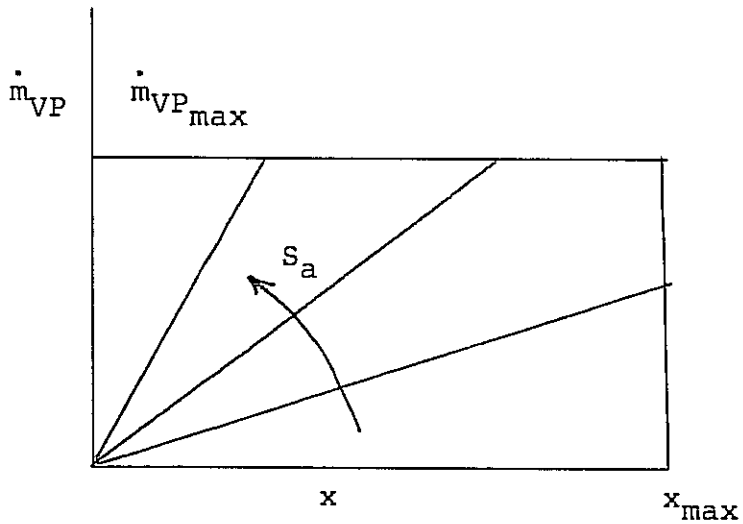
CHOICES FOR DOUBLING THE PRODUCTION RATE:

- 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  $\dot{m}_{VP}$  ( $\text{kg} / \text{m}^3 \text{ h}$ )
2. MAXIMIZE PRODUCT CONCENTRATION AND SELECTIVITY



$x$  ( $\frac{\text{kg cat.}}{\text{m}^3}$ ) - CATALYST CONCENTRATION

$S_a$  ( $\frac{\text{kg P}}{\text{kg cat h}}$ ) - 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

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

	GASES	LIQUIDS
DIFFUSIVITY (cm <sup>2</sup> /s)	0.01 TO 1	10 <sup>-6</sup> TO 10 <sup>-4</sup>
CONDUCTIVITY (w/mk)	5 x 10 <sup>-3</sup> TO 10 <sup>-1</sup>	5 x 10 <sup>-2</sup> TO 1

EXAMPLE

T = 25°C

O<sub>2</sub> - AIR

D = 0.23 cm<sup>2</sup>/s

O<sub>2</sub> - WATER

D = 2.1 x 10<sup>-5</sup> cm<sup>2</sup>/s

k<sub>L</sub> = 2.1 x 10<sup>-3</sup> cm<sup>2</sup>/s

H<sub>A</sub> = 7.9 x 10<sup>5</sup> ( $\frac{\text{atm cm}^3}{\text{mol}}$ )

IN GASES	P / D ↗ ;	T / D /	
IN LIQUIDS	P / D ↘ ;	T / D /	
IN GASES	P / λ ↗ ;	T / λ /	LOW P
	P / λ ↘ ;	T / λ ↘	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:

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

- 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*

Method	Basic form	$f(\text{flow})$	$f(D)$	Advantages	Disadvantages
Film theory	$k = \frac{D}{l}$	—	1.0	Simple; often good base for ideas	Film thickness $l$ is unknown
Penetration theory	$k = 2\sqrt{Dv^0/\pi L}$	$\frac{1}{2}$	$\frac{1}{2}$	Simplest including flow	Contact time ( $L/v^0$ ) often unknown
Surface-renewal theory	$k = \sqrt{D/\tau}$	—	$\frac{1}{2}$	Similar math to penetration theory, but better physical picture	Surface-renewal rate ( $\tau$ ) is unknown
Boundary layer theory	$k = 0.626 \frac{D}{L} \left(\frac{Lv^0}{\nu}\right)^{1/2} \left(\frac{\nu}{D}\right)^{1/3}$	$\frac{1}{2}$	$\frac{2}{3}$	Much better physical picture	Laminar flow past flat plate of length $L$ only; math hard.
Graetz-Nusselt theory	$k = \left(\frac{2}{3\Gamma(\frac{4}{3})}\right) \frac{D}{L} \left(\frac{L^2v^0}{DR}\right)^{1/3}$	$\frac{1}{3}$	$\frac{4}{3}$	Exact result for short tubes	Valid only in laminar flow

Table 9.3-2. A selection of mass transfer correlations<sup>a</sup> C FROM CUSLER (1984)

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

Spinning disc	$\frac{kd}{D} = 0.62 \left( \frac{d^2 \omega}{\nu} \right)^{1/2} \left( \frac{\nu}{D} \right)^{1/3}$	$d$ = disc diameter $\omega$ = disc rotation (radians/time)	Valid for Reynolds numbers between 100 and 20,000
Flow normal to capillary bed	$\frac{kd}{D} = f \left( \frac{dv^0}{\nu}, \frac{\nu}{D} \right)$	$d$ = tube diameter $v^0$ = average velocity	Large number of correlations with different exponents found by analogy with heat transfer
Packed beds	$\frac{k}{v^0} = 1.17 \left( \frac{dv^0}{\nu} \right)^{-0.42} \left( \frac{\nu}{D} \right)^{-0.67}$	$d$ = particle diameter $v^0$ = superficial velocity	The superficial velocity is that which would exist without packing
<i>Fluid-fluid interfaces</i> Drops or bubbles in stirred solution	$\frac{kL}{D} = 0.13 \left( \frac{L^4(P/V)}{\rho \nu^3} \right)^{1/4} \left( \frac{\nu}{D} \right)^{1/3}$	$L$ = stirrer length $P/V$ = power per volume	Correlations versus power per volume are common for dispersions
Large drops in unstirred solution	$\frac{kd}{D} = 0.42 \left( \frac{d^3 \Delta \rho g}{\rho \nu^2} \right)^{1/3} \left( \frac{\nu}{D} \right)^{1/2}$	$d$ = bubble diameter $\Delta \rho$ = density difference between bubble and surrounding fluid	"Large" is defined as ~0.3-cm diameter
Small drops of pure solute in unstirred solution Falling films	$\frac{kd}{D} = 1.13 \left( \frac{dv^0}{D} \right)^{0.8}$ $\frac{kz}{D} = 0.69 \left( \frac{zv^0}{D} \right)^{1/2}$	$d$ = bubble diameter $v^0$ = bubble velocity $z$ = position along film $v^0$ = average film velocity	These behave like rigid spheres Frequently embroiled and embellished

<sup>a</sup> 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.  
<sup>b</sup> The dimensionless groups are defined as follows:  $(dv^0/\nu)$  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;  $kz/D$  is the Sherwood number;  $k/v$  is the Stanton number.  
<sup>c</sup> 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**