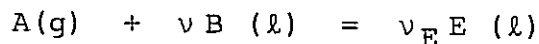


GAS ABSORPTION ACCOMPANIED BY REACTION

IN THE LIQUID



ASSUME: $\Omega_A = k_A B$

KEY PARAMETERS:

$$\frac{\tau_D}{\tau_R} = Ha^2 = \frac{k_B \ell D_{AL}}{k_{AL}^2} = \frac{\text{KINETIC RATE IN ABSENCE OF TRANSPORT EFFECTS}}{\text{MAXIMUM DIFFUSIONAL RATE OF A INTO LIQUID}}$$

HATTA NUMBER

$$E_i = 1 + \frac{D_{BL} B_\ell}{\nu D_{AL} A_i}$$

ENHANCEMENT FACTORS

$$E_L = \frac{\dot{N}_A}{k_L A_i} = \frac{\text{OBSERVED ABSORPTION FLUX}}{\text{MAX. FLUX OF PHYSICAL ABSORPTION INTO LIQUID FILM FROM INTERFACE}}$$

$$E_{LO} = \frac{\dot{N}_A}{K_L A^*} = \frac{\text{OBSERVED ABSORPTION FLUX}}{\text{MAX. FLUX OF PHYSICAL ABS. FROM GAS TO LIQUID}}$$

\dot{N}_A (mol/cm²s) - FLUX AT INTERFACE CALCULATED FROM VARIOUS MODELS

$$\frac{1}{K_L} = \frac{1}{k_L} + \frac{1}{k_g H}$$

$$\varphi = (N_A)_{act}$$

$$\left(\frac{\text{mol}}{\text{cm}^2 \text{ s}} \right)$$

$$H_C = H_A$$

$$\beta = H_L = \epsilon_L$$

$$p = P_{Ag}$$

Regime	Interface concentration profiles	Rate equations	
Instantaneous		$\varphi = \frac{P}{H_A} + \frac{D_B}{D_A} \frac{C_{B0}}{2}$ $= \frac{1}{k_L} + \frac{1}{H_A k_G}$	A
Instantaneous and surface		$\varphi = k_G P$	B
Rapid		$\varphi = \frac{P}{\frac{1}{k_G} + \frac{H_A}{E_L k_L}}$	C
Rapid pseudo 1st or nth order		$\varphi = \frac{P}{\frac{1}{k_G} + \frac{H_A}{\sqrt{D_A k_2 C_{B0}}}}$	D
Intermediate		No exact general expression developed	E
Intermediate		No exact general expression developed	F
Slow diffusional process		$\varphi = \frac{P}{\frac{1}{k_G} + \frac{H_A}{k_L} + \frac{H_A \alpha \beta}{\beta k_2 C_{B0}}}$	G
Very slow chemical process in the bulk of the liquid		$R_A = k_2 C_A^* C_{B0} \beta$	H

I

II

III

IV

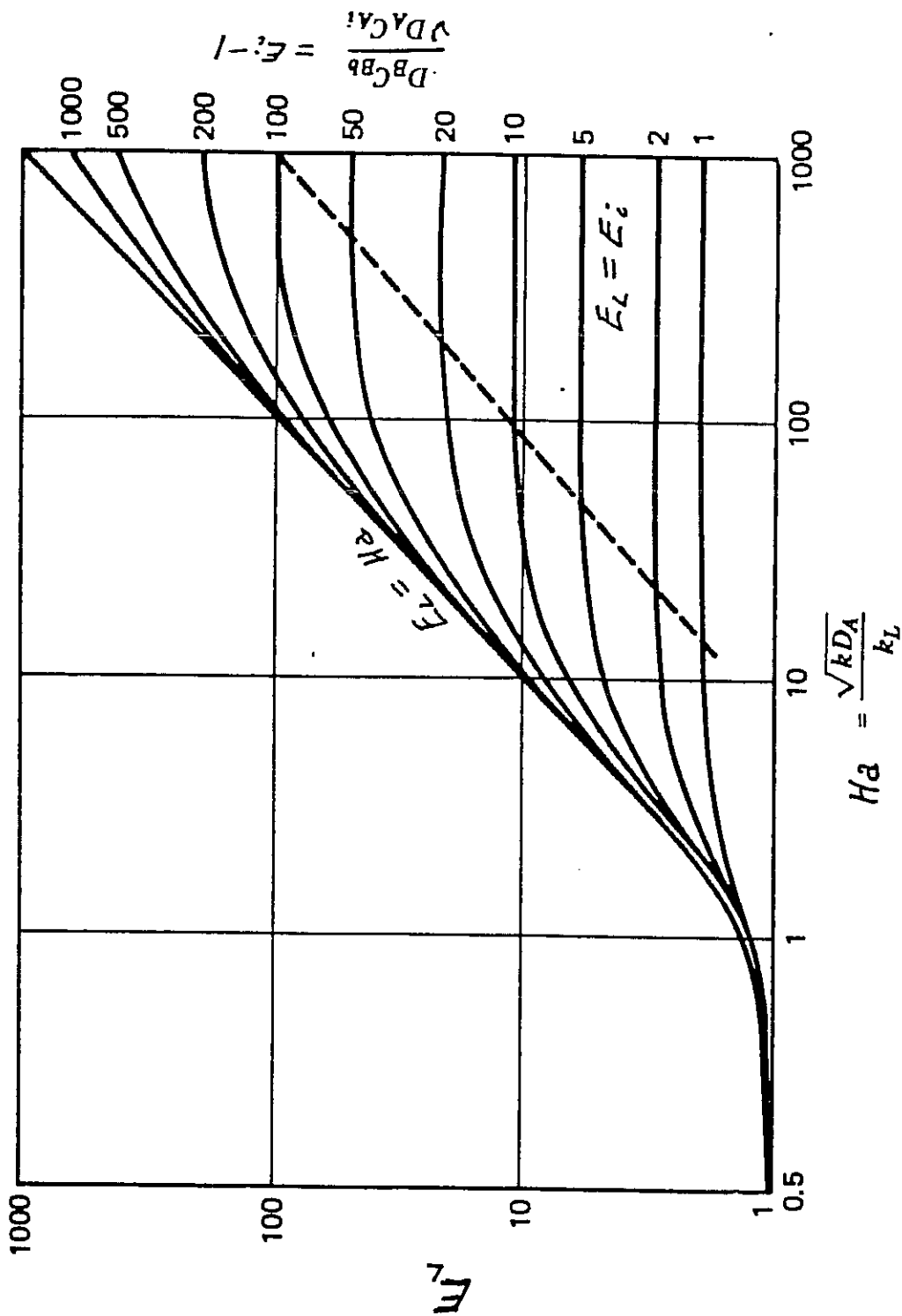


Figure Enhancement factor diagram for $C_{A_b} = 0$.

EIGHT (A - H) REGIMES CAN BE DISTINGUISHED:

A. INSTANTANEOUS REACTION OCCURS IN THE LIQUID FILM

$$Ha > 4E_i - 3$$

$$B_l < \frac{v D_{AL} k_{Ag} P_{Ag}}{k_{AL} D_{BL}}$$

$$E_L = E_i = E_{LO}$$

B. INSTANTANEOUS REACTION OCCURS AT GAS-LIQUID INTERFACE

$$Ha > 4E_i - 3$$

$$B_l > \frac{v D_{AL} k_{Ag} P_{Ag}}{k_{AL} D_{BL}}$$

$$E_L > \infty, \quad \dot{N}_A = k_g P_{Ag}$$

$$R_A = \dot{N}_A a_B$$

- HIGH GAS-LIQUID INTERFACIAL AREA DESIRED
- NONISOTHERMAL EFFECTS LIKELY

C. RAPID SECOND ORDER REACTION IN THE FILM. NO UNREACTED A PENETRATES INTO BULK LIQUID.

$$(4E_i - 3)^2 > Ha^2 > \frac{16 (E_i - E_L)}{E_i - 1}$$

$$\frac{D_{BL} B_\ell}{\nu D_{AL} A_i} = O(1)$$

$$E_L = \frac{Ha \sqrt{\frac{E_i - E_L}{E_i - 1}}}{\tanh \left[Ha \sqrt{\frac{E_i - E_L}{E_i - 1}} \right]}$$

D. PSEUDO FIRST ORDER REACTION IN FILM, SAME Ha NUMBER RANGE AS C.

$$\frac{D_{BL} B_\ell}{\nu D_{AL} A_i} \gg 1$$

$$E_L = \frac{Ha}{\tanh Ha} \approx Ha$$

ABSORPTION RATE PROPORTIONAL TO GAS-LIQUID AREA. NONISOTHERMAL EFFECTS STILL POSSIBLE.

E & F. INTERMEDIATE REGIME REACTION OCCURS BOTH IN
THE FILM AND BULK LIQUID

$$16 \frac{E_i - E}{E_i - 1} > Ha^2 > 0.01$$

TRANSPORT PROBLEM AT INTERFACE COUPLED WITH REACTOR RTD.

CAREFUL ANALYSIS NECESSARY. ENHANCEMENT FACTORS LOW,

BUT FILM RATES STILL HIGHER THAN RATE IN THE BULK.

$$\frac{V_{\text{FILM}}}{V_{\text{BULK LIQUID}}} = \frac{a_B \delta_f}{H_L} = \frac{a_B D_{AL}}{H_L k_L}$$

IS AN IMPORTANT PARAMETER.

MODERATE REACTION IN FILM AND FAST IN THE BULK.

NONISOTHERMAL EFFECTS NOT LIKELY.

NUMERICAL SOLUTIONS REQUIRED FOR E_L .

- G. SLOW REACTION IN THE BULK WITH FILM MASS TRANSFER RESISTANCE AND NEGLIGIBLE REACTION IN THE FILM

$$0.01 \geq Ha^2 > 0.05 \left(\frac{a_B D_{AL}}{H_L k_L} \right)$$

E_L HAS NO MEANING. EFFECTIVENESS FACTOR CONCEPT SHOULD BE USED.

- H. VERY SLOW REACTION IN THE BULK LIQUID WITH NO TRANSPORT RESISTANCE

$$Ha^2 \leq \left(\frac{a_B D_{AL}}{H_L k_L} \right)$$

TRUE KINETIC RATE OBSERVED

NONISOTHERMAL EFFECTS HIGHLY UNLIKELY

TO ASSESS THE CAPACITY OF THE MULTIPHASE CONTACTOR -
 REACTOR ONE MUST KNOW :

1. RTD OF EACH PHASE
2. FLOW DIRECTIONS: COCURRENT, COUNTERCURRENT, CROSS FLOW
3. HOLDUP OF EACH PHASE
4. INTERFACIAL AREA PER UNIT VOLUME
5. VARIOUS MASS TRANSFER COEFFICIENTS

TRENDS :

$$Ha < 0.2 \quad , \quad (H_L k_L / a_B D_{AL}) Ha^2 \ll 1$$

$$R_A \propto H_L$$

(H)

$$Ha < 0.2 \quad , \quad (H_L k_L / a_B D_{AL}) Ha^2 \gg 1$$

$$R_A \propto k_L a_B$$

(G)

$$2 < Ha \ll 1 + \frac{D_{BL} \bar{B}_l}{v D_{AL} A_i} \quad ; \quad R_A \propto a_B$$

(D)

$$Ha \gg 1 + \frac{D_{BL} \bar{B}_l}{v D_{AL} A_i} \quad , \quad R_A \propto k_L a_B E_i$$

(A)

WHEN $k_g H \gg k_L E_L$ GAS - FILM RESISTANCE UNIMPORTANT

MAXIMUM TEMPERATURE DIFFERENCE ACROSS FILM DEVELOPS
AT COMPLETE MASS TRANSFER LIMITATIONS.

$$(T_i - T_b)_{\max} = \frac{(-\Delta H_{RA}) A_b}{\rho C_p L_e^{2/3}} = \frac{\Delta T_{ad}}{Le^{2/3}} \quad (1)$$

$$Le = \frac{Sc}{Pr} = \frac{\lambda}{\rho C_p D_A} \quad \frac{\delta_h}{\delta_m} = Le^{1/3}$$

FOR LIQUIDS

FOR GASES

Le = 10 to 1000

Le = O(1)

TEMPERATURE DIFFERENCE FOR LIQUID FILM WITH REACTION

$$T_i - T_\ell = - \frac{[\Delta H_{rA} + \Delta H_{aA}]}{\rho C_p L_e^{2/3}} \frac{P_{Ag}/H E_A}{1 + \frac{k_L E_A}{k_g H}}$$

$$E_A = \frac{R_A}{k_L P_{Ag}/H}$$

TRIAL AND ERROR REQUIRED. NONISOTHERMALITY SEVERE FOR
FAST REACTIONS.

E.G. CHLORINATION OF TOLUENE

Table VII.12. Characteristic data of equipment for gas absorption with chemical reaction in aqueous systems

Type of gas-liquid contactor	Specific surface, a (m^{-1})	Volume fraction liquid phase, ϵ_L	$Sh = k_L d / D_A$	$\frac{V_L}{V_{FILM}} = \frac{(1 - \epsilon)/a\delta}{((1 - \epsilon)/ad)Sh}$
spray column	60	0.05	10-25	2-10
plate column	150	0.15	200-600	40-100
packed column	100	0.08	10-100	10-100
wetted-wall column	50	0.05	10-50	10-50
bubble column	20	0.98	400-1000	4000-10 ⁴
agitated bubble contactor	200	0.90	100-500	150-800

Type of Reactor	$100 \epsilon_L / (\epsilon_L + \epsilon_g)$	k_G (gmol/cm ² .s.atm) x 10 ⁴	k_L (cm/s) x 10 ²	a cm ² /cm ³ reactor	$k_L a$ (s ⁻¹) x 10 ²
Packed columns					
- counter-current	2 - 25	0.03 - 2	0.4 - 2	0.1 - 3.5	0.04 - 7
- co-current	2 - 95	0.1 - 3	0.4 - 6	0.1 - 17	0.04 - 102
Plate columns					
- bubble cap	10 - 95	0.5 - 2	1.5	1 - 4	1 - 20
- sieve plates	10 - 95	0.5 - 6	1 - 20	1 - 2	1 - 40
Bubble columns	60 - 98	0.5 - 2	1 - 4	0.5 - 6	0.5 - 24
Packed bubble columns	60 - 98	0.5 - 2	1 - 4	0.5 - 3	0.5 - 12
Tube reactors					
- horizontal and colloid	5 - 95	0.5 - 4	1 - 10	0.5 - 7	0.5 - 70
- vertical	5 - 95	0.5 - 8	2 - 5	1 - 10	2 - 100
Spray columns	2 - 20	0.5 - 2	0.7 - 1.5	0.1 - 1	0.07 - 1.5
Mechanically agitated bubble reactors					
	20 - 95	-	0.3 - 4	1 - 20	0.3 - 80
Submerged and plunging jet					
	94 - 99	-	0.15 - 0.5	0.2 - 1.2	0.03 - 0.06
- hydrocyclone	70 - 93	-	10 - 30	0.2 - 0.5	2 - 15
- ejector reactor	-	-	-	1 - 20	-
- Venturi	5 - 30	2 - 10	5 - 10	1.6 - 25	8 - 25

Table 1. Liquid holdup, mass transfer coefficients and effective interfacial area in gas-liquid reactors.

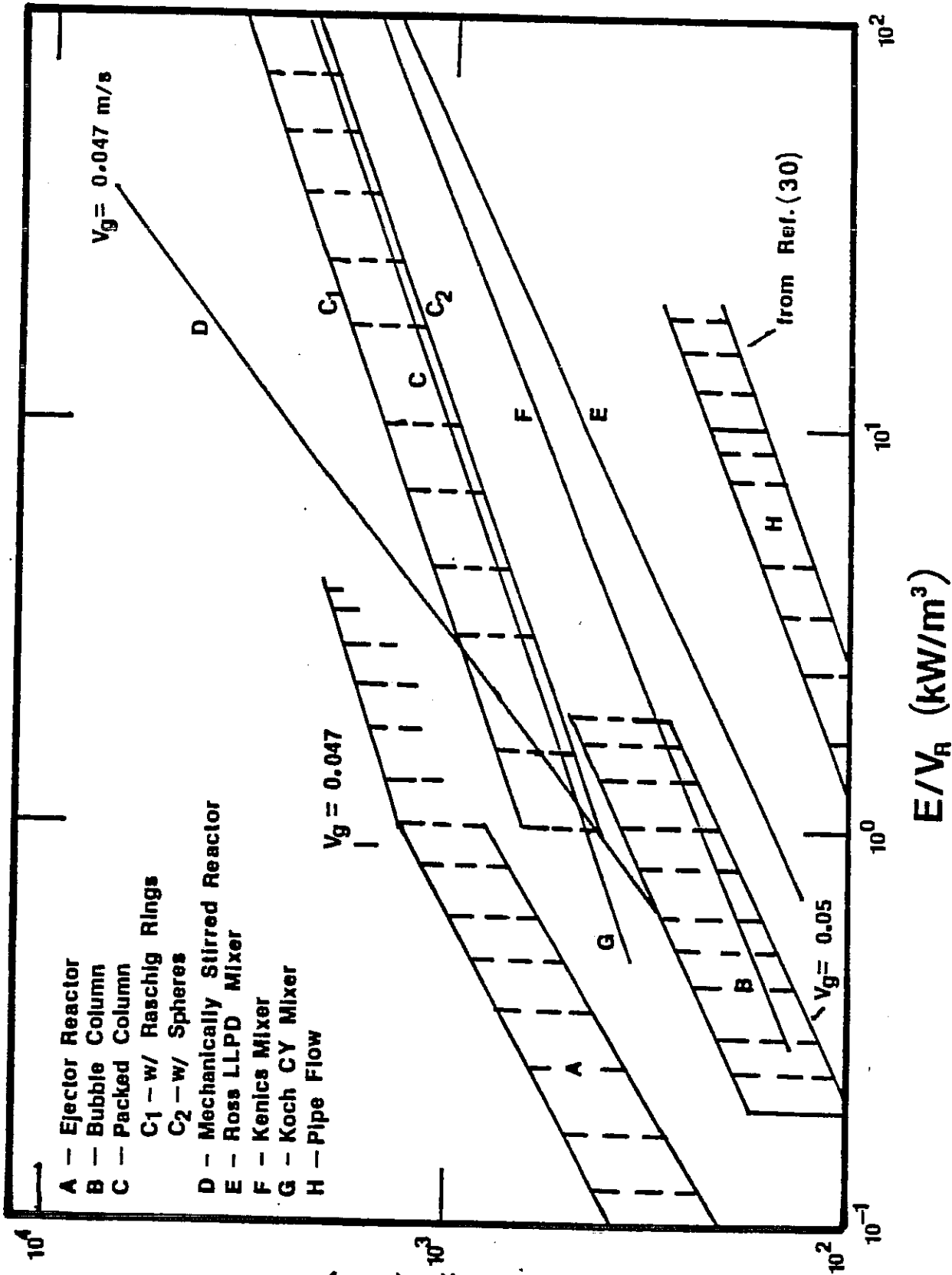


Figure 24. The Efficiencies of the Static Mixers Compared with Other Gas/Liquid Contacting Devices at One Gas Velocity

SCALE-UP STRATEGIES

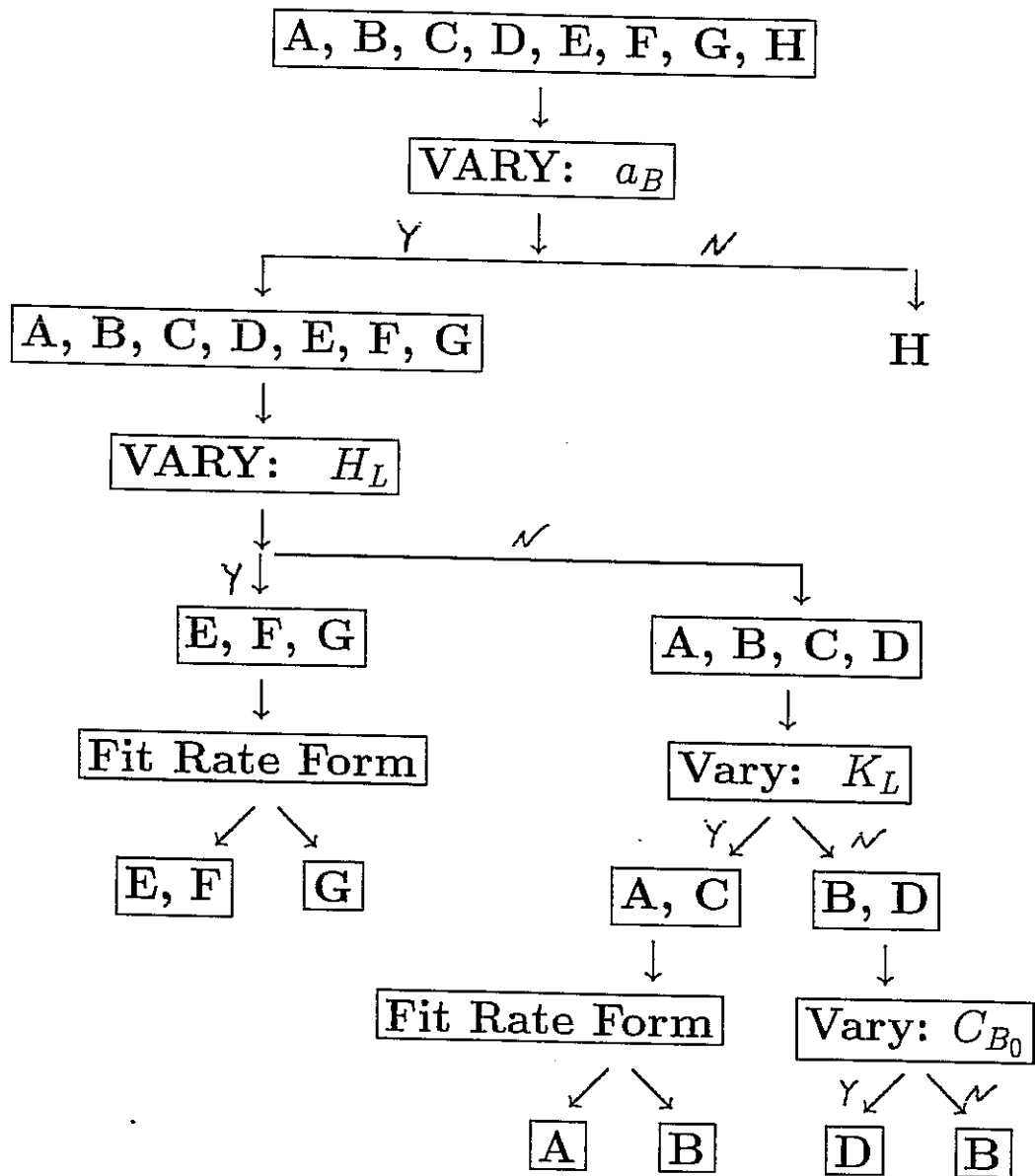
1. Run Small Scale Contactor
of Same Type As Plant Unit.
Use Correlations To Predict
Changes In Transport Coeff.
2. Simulate Different Points
In The Plant Unit By Lab.
Units Of Different Type
But With Same

$$K_L, K_G, \frac{a_B}{H_L}$$

In Addition Assess Effect Of

$$\frac{U_L}{a_B} \quad \frac{U_G}{U_L}$$

KINETIC REGIME DETERMINATION FROM LAB. REACTORS



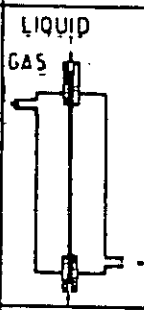
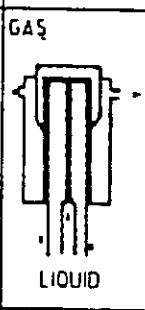
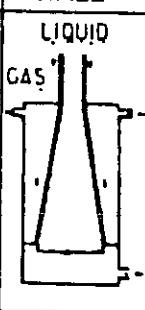
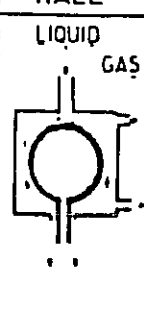
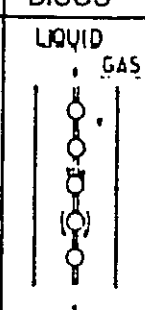
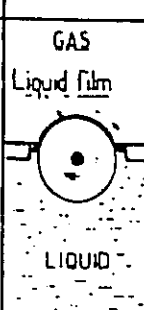
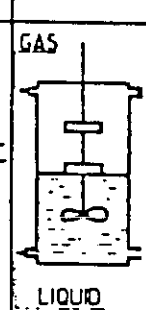
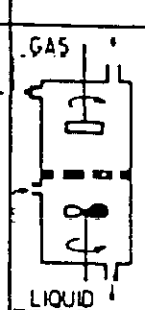
TYPE	LAMINAR JET	CYLINDRICAL WETTED WALL	CONIC WETTED WALL	SPHERICAL WETTED WALL	STRING OF DISCS	ROTATING DRUM	STIRRED VESSEL	STIRRED VESSEL
SCHEME								
k_L cm/s	0.016 -0.16	$3.6 \cdot 10^{-3}$ -0.016	$5 \cdot 10^{-3}$ -0.011	$5 \cdot 10^{-3}$ -0.016	$3.6 \cdot 10^{-3}$ -0.016	0.016 -0.36	$1.6 \cdot 10^{-3}$ -0.02	$2 \cdot 10^{-3}$ -0.02
CONTACT TIMES	10^{-3} - 10^{-1} s	10^{-1} -2 s	0.2-1 s	0.1-1 s	10^{-1} -2 s	$2 \cdot 10^{-4}$ -10 s	0.06-10 s	0.08-10 s
INTERFACIAL AREA	$0.3 \cdot 10 \text{ cm}^2$ high precision	$10 \cdot 100 \text{ cm}^2$ high precision	80 cm^2 high precision	$10 \cdot 40 \text{ cm}^2$ high precision	$30 \cdot 360 \text{ cm}^2$ moderate precision	diameter 10cm length 12cm high precision	80 cm^2 good precision	diameter 10cm length 15cm 2-30% open

Figure - Principal types of laboratory equipment.

MODEL	ROTATING DRUM	MOVING BAND	LAMINAR JET	WETTED WALL COLUMN			STRING OF DISCS - SPHERES	STIRRED VESSEL
				SPHERE	CYLINDER	CONE		
TIME OF CONTACT (s)	$2 \cdot 10^{-4}$ 10^{-1}	$6 \cdot 10^{-4}$ $6 \cdot 10^{-2}$	10^{-3} 10^{-1}	10^{-1} 1	10^{-1} 2	$2 \cdot 10^{-1}$ 1	10^{-1} 2	$8 \cdot 10^{-2}$ 10
INTERFACIAL AREA A_m (cm^2)	2 100	0.6 6	0.3 10	10 40	10 100	80	30 360	4 80
k_L ($\text{cm} \cdot \text{s}^{-1}$)	0.016 0.356	0.021 0.210	0.016 0.180	0.005 0.016	0.0036 0.016	0.005 0.011	0.0036 0.016	0.0016 0.021
$10^5 k_g$ ($\text{mole} \cdot \text{cm}^{-2} \cdot \text{s}^{-1} \cdot \text{atm}^{-1}$)	-	-	10 40	1 - 9			1 25	1 15
A_m / V_m (cm^{-1})	100 1250	80 400	20 80	20 60	25 60	40 70	20 60	0.002 0.540

Laboratory model	Contact time (s)	Industrial absorber	Contact time (s)	Laboratory model to be used for simulation
Cylindrical wetted wall	0.1 - 2	Plate column	0.019 - 0.04	Laminar jet Rotating drum
Spherical wetted wall	0.1 - 1	Packed column	0.03 - 1	Cylindrical wetted wall String of discs or of spheres Stirred vessel
Conical wetted wall	0.2 - 1	Venturi	0.004	Laminar jet
Laminar jet	0.001 - 0.1	Spray column	0.03 - 0.1	Laminar jet Rotating drum
String of discs or of spheres	0.1 - 2	Well stirred tank	0.01	Laminar jet Rotating drum
Rotating drum	0.0002 - 0.1	Bubble column	0.01	Laminar jet Rotating drum
Stirred vessel	0.06 - 10			

Table XX - Models for simulating absorbers based on equality of k_L

MEASUREMENT TECHNIQUES FOR a_L

- PHOTOGRAPHIC

$$\bar{d}_B = \sqrt{\frac{\sum n_i d_{BL}^2}{\sum n_i}} ; \quad a_B = \frac{6 \epsilon_g}{\bar{d}_B}$$

LOCAL VALUES

- LIGHT SCATTERING

$$a_B = \frac{4}{L} \ln \frac{I_0}{I}$$

LOCAL VALUES. LIMITED TO $a_B < 600 \text{ m}^{-1}$

- CONDUCTANCE

- CAPACITANCE

LOCAL VALUES

- γ - RAY ABSORPTION

LOCAL

- γ - RAY TOMOGRAPHY

DISTRIBUTION OF VALUES

- CHEMICAL ABSORPTION (2nd ORDER)

$$a_B = \frac{R_A}{k_L H a A_i} = \frac{R_A}{\sqrt{k D_{AL} \bar{B}_l A_i}}$$

GAS - INTERFACIAL AREA MEASUREMENT BY CHEMICAL
ABSORPTION IS POPULAR

PROBLEMS:

- AREA DEPENDS ON REACTION USED
- PHYSICAL PROPERTIES MAY AFFECT IT AND CHANGE IT
FROM MEASURED TO MODELED SYSTEMS
- CONDITION $2 < Ha < E_1$ MAY NOT BE SATISFIED
EVERYWHERE IN REACTOR IF NOT DIFFERENTIAL OR
NOT CSTR
- THE MEASURED AREA DEPENDS ON RATIO OF REACTION
CAPACITY INCREASE TO ENHANCEMENT FACTOR

SYSTEMS USED EXTENSIVELY:

- $CO_2 + NaOH$ DANCKWERTS, GAS-LIQUID REACTIONS
MCGRAW-HILL, 1970
- $O_2 + Na_2SO_3$ SOLUTION + Co^{++} LINEK AND VACEK
CHEM. ENG. SCI.
36, 1747 (1981)

FOR OTHER SYSTEMS SEE:

DORAISWAMY AND SHARMA
HETEROGENEOUS REACTIONS VOL. 2
WILEY 1986

MEASUREMENT OF $k_L a$ SHOULD BE DONE WITH PURE GAS
OR OTHERWISE ELIMINATING GAS SIDE RESISTANCE

STEADY STATE

1. MASS TRANSFER NO REACTION

$$k_L a = \frac{R_A}{A_i - \bar{A}_\ell}$$

$$k_L a H_L V / Q_L \ll 1 \quad \text{i.e.} \quad \bar{A}_\ell \ll A_i$$

AFFECTED BY RTD OF LIQUID

2. MASS TRANSFER WITH SLOW REACTION

$$Ha < 0.2 \quad (H_L k_L / a D_a) \quad Ha^2 \gg 1$$

$$k_L a_\beta = \frac{R_A}{A_i}$$

INDEPENDENT OF LIQUID RTD

3. MASS TRANSFER WITH INSTANTANEOUS REACTION

$$k_L a_\beta = \frac{R_A}{A_i \left(1 + \frac{D_{BL} \bar{B}_\ell}{\nu D_{AL} A_i} \right)}$$

4. DYNAMIC METHODS WITH/WITHOUT REACTION

MEASUREMENT OF $k_g a_g$

- ABSORPTION OF VERY SOLUBLE GASES
- ABSORPTION WITH INSTANTANEOUS REACTION ON GAS-LIQUID INTERPHASE

MEASUREMENT OF k_s

- DISSOLUTION OF SOLID PARTICLES (e.g. NAPHTHALENE, BENZOIC ACID, β -NAPHTHOL, etc.)
- DYNAMIC METHODS

EVALUATION OF k_L

- FROM $k_L a_g$ AND a_g MAY VARY DEPENDENT ON SYSTEM
- BY DANCKWERTS METHOD OF CHEMICAL ABSORPTION

$$\left(\frac{R_A}{A_i}\right)^2 = \underbrace{a_g^2 D_{AL}}_{\text{SLOPE}} (k_B a_g) + \underbrace{(k_{AL} a_g)^2}_{\text{INTERCEPT}}$$

- BY SIMULTANEOUS ABSORPTION OF REACTANT

($E_L = H a + a$) AND INERT ($k_L a_g$)

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Chapter 2. Nomenclature

- A - concentration of species A from gas phase;
- A/V_R - gas-liquid interfacial area per unit reaction volume;
- a_B - gas-liquid interfacial area per unit reactor volume;
- a_p - liquid-solid interfacial area per unit reactor volume;
- B - concentration of species B from liquid phase;
- Bi_m - Biot number for mass transfer = ratio of diffusional resistance in the particle and external mass transfer resistance;
- D - diffusivity;
- D_e - effective diffusivity;
- \bar{d}_B - mean bubble diameter;
- d_p - particle diameter;
- E - concentration of species E;
- E_L - enhancement factor i.e. ratio of actual flux to maximum transport rate from gas-liquid interface to liquid bulk;
- E_{LD} - overall enhancement factor for gas-liquid absorption i.e. ratio of actual flux to maximum mass transport flux from bulk gas phase to bulk of the liquid;
- E_i - enhancement factor for instantaneous reaction;
- E/V_R - dissipated energy per unit reactor volume;
- H_A - Henry's constant for gaseous species A;
- Ha - Hatta number;
- H_L - liquid holdup i.e. fraction of reactor volume occupied by liquid;
- h_p - heat transfer coefficient from particles to fluid;
- I - light intensity
- K_L - overall gas-liquid mass transfer coefficient for concentration driving force;
- K_G - overall gas-liquid mass transfer coefficient for partial pressure driving force;
- K - equilibrium constant for reaction or adsorption;
- k - reaction rate constant for reaction per unit volume of medium;

k_w - reaction rate constant for reaction per unit mass of catalyst;
 k_o - frequency factor in Arrhenius representation of the rate constant;
 k_{jL} - liquid side gas-liquid mass transfer coefficient for species j;
 k_s, k_{LS} - liquid-solid mass transfer coefficient;
 k_{jg} - gas side gas-liquid mass transfer coefficient for species j;
 L - characteristic length;
 Le - Lewis Number i.e.; ratio of Schmidt and Prandtl numbers;
 M_A - overall gas-liquid-solid mass transfer coefficient for species A;
 m - modulus, also partial reaction order;
 \dot{m}_{VP} - volumetric productivity i.e. mass production rate per unit reactor volume;
 \dot{N}_j - molar flux across gas-liquid interface of species j;
 n - reaction order;
 P - pressure;
 P_{jg} - partial pressure of species j in the gas phase;
 p - partial reaction order;
 PR - particle resistance;
 Q_L - liquid volumetric flow rate;
 q - partial reaction order;
 R_j - observed reaction rate of species j per unit reactor volume;
 R - radius of particle or reactor, universal gas constant;
 Sh - Sherwood number;
 S_p - particle external surface area;
 T - temperature;
 u - superficial velocity;
 V - reactor volume;
 V_p - particle volume;
 x_j - fractional conversion of species j;
 y_j - mole fraction of species j;

Greek Letters

- α - shape factor;
- β - Prater number, dimensionless adiabatic temperature rise;
- γ - dimensionless activation energy;
- δ_f - liquid film thickness;
- δ_h - energy boundary layer thickness;
- δ_m - mass boundary layer thickness;
- ΔT_{ad} - adiabatic temperature rise;
- ΔH_a - heat of absorption;
- ΔH_R - heat of reaction;
- ϵ_B - bed porosity;
- ϵ_g - gas holdup;
- ϵ_L - liquid holdup;
- ϵ_p - particle porosity;
- η_p - particle effectiveness factor;
- η_o - overall effectiveness factor;
- Λ_p - particle modulus;
- λ - conductivity;
- λ_e - effective bed or particle conductivity;
- ν - kinematic viscosity;
- ρ_p - particle density;
- ρ_j - density of phase j;
- \mathcal{G} - interfacial flux;
- ϕ - modulus;
- Φ - observable (Wagner) modulus;
- τ_D - characteristic diffusion time;
- τ_R - characteristic reaction time;
- Ω_j - kinetic reaction rate of species j per unit volume of catalyst;
- Ω'_j - kinetic reaction rate of species j per unit reactor volume;

Subscripts

- A - reactant A;
- B - reactant B;
- b - in bulk phase;
- g - in gas phase
- i - at the interface
- L - in liquid phase
- l - in liquid phase
- j^l, j^L - species j in liquid
- j^g - species j in gas
- o - inlet or initial
- s - at the catalyst exterior surface
- SL - in slurry
- TBR - in trickle-bed

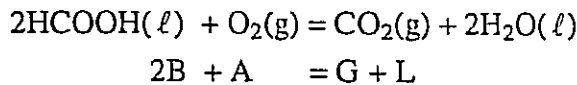
Superscripts

- * - at equilibrium (or saturation)

Problems To Do

1. Consider air oxidation of formic acid in a differential trickle bed reactor over Cu_{0.2}nO catalyst.

The reaction is:



The following conditions apply:

$$T = 240^\circ\text{C}$$

$$P = 20 \text{ atm}$$

$$\text{Formic Acid Concentration} \approx 2 \times 10^{-6} \text{ mol/cm}^3$$

$$\text{Henry's constant for O}_2 = 88.7 \text{ (mol/cm}^3 \text{ gas)/(mol/cm}^3 \text{ liquid)}$$

$$k_w = 4.45 \times 10^5 \text{ (cm}^6 \text{/mol g s)} - \text{2nd order rate constant}$$

$$k_{L\text{A}B} = 9 \times 10^{-3} \text{ (s}^{-1}\text{)} - \text{volumetric mass transfer coefficient}$$

$$d_p = 0.24 \text{ cm (catalyst particle diameter)}$$

$$(k_s a_p)_A = 0.04 \text{ (s}^{-1}\text{)} - \text{liquid solid mass transfer coefficient for O}_2$$

$$(k_s a_p)_B = 0.035 \text{ (s}^{-1}\text{)} - \text{liquid solid mass transfer coefficient for F.A.}$$

$$\rho_p = 2.35 \text{ (g/cm}^3\text{)} \text{ pellet density}$$

$$\varepsilon_B = 0.44 \text{ bed external voidage}$$

$$D_{eA} = 2.6 \times 10^{-4} \text{ cm}^2 \text{/s} - \text{effective diff. of O}_2$$

$$D_{eB} = 2.08 \times 10^{-4} \text{ cm}^2 - \text{effective diff. for F.A.}$$

Find:

- the overall effectiveness factor
- the dominant resistance
- the rate of oxidation of formic acid

2. Consider hydrogenation of α -methylstyrene. At 50°C, P = 1 atm, the observed rate was $1.86 \times 10^{-7} \text{ (mol/s cm}^3 \text{ pellets)}$.

$$d_p = 0.825 \text{ cm} - \text{particle diameter}$$

$$A^* = 3.54 \times 10^{-6} \text{ MOL H}_2 \text{/cm}^3 - \text{H}_2 \text{ solubility}$$

$$D_{Ac} = 5.5 \times 10^{-5} \text{ cm}^2 \text{/s} - \text{effective diffusivity}$$

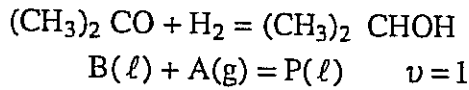
$$k_{gls} = 0.0138 \text{ (cm/s)} - \text{gas-liquid-solid mass transfer coefficient}$$

The above reaction is conducted on a string of spherical catalysts. Liquid film thickness is $\delta_f = 0.012 \text{ cm}$.

Find:

- the extent of the external mass transfer resistance
- the overall effectiveness factor
- the rate constant at 50°C.

3. Hydrogenation of acetone (dimethyl ketone) to isopropanol on a Raney nickel catalyst in a slurry reactor obeys a half-order behavior with respect to hydrogen.



At $T = 14^\circ\text{C}$, $P = 10 \text{ atm}$, $k_w = 2.35 \times 10^{-3} (\text{cm}^3/\text{mole})^{1/2}/\text{g s}$;

$A^* = 2.75 \times 10^{-5} (\text{mole}/\text{cm}^3)$; $k_{L\text{AB}} = 0.0186 \text{ s}^{-1}$; $k_{sp} = 0.266 \text{ s}^{-1}$;

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

Catalyst particles are small enough that the particle effectiveness factor is unity. Calculate the overall effectiveness factor and predict the hydrogenation rate per unit volume of the slurry.

4. Compare the local reaction rate for a gas limited reaction in an agitated slurry reactor and trickle bed reactor under conditions yielding the following data:

Slurry

$$d_p = 10 \mu\text{m} \quad \Lambda_p = 0.1 \quad \text{for } k_v = 0.2 (\text{s}^{-1})$$

$$k_{L\text{AB}} = 0.05 (\text{s}^{-1})$$

$k_s = \text{large enough so that liquid-solid mass transfer resistance can be ignored.}$

- What is the dominant resistance in each reactor.
 - If the reactors operate at the same pressure and use pure gas reactant, how do the two rates perform?
 - If the pressure in the trickle bed is 10 times higher than in the slurry, how do the two rates compare?
 - Repeat the above for a reaction with a $k_v = 20 (\text{s}^{-1})$. Assume same diffusional properties in the particle.
5. Consider CO_2 absorption in MEA solution and determine the reaction regime under the conditions indicated below.

DATA:

$$y_{\text{Ab}} = 0.25; B_{(\ell)} = 2.5 \times 10^{-3} \text{ mol}/\text{cm}^3, P = 1 \text{ atm}$$

$$D_A = 1.4 \times 10^{-5} \text{ cm}^2; D_B = 7.7 \times 10^{-6} \text{ cm}^2/\text{s}$$

$$k_L = 0.022 \text{ cm}/\text{s}; k = 1.02 \times 10^7 (\text{cm}^3/\text{mol s})$$

$$a_B = 1.4 \text{ cm}^{-1}; \nu = 2$$

$$H_A = 4 \times 10^4 \text{ cm}^3 \text{ atm}/\text{mol}$$

- What rate of absorption can you expect under these conditions?
- What type of contactor do you recommend for this type of reaction and why?

6. Consider H_2S absorption in the amine solution and determine the reaction regime under the conditions indicated below:

DATA:

$$B_L = 2.5 \times 10^{-4} \text{ (mol/cm}^3\text{)} ; y_{Ab} = 0.01 , P = 20 \text{ atm}$$

$$\frac{D_A}{D_B} = 1.5 ; k_L a_b = 0.03 \text{ (s}^{-1}\text{)}$$

$$H_A = 10^4 \frac{\text{cm}^3 \text{ atm}}{\text{mol}} ; k_{Ag} a_B = 8.1 \times 10^{-5} \frac{\text{mol}}{\text{cm}^3 \text{ atm s}}$$

$$a_B = 10 \text{ cm}^{-1}$$

- a) What rate of absorption can you expect under these conditions?
- b) What type of contactor do you recommend and why?

CHAPTER 2

APPENDIX

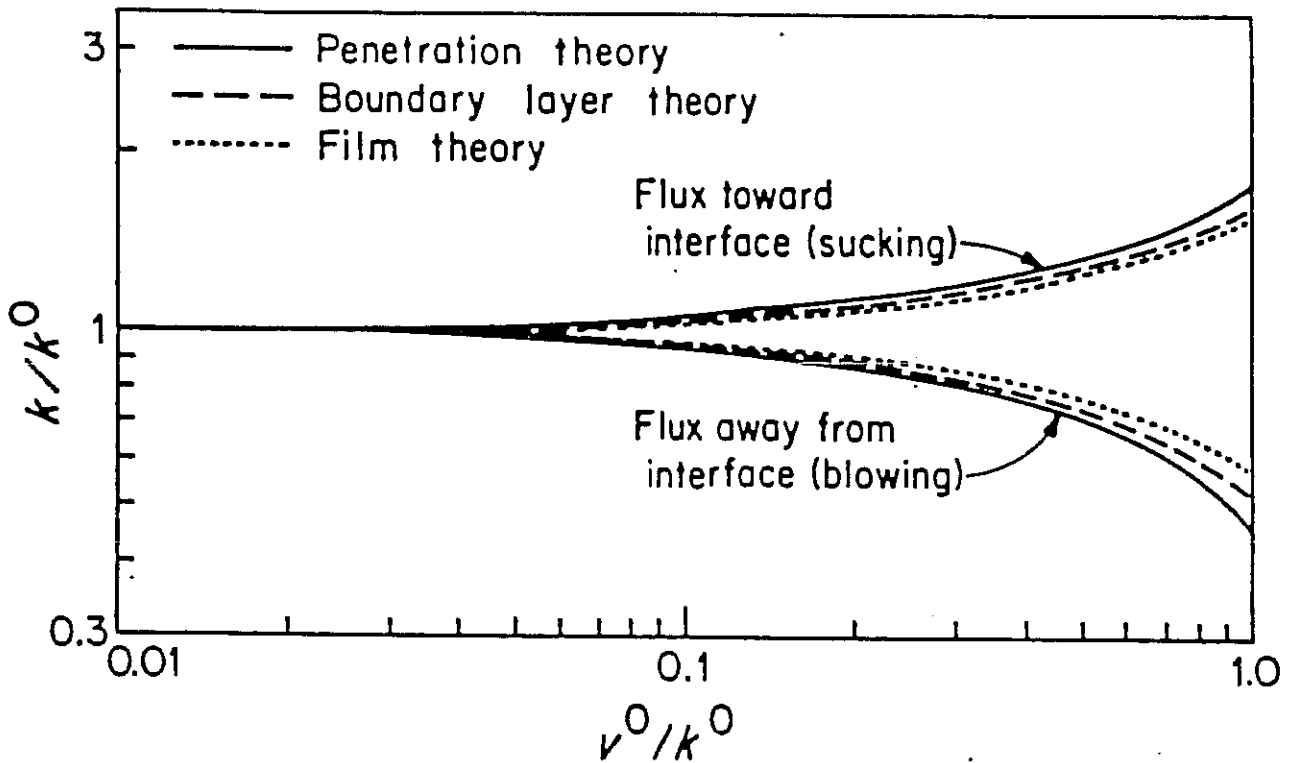


Fig. 11.5-2. Correction factors for rapid mass transfer. This figure gives the mass transfer coefficient k as a function of the interfacial convection v^0 . In dilute solution, v^0 is small, and k approaches the slow mass transfer limit k^0 . In concentrated solution, k may reach a new value, although estimates of this value from different theories are about the same (the boundary layer theory shown is for a Schmidt number of 1,000).

CORRECTION FOR MASS TRANSFER
COEFFICIENTS DUE TO RAPID FLUXES

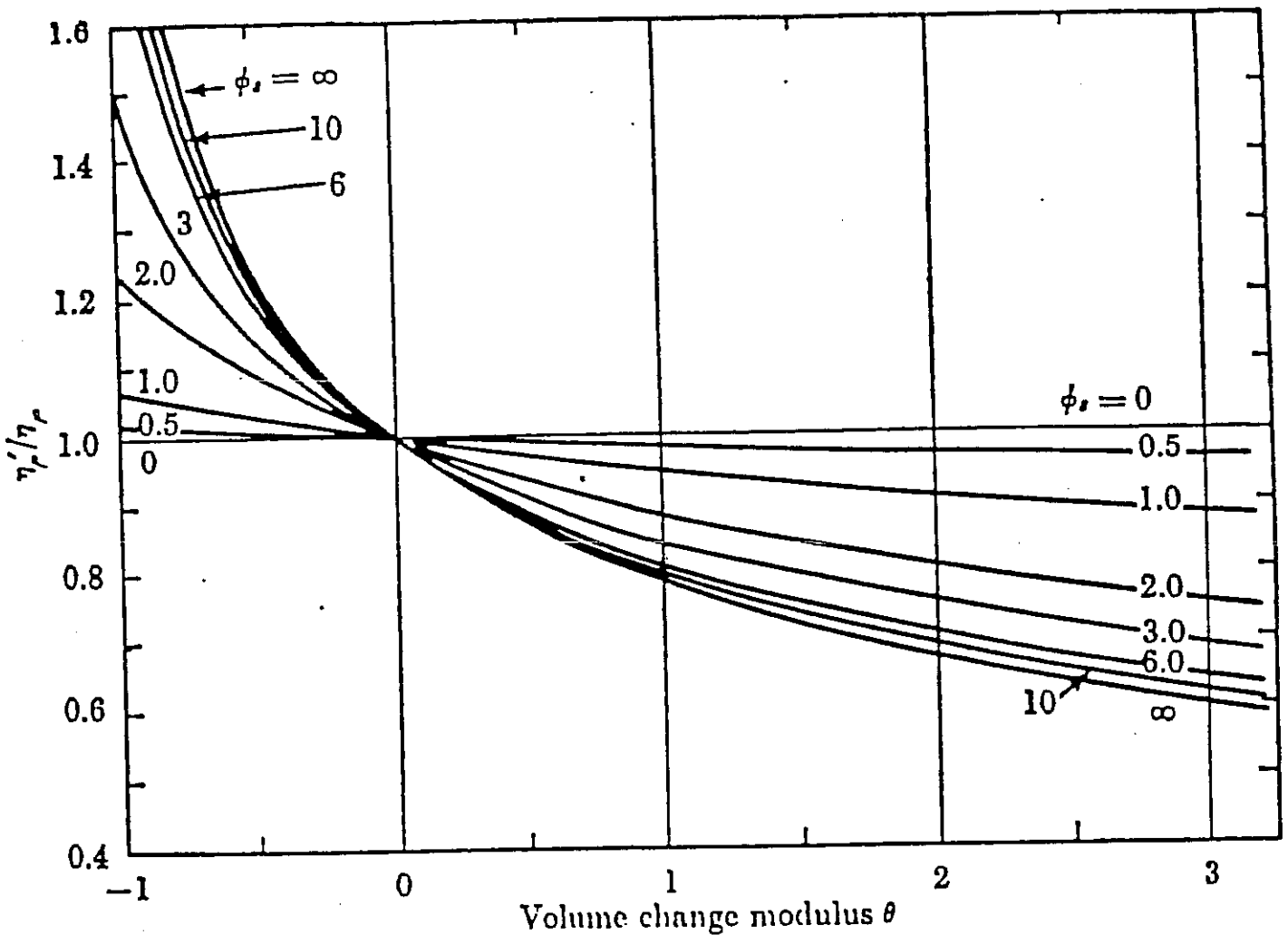
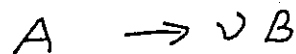


Figure 4.10. Effect of volume change on effectiveness factor. $\theta = (\nu - 1) Y_{A,s}$. First-order reaction, spherical geometry, bulk diffusion. Weckman and Gorring [363].

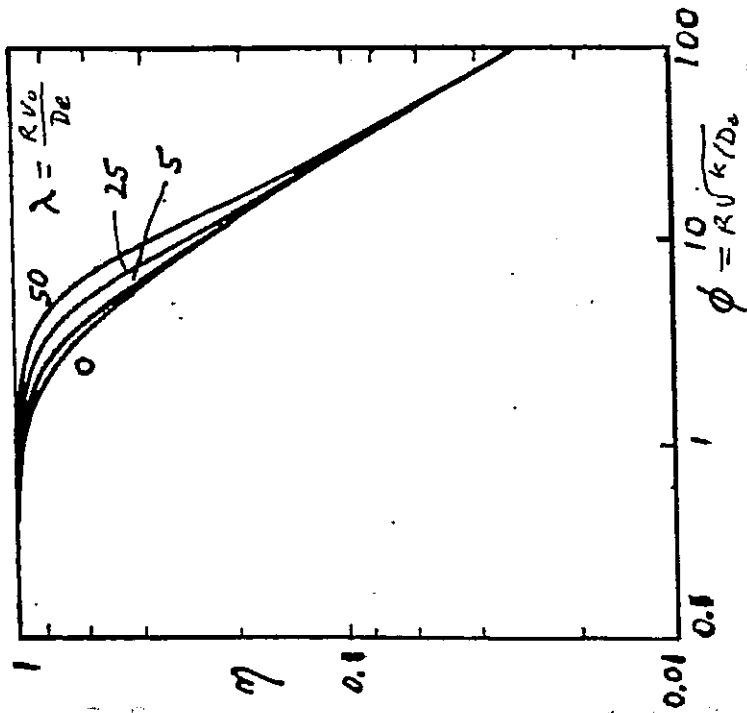
EFFECT OF CHANGE IN VOLUME
CAUSED BY REACTION ON
PELLET EFFECTIVENESS



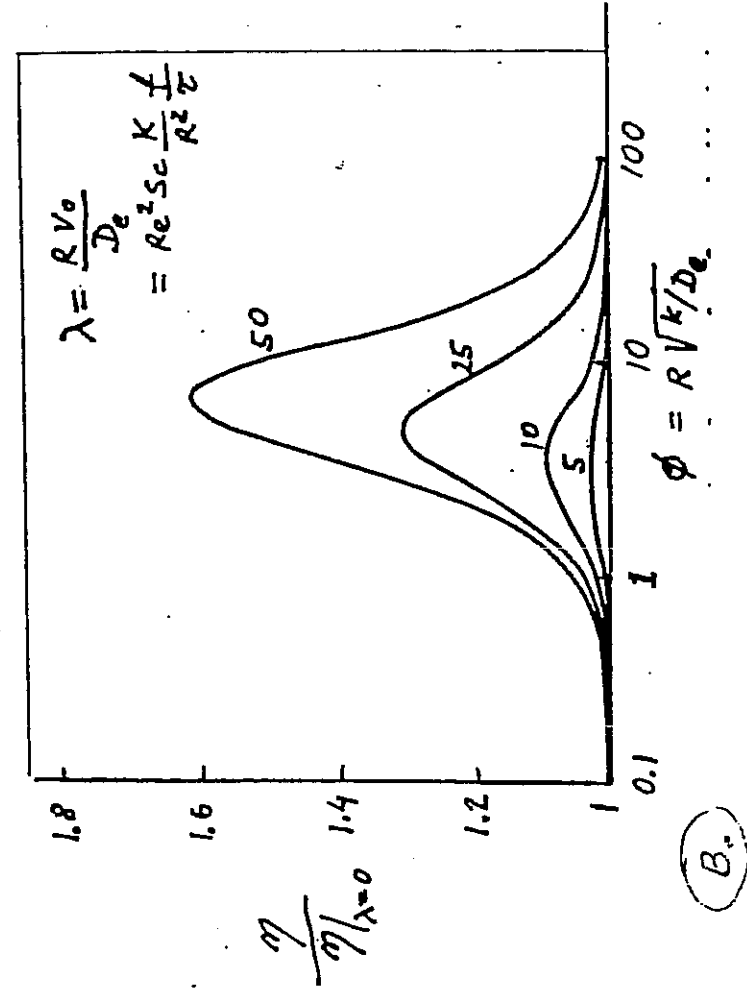
$$\theta = (\nu - 1) Y_{A,s} \quad , \quad \eta_p = \text{PELLET EFFECTIVENESS AT } \theta = 0$$

$Y_{A,s}$ = MOLE FRACTION
OF A ON OUTSIDE
SURFACE

$$\phi_s = R \sqrt{\frac{k}{D_c}} = 3 \Lambda_p$$



(A.)



(B.)

EFFECTIVENESS FACTOR AS FUNCTION OF MODULUS FOR A SPHERICAL PARTICLE WITH INTERFACIAL CONVECTION (A) AND RATIO OF EFFECTIVENESS FACTORS WITH/ WITHOUT CONVECTION (B)

FOR $\phi > 1, \phi^2 \gg \lambda$

$$\eta = \frac{3}{2\phi^2} \left\{ \frac{\lambda}{2} \sqrt{1 + \frac{4\phi^2}{\lambda^2}} + \frac{2\phi^2}{\lambda} \cdot \sinh^{-1} \left(\frac{\lambda}{2\phi} \right) \right\}$$

FOR $\lambda \gg 1$

$$\eta = \frac{3}{2\phi^2} \left\{ \frac{1}{2} - \frac{\lambda^2}{4\phi^2} \left[1 - \left(1 + \frac{2\phi^2}{\lambda} \right) e^{-2\phi/\lambda} \right] \right\}$$

FROM MIR & PISHEW, CHEM. ENG. SCI 32, 35 (1977).

GAS-LIMITED REACTION

GENERALIZATION TO ANY KINETIC RATE FORM

$$M_A (A^* - A_s) = \frac{w}{\rho_p} \eta_p \Omega_{As} \quad (1)$$

$$\Lambda_p^2 = \left(\frac{V_p}{S_p} \right)^2 \frac{\Omega_{As}}{D_{Ae} A_s} \quad (2)$$

$$m_1 = \frac{(1+\alpha) \Lambda_p}{2 \int_{a_e}^1 \Omega^* da} \quad (3)$$

$$m_2 = \frac{(1+\alpha) \Lambda_p}{\sqrt{\left. \frac{d\Omega^*}{da} \right|_1}} \quad (4)$$

$$m = m_2 \sqrt{\frac{1 + \alpha + 0.7 m_1^2}{1 + \alpha + 0.7 m_2^2}} \quad (5)$$

$$\eta_p = \frac{\tanh (m/(1+\alpha))}{m} \quad (6)$$

$$\eta_o = \eta_p \frac{\Omega_{As}}{\Omega_{Ag}} \quad (7)$$

$$R_A = \eta_o \Omega_{Ag} (1 - \epsilon_B) \quad (8)$$

$\alpha = 0, 1, 2$ PARTICLE SHAPE FACTOR (SLAB, CYLINDER, SPHERE)

$$\Omega^* = \frac{\Omega}{\Omega_s}$$

$$a = \frac{A}{A_s}$$

VALID FOR $\left. \frac{d\Omega^*}{da} \right|_1 < 0$

PROCEDURE FOR CALCULATING THE OVERALL EFFECTIVENESS

1. START COUNTER AT $n = 1$

2. ASSUME $A_{s1} = A_g = A^*$ IF $M_A \gg w \Omega_{Ag}/A^*$ OR $A_{s1} = A^*/2$

$$\text{IF } M_A \ll \frac{w \Omega_{Ag}}{A^*}$$

3. USING THE GIVEN KINETIC FORM $\Omega(A)$ CALCULATE FOR THE DESIRED PARTICLE SHAPE $\Lambda_p, m_1, m_2, m, \eta_p$ FROM EQS (2-6)

4. ESTIMATE M_A

5. FROM EQ(1) ESTIMATE NEW PARTICLE SURFACE CONCENTRATION

$$A_{sn}^c = A^* - \frac{w \eta_p \Omega_{AS}(A_{sn})}{\rho_p M_A}$$

6. CORRECT PARTICLE SURFACE CONCENTRATION BY RELAXATION METHOD

$$A_{sn+1} = \omega A_{sn} + (1-\omega) A_{sn}^c$$

7. CHECK WHETHER CONVERGENCE IS ACCOMPLISHED

$$|A_{sn} - A_{sn}^c| < \epsilon$$

IF SO GO TO STEP 8, IF NOT GO TO STEP 3

8. CALCULATE η_o BY EQ (7)

NOTE: MANY VARIATIONS ON THIS PROCEDURE CAN BE DEVELOPED.

$$\text{LET } \Omega_{Ag} = k A^{*n}$$

$$R_A = \eta_o \Omega_{Ag} (1 - \epsilon_B) = \eta_p \Omega_{As} (1 - \epsilon_B) = M_A (A^* - A_S) = k_L a_B (A^* - A_g)$$

$$\frac{A^* - A_S}{A^*} = \frac{R_A}{M_A A^*} = \frac{\eta_o \Omega_{Ag}}{M_A A^*} = \psi$$

$\psi < 0.1$ NO EXTERNAL EFFECTS

$\psi > 0.5$ DOMINANT EXTERNAL RESISTANCE

CASE 1 $m/\alpha < 0.3$; $\eta_p = 1$

NO INTERNAL DIFFUSIONAL EFFECTS

a) $\psi < 0.1$; $\eta_o = 1$; $R_A = \Omega_{Ag} (1 - \epsilon_B) = k (1 - \epsilon_B) A^{*n}$

TRUE KINETICS OBSERVED

b) $\psi > 0.9$; $\eta_o < 1$; $R_A = M_A A^*$ 1st ORDER

MASS TRANSFER CONTROLS

CASE 2 $m/\alpha > 5$, $\eta_p = 1/m = \frac{1}{\Lambda_p}$

STRONG PORE DIFFUSIONAL EFFECTS

a) $\psi < 0.1$; $\eta_o \approx \eta_p$

$$R_A = (1 - \epsilon_B) \sqrt{\frac{n}{n+1}} k D_{Ae} \left(\frac{S_P}{V_P}\right) A^{*(n+1) 1/2}$$

MASKED KINETICS OBSERVED

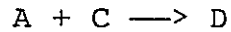
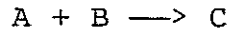
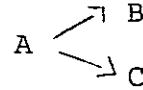
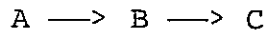
b) $\psi > 0.9$; $\eta_o \ll \eta_p$; $R_A = M_A A^*$

FIRST ORDER PROCESS OBSERVED

EXTERNAL MASS TRANSFER

CONTROLS THE RATE

COMPLEX REACTION SCHEMES



MULTIPLE MASS BALANCES MUST BE WRITTEN OF THE TYPE (FOR COMPONENT J)

$$M_j (C_{jl} - C_{js}) = \frac{w}{\rho_p} \Omega_{js}$$

FOR INTERNAL PORE DIFFUSIONAL EFFECTS CONSULT THE LITERATURE FOR REFERENCES

ARIS, R., MATHEMATICAL THEORY OF DIFFUSION AND REACTION
OXFORD, 1975.

FROMENT, G. AND BISCHOFF, K. B., CHEMICAL REACTOR ANALYSIS
AND DESIGN, WILEY, 1979

DORAISWAMY, L. K. AND SHARMA, M. M., HETEROGENEOUS REACTIONS,
VOLUMES 1 and 2, WILEY, 1984.

SAME METHODOLOGY APPLIES
EXECUTION MORE DIFFICULT
MULTICOMPONENT DIFFUSION EFFECTS POSSIBLE