Gas – Liquid
and
Gas- Liquid –Solid Reactions

A. Gas –Liquid Systems
Proper Approach to Gas-Liquid Reactions

References

• Mass Transfer theories
• Gas-liquid reaction regimes
• Multiphase reactors and selection criterion
• Film model: Governing equations, problem complexities
• Examples and Illustrative Results
• Solution Algorithm (computational concepts)
Theories for Analysis of Transport Effects in Gas-Liquid Reactions

Two-film theory

Penetration theory

Surface renewal theory

Rigorous multicomponent diffusion theory
Two-film Theory Assumptions

1. A stagnant layer exists in both the gas and the liquid phases.

2. The stagnant layers or films have negligible capacitance and hence a local steady-state exists.

3. Concentration gradients in the film are one-dimensional.

4. Local equilibrium exists between the the gas and liquid phases as the gas-liquid interface

5. Local concentration gradients beyond the films are absent due to turbulence.
Two-Film Theory Concept


\[ p_{Ai} = H_A C_{Ai} \]

\[ x = \delta_G \quad x = 0 \quad x = \delta_L \]
Two-Film Theory
- Single Reaction in the Liquid Film -

\[ A \text{ (g) } + b \text{ B (liq) } \rightarrow P \text{ (liq)} \]

B & P are nonvolatile

\[ R_A \left[ \frac{\text{kg-moles A}}{m^3 \text{ liquid - s}} \right] = - k_{mn} C_A^m C_B^n \]

Closed form solutions only possible for linear kinetics or when linear approximations are introduced
Film Theory Model for a Single Nonvolatile Gas-Liquid Reaction

- Diffusion-reaction equations for a single reaction in the liquid film are:

\[ A(g) + bB(l) \rightarrow P(l) \]

\[ D_A \frac{d^2 A}{dx^2} = r \quad \text{at } x = 0 \quad A = A^* \quad \text{at } x = \delta \quad A = A_L \]

\[ D_B \frac{d^2 B}{dx^2} = br \quad \text{at } x = 0 \quad \frac{dB}{dx} = 0 \quad \text{at } x = \delta \quad B = B_L \]

- In dimensionless form, the equations become dependent on two dimensionless parameters, the Hatta number Ha and q*:

\[ r = k_{mn} A^m B^n \]  

\[ Ha = \frac{t_D}{t_R} = \left[ \frac{2}{m+1} D_A k_{mn} (A^*)^{m-1} B_L^n \right]^{1/2} \quad q^* = \frac{B_L D_B}{bA^n D_A} \]
Penetration Theory Model

- Diffusion - reaction equations for a single reaction in the liquid film are:

\[
\frac{\partial C_A}{\partial t} = D_A \frac{\partial^2 C_A}{\partial x^2} + R_A
\]

\[
\frac{\partial C_B}{\partial t} = D_B \frac{\partial^2 C_B}{\partial x^2} + R_B
\]
Comparison Between Theories

- **Film theory:**
  - \( k_L \propto D, \delta \) - film thickness
  \[ k_L = \frac{R_A'}{C^* - C} = \frac{D}{\delta} \]

- **Penetration theory:**
  - \( k_L \propto D^{1/2} \)
  - **Higbie model**
    - * - life of surface liquid element
  \[ k_L = \frac{R_A'}{C^* - C} = 2\sqrt{\frac{D}{\pi t^*}} \]
  - **Danckwerts model**
    - s - average rate of surface renewal
  \[ k_L = \frac{R_A'}{C^* - C} = \sqrt{Ds} \]
Gas-Liquid Reaction Regimes

- Instantaneous
- Fast (m, n)
- Instantaneous & Surface
- General (m,n) or Intermediate
- Slow Diffusional
- Rapid pseudo 1st or mth order
- Very Slow
Characteristic Diffusion & Reaction Times

- **Diffusion time**
  \[ t_D = \frac{D}{k_L^2} \]

- **Reaction time**
  \[ t_R = \frac{C - C_E}{r} \]

- **Mass transfer time**
  \[ t_M = \frac{1}{k_L \alpha_B} \]
Reaction-Diffusion Regimes Defined by Characteristic Times

- Slow reaction regime: $t_D << t_R$, $k_L = k_L^0$
  - Slow reaction-diffusion regime: $t_D << t_R << t_M$
  - Slow reaction kinetic regime: $t_D << t_M << t_R$

- Fast reaction regime: $t_D >> t_R$, $k_L = E_A k_L^0 > k_L^0$
  - Instantaneous reaction regime: $k_L = E_{A\infty} k_L^0$
For reaction of a gas reactant in the liquid with liquid reactant with/without assistance of a dissolved catalyst

\[ A(g) + b \beta(\ell) = P(\ell) \]

The rate in the composition region of interest can usually be approximated as

\[ -R_A \left( \frac{k \text{ mol A}}{m^3 s} \right) = k C_A^m C_B^n \]

Where \( C_A, C_B \) are dissolved A concentration and concentration of liquid reactant B in the liquid. Reaction rate constant \( k \) is a function of dissolved catalyst concentration when catalyst is involved.

For reactions that are extremely fast compared to rate of mass transfer form gas to liquid one evaluates the enhancement of the absorption rate due to reaction.

\[ (-R_A) = k_L a E_{Lo} \left( \frac{p_{A_g}}{H_A} \right) \varepsilon_L \]

For not so fast reactions the rate is

\[ (-R_A) = \eta k \left( \frac{p_{A_g}}{H_A} \right)^m C_B^n \varepsilon_L \]

Where \( \eta \) effectiveness factor yields the slow down due to transport resistances.
Gas Absorption Accompanied by Reaction in the Liquid

\[ \begin{align*}
A(g) + v B(l) &= v_E E(l) \\
\end{align*} \]

Assume: \( \Omega_A = k A B \) - 2nd order rate

Hatta Number:
\[ \frac{\tau_D}{\tau_R} = Ha^2 = \frac{k BL D_{AL}}{k_{AL}^2} \]

Ei Number:
\[ E_i = 1 + \frac{D_{BL} B_L}{v D_{AL} A_i} \]

Enhancement Factor:
\[ E_L = \frac{N_A}{k_{LA_i}} = \text{OBSERVED ABSORPTION FLUX} \]
\[ E_{LO} = \frac{\dot{N}_A}{k_{LA}} = \text{OBSERVED ABSORPTION FLUX} \]
\[ N_A \text{ (mol/cm}^2\text{s}) \rightarrow \text{FLUX AT INTERFACE CALCULATED FROM VARIOUS MODELS} \]

\[ \frac{1}{K_L} = \frac{1}{k_L} + \frac{1}{k_g H} \]
If $E_i > 5 M_H$ we then have pseudo first order reaction by the $G/L$ interface in which case $E = M_H$
More precisely

$$E = M_H \left(1 - \frac{M_H - 1}{2E_i}\right) + \ldots$$

Reaction zone approaches interface

No reaction in $L$ film

All reaction occurs on $L$ film, no penetration of $A$ into $L$ bulk.

Fast second order reaction in $L$ film $5E_i > M_H > \frac{E_i}{5}$

$E_i = 1 + \frac{\psi_B C_B H_A}{b \beta_A P_A}$

$M_H = \frac{\sqrt{\omega_A k C_B}}{k_{AI}}$

If $E_i < \frac{M_H}{5}$ then we have instantaneous reaction at a plane on the $L$ film in which case $E = E_i$
More precisely:

$$E = E_i - \frac{E_i^2 (E_i - 1)}{M_H^2} + \ldots$$
In this notation $\varphi = \dot{N}_A \left( k \text{ mol } A/m^2 \text{s} \right)$ is the gas to liquid flux

$$-R_A' = \dot{N}_A a \left( k \text{ mol/m}^3 \text{ liquid s} \right)$$

$$-R_A = \varepsilon_L \left( -R_A' \right) \left( k \text{ mol/m}^3 \text{ reactor s} \right)$$
Eight (A – H) regimes can be distinguished:

A. Instantaneous reaction occurs in the liquid film

\[ H_a > 4E_i - 3 \]

\[ B_L < \frac{\nu D_{AL} k_{Ag} P_{Ag}}{k_{AL} D_{BL}} \]

\[ E_L = E_i = E_{LO} \]

B. Instantaneous reaction occurs at gas-liquid interface

\[ H_a > 4E_i - 3 \]

\[ B_L > \frac{\nu \nu_{AL} k_{Ag} P_{Ag}}{k_{AL} D_{BL}} \]

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

\[ R_A = \dot{N}_A a_B \]

- High gas-liquid interfacial area desired
- Non-isothermal effects likely
C. Rapid second order reaction in the film. No unreacted A penetrates into bulk liquid

\[(4E_i - 3)^2 > H_a^2 > \frac{16 (E_i - E_L)}{E_i - 1}\]

\[\frac{D_{BL} B_L}{\nu D_{AL} A_i} = O(1)\]

\[E_L = \frac{H_a \sqrt{E_i - E_L}}{E_i - 1} \cdot \tanh [H_a \sqrt{\frac{E_i - E_L}{E_i - 1}}] \]

D. Pseudo first order reaction in film; same Ha number range as C.

\[\frac{D_{BL} B_L}{\nu D_{AL} A_i} > > 1\]

\[E_L = \frac{H_a}{\tanh H_a} \approx H_a\]

Absorption rate proportional to gas-liquid area. Non-isothermal 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.

\[ \frac{V_{FILM}}{V_{BULK LIQUID}} = \frac{a_B \delta_f}{H_L} = \frac{a_B^{DAL}}{H_L k_L} \]

IS AN IMPORTANT PARAMETER.

MODERATE REACTION IN FILM AND FAST IN THE BULK.

NONISOTHERMAL EFFECTS NOT LIKELY.

NUMERICAL SOLUTIONS REQUIRED FOR \( E_L \).
Maximum temperature difference across film develops at complete mass transfer limitations

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

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

FOR LIQUIDS

Le = 10 to 1000

FOR GASES

Le = O(1)

Temperature difference for liquid film with reaction

\[
T_i - T_l = -\frac{[\Delta H_{RA} + \Delta H_{A}]_{\text{A}}}{\rho C_p L_e^{2/3}} \frac{P_{Ag/H} E_A}{1 + \frac{k_{LEA}}{k_{g/H}}} \quad E_A = \frac{R_A}{k_{L}P_{Ag/H}}
\]

Trial and error required. Nonisothermality severe for fast reactions.

e.g. Chlorination of toluene
- Summary -

Limiting Reaction-Diffusion Regimes

Slow reaction kinetic regime
- Rate proportional to liquid holdup and reaction rate and influenced by the overall concentration driving force
- Rate independent of $k_i a_B$ and overall concentration driving force

Slow reaction-diffusion regime
- Rate proportional to $k_i a_B$ and overall concentration driving force
- Rate independent of liquid holdup and often of reaction rate

Fast reaction regime
- Rate proportional to $a_B$, square root of reaction rate and driving force to the power $(n+1)/2$ (nth order reaction)
- Rate independent of $k_i$ and liquid holdup

Instantaneous reaction regime
- Rate proportional to $k_L$ and $a_B$
- Rate independent of liquid holdup, reaction rate and is a weak function of the solubility of the gas reactant
Key Issues

- Evaluate possible mechanisms and identify reaction pathways, key intermediates and rate parameters
- Evaluate the reaction regime and transport parameters on the rate and assess best reactor type
- Assess reactor flow pattern and flow regime on the rate
- Select best reactor, flow regime and catalyst concentration

Approximately for 2\textsuperscript{nd} order reaction \( A(g) + b \, B(\ell) \rightarrow P(\ell) \)

\[
-R_A = \frac{P_A / H_A}{k_{A_g} \, a \, H_A} + \frac{1}{k_{A_L} \, a \, E_L} + \frac{1}{k \, C_{\beta} \, \varepsilon_L}
\]

\[-R_A \left( \frac{\text{k mol A}}{\text{m}^3 \text{s}} \right) = \text{observed local reaction rate per unit volume of reactor} \]

\( p_A(\text{atm}) = \text{local partial pressure of A in the gas phase} \)

\( H_A \left( \frac{\text{atm m}^3 \text{ liquid}}{\text{k mol A}} \right) = \text{Henry's constant for A} \)

\( k_{A_g} \, a \, H_A, \, k_{A_L} \, a(1/\text{s}) = \text{volumetric mass transfer coefficient for gas and liquid film, respectively.} \)

\( E_L = \text{dimensionless enhancement factor} \)

\( E_L \left( \frac{\text{m}^3 \text{ liquid}}{\text{m}^3 \text{ reactor}} \right) = \text{local liquid volume fraction in reactor} \)
Gas- liquid – solid systems
Gas-Liquid-Solid Reactions

Let us consider: \[ A + νB \xrightarrow{\text{Catalyst}} ν_E E \]

**Reaction occurring in the pores of the catalyst particles and is gas reactant limited**
- A  Reactant in the gas phase
- B  Non-volatile reaction in the liquid phase

**Number of steps:**
- Transport of A from bulk gas phase to gas-liquid interface
- Transport of A from gas-liquid interface to bulk liquid
- Transport of A&B from bulk liquid to catalyst surface
- Intraparticle diffusion in the pores
- Adsorption of the reactants on the catalyst surface
- Surface reaction to yield product

The overall local rate of reaction is given as

\[
R_A = \bar{A}^* \left[ \frac{1}{k_L a} + \frac{1}{k_s a_p} + \frac{1}{\eta_c w k_2 B_l} \right]^{-1}
\]
Gas – Liquid Solid Catalyzed Reaction \( A(g) + B(l) = P(l) \)

**Gas Limiting Reactant (Completely Wetted Catalyst)**

KINETIC RATE \( : k_v A \left( \frac{mol}{m^3 \text{ cat.s}} \right) = \Omega_A \)
(per unit catalyst volume)

RATE IN CATALYST: \( k_v \eta_p \left( 1 - \varepsilon_B \right) A_s \left( \frac{mol}{m^3 \text{ react. s}} \right) \)
(per unit reactor volume)

TRANSPORT RATE \( \left( \frac{mol}{m^3 \text{ react. s}} \right) \)
(per unit reactor volume)

- Gas - liquid \( : K_1 a_B \left( \frac{A_g}{H_a} - A_l \right) \)

- Liquid - solid \( : k_s a_p \left( A_l - A_s \right) \)

OVERALL (APPARENT) RATE \( \left( \frac{mol}{m^3 \text{ react.s}} \right) : \)

\[
R_A = \eta_o k_v \left( 1 - \varepsilon_B \right) \frac{A_g}{H_a} = \frac{A_g}{H_a} \left( \frac{1}{K_i a_B} + \frac{1}{k_s a_p} + \frac{1}{(1 - \varepsilon_B) k_v \eta_p} \right)
\]
Dependence of Apparent Rate Constant ($k_{app}$) on Transport ($k_{ls}$, $\eta_p$) and Kinetic Parameters ($k_v$)

Reaction: \( A(g) + B(l) = P(l) \)

**Liquid limiting reactant (nonvolatile) – Case of completely wetted catalyst**

- Kinetic rate (per unit catalyst volume): \( k_v B (mol/\text{m}^3 \text{cat.s}) \)
- Rate in catalyst (per unit reactor volume): \( k_v \eta_p B_s (1 - \varepsilon_B) (mol/\text{m}^3 \text{react.s}) \)
- Transport rate (per unit reactor volume): \( k_{ls} (B_l - B_s) a_p (mol/\text{m}^3 \text{react.s}) \)

**Overall (apparent) rate (mol/\text{m}^3 \text{react.s})**

\[
\eta_p k_v (1 - \varepsilon_B) B_l - k_{app} B_L = \frac{B_L}{1 + \frac{1}{k_{ls} a_p + \eta_p k_v (1 - \varepsilon_B)}}
\]
Our task in catalytic reactor selection, scale-up and design is to either maximize volumetric productivity, selectivity or product concentration or an objective function of all of the above. The key to our success is the catalyst. For each reactor type considered we can plot feasible operating points on a plot of volumetric productivity versus catalyst concentration.

Clearly $\dot{m}_{v_{\text{max}}}$ is determined by transport limitations and $x_{\text{max}}$ by reactor type and flow regime.

Improving $S_a$ only improves $\dot{m}_v$ if we are not already transport limited.
Chemists or biochemists need to improve $S_a$ and together with engineers work on increasing $x_{\text{max}}$.

Engineers by manipulation of flow patterns affect $\dot{m}_{\text{max}}$.

In **Kinetically Controlled Regime**

$$\dot{m}_v \propto x, \quad S_a$$

$x_{\text{max}}$ limited by catalyst and support or matrix loading capacity for cells or enzymes

In **Transport Limited Regime**

$$\dot{m}_v \propto S_a^p, \quad x^p$$

$$0 \leq p \leq 1/2$$

Mass transfer between gas-liquid, liquid-solid etc. entirely limit $\dot{m}_v$ and set $\dot{m}_{\text{max}}$. Changes in $S_a$, do not help; alternating flow regime or contact pattern may help!

$\therefore$ **Important to know the regime of operation**
Key Multiphase Reactors

- Bubble Column
- Mechanically Agitated Tank
- Packed Column
- Trickle bed
- Three-phase fluidized bed
Bubble Column in different modes

- Single Stage
- Multi Stage
- Multi Channel
- With Motionless Mixers

- Loop Reactor
- Jet Reactor
- Downflow Bubble Column

- Three-Phase Fluidized-Bed Reactor
- Slurry Reactor
## Key Multiphase Reactor Parameters

**Main Characteristics of Different Types of Three-phase Reactor**

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Catalyst in suspension</th>
<th>Fixed bed</th>
<th>Three-phase fluidized bed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bubble column</td>
<td>Downward cocurrent</td>
<td>Upward cocurrent</td>
</tr>
<tr>
<td>$\varepsilon_p$&lt;sup&gt;(1)&lt;/sup&gt;</td>
<td>0.01</td>
<td>0.6-0.7</td>
<td>0.6-0.7</td>
</tr>
<tr>
<td>$\varepsilon_L$&lt;sup&gt;(1)&lt;/sup&gt;</td>
<td>0.8-0.9</td>
<td>0.05-0.25</td>
<td>0.2-0.3</td>
</tr>
<tr>
<td>$\varepsilon_G$&lt;sup&gt;(1)&lt;/sup&gt;</td>
<td>0.1-0.2</td>
<td>0.2-0.35</td>
<td>0.05-0.1</td>
</tr>
<tr>
<td>$d_p$ (mm)</td>
<td>$\leq 0.1$</td>
<td>1-5</td>
<td>1-5</td>
</tr>
<tr>
<td>$A_s$ (m&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>500</td>
<td>1000-2000</td>
<td>1000-2000</td>
</tr>
<tr>
<td>$A_{GL}$ (m&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>100-400</td>
<td>100-1000</td>
<td>100-1000</td>
</tr>
<tr>
<td>$\eta$ (Isothermal)</td>
<td>1</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
</tr>
</tbody>
</table>

1. The values given here correspond only to the part of the reactor occupied by the catalyst and not the entire reactor.
2. Value corresponding to special shapes of particles.

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Depending on the reaction regime one should select reactor type

- For slow reactions with or without transport limitations choose reactor with large liquid holdup e.g. bubble columns or stirred tanks
- Then create flow pattern of liquid well mixed or plug flow (by staging) depending on the reaction pathway demands

This has not been done systematically

- Stirred tanks
- Stirred tanks in series
- Bubble columns &
- Staged bubble columns

Have been used (e.g. cyclohexane oxidation).

One attempts to keep gas and liquid in plug flow, use small gas bubbles to increase $a$ and decrease gas liquid resistance.

Not explained in terms of basic reaction pathways. Unknown transport resistances.
Table VII.12. Characteristic data of equipment for gas absorption with chemical reaction in aqueous systems

<table>
<thead>
<tr>
<th>Type of gas–liquid contactor</th>
<th>Specific surface, $a$ (m$^{-1}$)</th>
<th>Volume fraction liquid phase, $\varepsilon_L$</th>
<th>$Sh = \frac{k_L d}{D_A}$</th>
<th>$(1 - \varepsilon)/a\varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>spray column</td>
<td>60</td>
<td>0.05</td>
<td>10–25</td>
<td>2-10</td>
</tr>
<tr>
<td>plate column</td>
<td>150</td>
<td>0.15</td>
<td>200–600</td>
<td>40-100</td>
</tr>
<tr>
<td>packed column</td>
<td>100</td>
<td>0.08</td>
<td>10–100</td>
<td>10-100</td>
</tr>
<tr>
<td>wetted-wall column</td>
<td>50</td>
<td>0.05</td>
<td>10–50</td>
<td>10-50</td>
</tr>
<tr>
<td>bubble column</td>
<td>20</td>
<td>0.98</td>
<td>400–1000</td>
<td>$4000 - 10^4$</td>
</tr>
<tr>
<td>agitated bubble contactor</td>
<td>200</td>
<td>0.90</td>
<td>100–500</td>
<td>150-800</td>
</tr>
<tr>
<td>Type of Reactor</td>
<td>$100 \frac{c_L}{(c_L - c_g)}$</td>
<td>$(\text{gmol/cm}^2\text{s.atm}) \times 10^4$</td>
<td>$k_z$</td>
<td>$a$</td>
</tr>
<tr>
<td>-------------------------------------</td>
<td>---------------------------------</td>
<td>--------------------------------</td>
<td>-------</td>
<td>-----</td>
</tr>
<tr>
<td>Packed columns</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- counter-current</td>
<td>2 - 25</td>
<td>0.03 - 2</td>
<td>0.4 - 2</td>
<td>0.1 - 3.5</td>
</tr>
<tr>
<td>- co-current</td>
<td>2 - 95</td>
<td>0.1 - 3</td>
<td>0.4 - 6</td>
<td>0.1 - 17</td>
</tr>
<tr>
<td>Plate columns</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- bubble cap</td>
<td>10 - 95</td>
<td>0.5 - 2</td>
<td>1.5</td>
<td>1 - 4</td>
</tr>
<tr>
<td>- siever plates</td>
<td>10 - 95</td>
<td>0.5 - 6</td>
<td>1 - 20</td>
<td>1 - 2</td>
</tr>
<tr>
<td>Bubble columns</td>
<td>60 - 98</td>
<td>0.5 - 2</td>
<td>1 - 4</td>
<td>0.5 - 6</td>
</tr>
<tr>
<td>Packed bubble columns</td>
<td>60 - 93</td>
<td>0.5 - 2</td>
<td>1 - 4</td>
<td>0.5 - 3</td>
</tr>
<tr>
<td>Tube reactors</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- horizontal and colloid</td>
<td>5 - 95</td>
<td>0.5 - 4</td>
<td>1 - 10</td>
<td>0.5 - 7</td>
</tr>
<tr>
<td>- vertical</td>
<td>5 - 95</td>
<td>0.5 - 8</td>
<td>2 - 5</td>
<td>1 - 10</td>
</tr>
<tr>
<td>Spray columns</td>
<td>2 - 20</td>
<td>0.5 - 2</td>
<td>0.7 - 1.5</td>
<td>0.1 - 1</td>
</tr>
<tr>
<td>Mechanically agitated bubble reactors</td>
<td>20 - 95</td>
<td>-</td>
<td>0.3 - 4</td>
<td>1 - 20</td>
</tr>
<tr>
<td>Submerged and plunging jet</td>
<td>94 - 99</td>
<td>-</td>
<td>0.15 - 0.5</td>
<td>0.2 - 1.2</td>
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<tr>
<td>- hydrocyclone</td>
<td>70 - 93</td>
<td>-</td>
<td>10 - 30</td>
<td>0.2 - 0.5</td>
</tr>
<tr>
<td>- ejector reactor</td>
<td>-</td>
<td>-</td>
<td>1 - 20</td>
<td>-</td>
</tr>
<tr>
<td>- Venturi</td>
<td>5 - 30</td>
<td>2 - 10</td>
<td>5 - 10</td>
<td>1.6 - 25</td>
</tr>
</tbody>
</table>

Table 1. Liquid holdup, mass transfer coefficients and effective interfacial area in gas-liquid reactors.
## Multiphase Reactor Types for Chemical, Specialty, and Petroleum Processes

<table>
<thead>
<tr>
<th>Reactor Type</th>
<th>Catalyst Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mechanically agitated tanks</td>
<td>Soluble catalysts</td>
</tr>
<tr>
<td>Multistage agitated columns</td>
<td>&amp; Powdered catalysts</td>
</tr>
<tr>
<td>Bubble columns</td>
<td></td>
</tr>
<tr>
<td>Draft-tube reactors</td>
<td></td>
</tr>
<tr>
<td>Loop reactors</td>
<td></td>
</tr>
<tr>
<td>Packed columns</td>
<td>Soluble catalysts</td>
</tr>
<tr>
<td>Trickle-beds</td>
<td>&amp; Tableted catalysts</td>
</tr>
<tr>
<td>Packed bubble columns</td>
<td></td>
</tr>
<tr>
<td>Ebullated-bed reactors</td>
<td></td>
</tr>
</tbody>
</table>

*P. L. Mills*

*Multiphase CRE*
3. Basic Design Equations for Multiphase Reactors

P.A. Ramachandran, P. L. Mills and M. P. Dudukovic
rama@wustl.edu; dudu@wustl.edu


4. Dudukovic, Mills and Ramachandran, Course Notes (1990s and 2000s)
# Types of Multiphase Reactions

<table>
<thead>
<tr>
<th>Reaction Type</th>
<th>Degree of Difficulty</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas-liquid without catalyst</td>
<td>Straightforward</td>
</tr>
<tr>
<td>Gas-liquid with soluble catalyst</td>
<td></td>
</tr>
<tr>
<td>Gas-liquid with solid catalyst</td>
<td></td>
</tr>
<tr>
<td>Gas-liquid-liquid with soluble or solid catalyst</td>
<td>Complex</td>
</tr>
<tr>
<td>Gas-liquid-liquid with soluble or solid catalyst (two liquid phases)</td>
<td></td>
</tr>
</tbody>
</table>
Hierarchy of Multiphase Reactor Models

<table>
<thead>
<tr>
<th>Model Type</th>
<th>Implementation</th>
<th>Insight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical</td>
<td>Straightforward</td>
<td>Very little</td>
</tr>
<tr>
<td>Ideal Flow Patterns</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenomenological</td>
<td>Very Difficult or Impossible</td>
<td>Significant</td>
</tr>
<tr>
<td>Volume-Averaged Conservation Laws</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Point-wise Conservation Laws</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Basic Reactor Types for Systems With Solid Catalyst (three or four phase systems)

- Systems with moving catalysts
  - stirred tank slurry systems
  - slurry bubble columns
  - loop slurry reactors
  - three phase fluidized beds (ebulated beds)

- Systems with stagnant catalysts
  - packed beds with two phase flow: down flow, up flow, counter-current flow
  - monoliths and structured packing
  - rotating packed beds
Phenomena Affecting Slurry Reactor Performance

Flow dynamics of the multi-phase dispersion
- Fluid holdups & holdup distribution
- Fluid and particle specific interfacial areas
- Bubble size & catalyst size distributions

Fluid macro-mixing
- PDF’s of RTDs for the various phases

Fluid micro-mixing
- Bubble coalescence & breakage
- Catalyst particle agglomeration & attrition

Heat transfer phenomena
- Liquid evaporation & condensation
- Fluid-to-wall, fluid-to-internal coils, etc.

Energy dissipation
- Power input from various sources (e.g., stirrers, fluid-fluid interactions,...)

Reactor Model
Phenomena Affecting Fixed-Bed Reactor Performance

Fluid dynamics of the multi-phase flows
- Flow regimes & pressure drop
- Fluid holdups & holdup distribution
- Fluid-fluid & fluid-particle specific interfacial areas
- Fluid distribution

Fluid macro-mixing
- PDF’s of RTDs for the various phases

Heat transfer phenomena
- Liquid evaporation & condensation
- Fluid-to-wall, fluid-to-internal coils, etc.

Energy dissipation
- Pressure drop
  (e.g., stirrers, fluid-fluid interactions, …)
# Elements of the Reactor Model

<table>
<thead>
<tr>
<th>Micro or Local Analysis</th>
<th>Macro or Global Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Gas - liquid mass transfer</td>
<td>• Flow patterns for the gas, liquid, and solids</td>
</tr>
<tr>
<td>• Liquid - solid mass transfer</td>
<td>• Dynamics of gas, liquid, and solids flows</td>
</tr>
<tr>
<td>• Interparticle and inter-phase mass transfer</td>
<td>• Macro distributions of the gas, liquid and solids</td>
</tr>
<tr>
<td>• Intraparticle and intra-phase diffusion</td>
<td>• Heat exchange</td>
</tr>
<tr>
<td>• Intraparticle and intra-phase heat transfer</td>
<td>• Other types of transport phenomena</td>
</tr>
<tr>
<td>• Catalyst particle wetting</td>
<td></td>
</tr>
</tbody>
</table>
Reactor Design Variables

Reactor = f (Process Variables, Reaction Rates, Flow Patterns)

- Conversion
- Selectivity
- Activity

Feed: \(Q_{\text{in}}, T_{\text{in}}, C_{\text{in}}\)

Product: \(Q_{\text{out}}, T_{\text{out}}, C_{\text{out}}\)

Reactor Performance Variables:
- Flow rates
- Kinetics
- Inlet C & T
- Transport
- Heat exchange
- Macro
- Micro

Heat exchange
## Idealized Mixing Models for Multi-phase (Three Phase) Reactors

<table>
<thead>
<tr>
<th>Model</th>
<th>Gas-Phase</th>
<th>Liquid Phase</th>
<th>Solid-Phase</th>
<th>Reactor Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Plug-flow</td>
<td>Plug-flow</td>
<td>Fixed</td>
<td>Trickle-Bed, Flooded-Bed</td>
</tr>
<tr>
<td>2</td>
<td>Back mixed</td>
<td>Back mixed</td>
<td>Back mixed</td>
<td>Mechanically agitated</td>
</tr>
<tr>
<td>3</td>
<td>Plug-Flow</td>
<td>Back mixed</td>
<td>Back mixed</td>
<td>Bubble column, Bullated - bed, Gas-Lift &amp; Loop</td>
</tr>
</tbody>
</table>
Ideal Flow Patterns in Multiphase Reactors

Example: Mechanically Agitated Reactors

\[ \begin{align*}
V_R &= V_G + V_L + V_C \\
1 &= \varepsilon_G + \varepsilon_L + \varepsilon_C \\
\tau_G &= \frac{V_r \varepsilon_G}{Q_G} \\
\tau_L &= \frac{V_r (1 - \varepsilon_G - \varepsilon_L)}{Q_L}
\end{align*} \]
First Absolute Moment of the Tracer Response for Multi-phase Systems

For a single mobile phase in contact with $p$ stagnant phases:

$$\mu_1 = \frac{V_1 + \sum_{j=2}^{p} K_{1j} V_j}{Q_1}$$

For $p$ mobile phases in contact with $p - 1$ mobile phases:

$$\mu_1 = \frac{V_1 + \sum_{j=2}^{p} K_{1j} V_j}{Q_1 + \sum_{j=2}^{p} K_{1j} Q_j}$$

$$K_{1j} = \left( \frac{C_j}{C_1} \right)_{\text{equil.}}$$

is the partition coefficient of the tracer between phase 1 and j
“For any system where the covariance of sojourn times is zero (i.e., when the tracer leaves and re-enters the flowing stream at the same spatial position), the PDF of sojourn times in the reaction environment can be obtained from the exit-age PDF for a non-adsorbing tracer that remains confined to the flowing phase external to other phases present in the system.”

For a first-order process:

$$1 - X_A = \int_0^\infty e^{-H_p(k_c)t} E_{ext}(t) \, dt$$

$$H_p(k_c) = \text{pdf for the stagnant phase}$$

$$= \int_0^\infty e^{-\left(k_W W / Q_1\right)t} E_{ext}(t) \, dt$$
Illustrations of Ideal-Mixing Models for Multiphase Reactors

- **Stirred tank**
  - \( \Delta z \)
  - G
  - L
  - Plug-flow of gas
  - Backmixed liquid & catalyst
  - Batch catalyst
  - Catalyst is fully wetted

- **Bubble Column**
  - \( \Delta z \)
  - G
  - L
  - Plug-flow of gas
  - Backmixed liquid & catalyst
  - Batch catalyst
  - Catalyst is fully wetted

- **Trickle - Bed**
  - \( \Delta z \)
  - G
  - L
  - Plug-flow of gas
  - Plug-flow of liquid
  - Fixed-bed of catalyst
  - Catalyst is fully wetted

- **Floated - Bed**
Limiting Forms of Intrinsic Reaction Rates

Reaction Scheme: A (g) + vB (l) \rightarrow C (l)

2nd Order React.: \[ R_A = k_{11} C_{Ae} C_{Be} \left( \frac{\text{moles A}}{\text{g cat.} \cdot \text{s}} \right) \]

\[ R_B = v k_{11} C_{Ae} C_{Be} = v R_A \left( \frac{\text{moles B}}{\text{g cat.} \cdot \text{s}} \right) \]

Equivalent Form:

\[ R_A = k_{11} A^* B_e \left[ C_{Ae} = A^* ; C_{Be} = B_e \right] \]

Gas Limiting:

\[ R_A = (k_{11} B_e) A^* = k_i A^* \left[ k_i = k_{11} B_e \right] \]

\[ \Rightarrow v A^* \ll B_e \]

Liquid Limiting:

\[ R_B = v (k_{11} A^*) B_e = v k_i B_e \left[ k_i = k_{11} A^* \right] \]

\[ \Rightarrow B_e \ll v A^* \]

Gas & Liquid Both Limiting:

\[ R_A = k_{11} A^* B_e \]

\[ R_B = v R_A = v k_{11} A^* B_e \]

\[ \Rightarrow v A^* \ll B_e \]
Gas Limiting Reactant and Plug-Flow of Liquid

**Reaction Scheme:** \( A (g) + vB (l) \rightarrow C (l) \)

**Key Assumptions**

1. Gaseous reactant is limiting
2. First-order reaction wrt dissolved gas
3. Constant gas-phase concentration
4. Plug-flow of liquid
5. Isothermal operation
6. Liquid is nonvolatile
7. Catalyst concentration is constant
8. Finite gas-liquid, liquid-solid, and intraparticle gradients

\[
\frac{C_B}{C_A} >> 1 \quad D_{B_L} C_B / vD_{A_L} C_A >> 1
\]
Gas Reactant Limiting and Plug Flow of Liquid

Constant gas phase concentration \( \rightarrow \) valid for pure gas at high flow rate

\[
\frac{dz}{dz} = k_{\text{rev}} \frac{A}{A} \left( \frac{A^*}{A} \right) A_r dz - k_s a_p \left( A_l - A_s \right) A_r dz = 0
\]

(1)

Dividing by \( A_r dz \) and taking limit \( dz \rightarrow \infty \)

\[
-(\frac{Q_l A_l}{A_r}) \left( \frac{dA_l}{dz} \right) + K_{l \text{ab}} (A^* - A_x) = \frac{Q_s a_p}{A_r} (A_x - A_s) \quad u_x = \frac{Q_s}{A_r}
\]

(3)

(4)
At the catalyst surface:

\[ \text{net Rate of} \]
\[ \left( \text{Liquid-Solid Transport} \right) = \left( \text{Rate of Rxn at the catalyst surface} \right) \]
\[ \dot{q}_s ap (A_e - A_s) \left[ \text{mole} \cdot \text{m}^{-3} \cdot \text{h}^{-1} \cdot \text{g}^{-1} \cdot \text{s} \right] = \eta_c q_i A_s \left[ \frac{\text{mole} \cdot \text{s}}{\text{m}^2 \cdot \text{g} \cdot \text{atm} \cdot \text{s}} \right] \cdot W \left[ \frac{\text{g cat}}{\text{m}^2 \cdot \text{liquid}} \right] \]

\[ \sum \text{Summary} \]

\[ \eta_c = \eta_p \] particle effectiveness factor

\[ -u_e \frac{dA_e}{dz} + k_{qb} (A^e - A_e) = \dot{q}_s ap (A_e - A_s) \] ... (1)

\[ \dot{q}_s ap (A_e - A_s) = \eta_c q_i W A_s \] \( \text{conc. of dissolved} \)
\( \text{gas at the reactor inlet} \)

at \( z = 0 \) [inlet]: \( A_e = A_{ei} \)

For Reactant B:
\[ (\Phi B_e)_2 - (\Phi B_e)_3 + \Delta \dot{z} = \eta_c u_e \frac{q_i W A_s}{A_r} A_{ei} \cdot \xi_e \]
\[ \text{div by} \ A_r, \text{take limit} \ a_r \Delta \dot{z} \to 0 \]
\[ -u_e \frac{dB_e}{dz} = \eta_c u_e \frac{q_i W A_s}{A_r} \] ... (2)

at \( z = 0 \) [inlet]: \( B_e = B_{ei} \)
Gas Reactant Limiting and Plug Flow of Liquid
Solving the Model Equations

\[ \frac{\partial}{\partial \eta} \left( \rho_s \alpha_p (A_e - A_s) \right) + \frac{\partial}{\partial \eta} \left( \rho_s \alpha_p \frac{A_e}{\eta_c \rho, w + \rho_s \alpha_p} \right) = \frac{\partial}{\partial \eta} \left( \rho_s \alpha_p \frac{A_e}{\eta_c \rho, w + \rho_s \alpha_p} \right) \]

Solve for \( A_s \in [A_e - A_s] \)

\[ A_s = \frac{D_s \alpha_p A_e}{\eta_c \rho, w + \rho_s \alpha_p} \]

\[ A_e - A_s = \frac{\rho_s \alpha_p A_e}{\eta_c \rho, w + \rho_s \alpha_p} \]

\[ -u_e \frac{dA_e}{d\eta} + K_{LQ} A_e^x = \left( K_{LQ} + \frac{1}{\rho_s \alpha_p \eta_c \rho, w} \right) A_e \]

Let \( \eta = \frac{\bar{z}}{L} = \text{dimensionless axial coordinate} \)

\[ -u_e \frac{dA_e}{d\eta} + K_{LQ} A_e^x = \left( K_{LQ} + \frac{1}{\rho_s \alpha_p \eta_c \rho, w} \right) A_e \]

\[ 0 < \eta < 1 \]

\[ \frac{dA_e}{d\eta} + (\alpha_g + \beta_s) A_e = \alpha_e A_e^x \]

\[ \alpha_e = \frac{K_{LQ} L}{u_e} \]

\[ \beta_s = \frac{\alpha_s \alpha_r}{\alpha_r + \alpha_s} \]

\[ \alpha_r = \frac{\rho_s \alpha_p \eta_c \rho, w}{u_e} \]

\[ \frac{A_e}{A_e^x} = \frac{\alpha_e}{\alpha_g + \beta_s} \]

\[ \frac{A_e^x}{A_e} = \frac{\alpha_g + \beta_s}{\alpha_e} \]

\[ \frac{\alpha_g + \beta_s}{\alpha_e} \]

Dimensionless concentration of dissolved gas
Concept of Reactor Efficiency

\[ \eta_R = \frac{\text{Rate of rxn in the Entire Reactor with Transport Effects}}{\text{Maximum Possible Rate}} \]

\[ \eta_R = \frac{A_e}{A^*} = \frac{a_{el}}{a_{el} + \beta_{es}} \]

\[ \eta_R = \frac{\beta_{es}}{\alpha_r (\alpha_{el} + \beta_{es})} \left[ \alpha_{el} + \left( a_{el} - \frac{\alpha_{el}}{\alpha_{el} + \beta_{es}} \right) \right] \]

\[ \int_0^1 \frac{A_e(\eta) d\eta}{A^*} = \int_0^1 a_{el}(\eta) d\eta = \int_0^1 a_{el}(\eta) d\eta \]
Conversion of Reactant B
(in terms of Reactor Efficiency)

From eq (3):

\[-u_x \frac{dB_x}{d \eta} = \eta_c \nu_x \frac{L}{W} A_x\]

\[-\int_{B_{10}}^{B_x} \frac{d B_x}{d \eta} = \frac{\eta_c \nu_x L}{u_x (u_x/\xi)} \int_{0}^{L} A_x(\eta)\,d\eta\]

\[B_x = \frac{B_{10} - B_{10}}{B_{10}} = \frac{\nu_x L}{u_x/\xi} \int_{0}^{1} A_x(\eta)\,d\eta\]

\[= \frac{\nu_x L}{B_{10}} \int_{0}^{1} \frac{A_x(\eta)}{u_x/\xi} \,d\eta\]

\[= \frac{\nu A_x}{B_{10}} \int_{0}^{1} \frac{u_x/\xi}{\eta c \nu_x L/\xi} \,d\eta\]

\[= \frac{\nu A_x}{B_{10}} \int_{0}^{1} \frac{A_x(\eta)}{\eta c \nu_x L/\xi} \,d\eta\]

\[= \frac{\nu A_x}{B_{10}} \int_{0}^{1} \frac{A_x(\eta)}{\eta c \nu_x L/\xi} \,d\eta\]

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\[= \frac{\nu A_x}{B_{10}} \int_{0}^{1} \frac{A_x(\eta)}{\eta c \nu_x L/\xi} \,d\eta\]
Gas Reactant Limiting and Backmixed Liquid

**Key Assumptions**

1. Gaseous reactant is limiting
2. First-order reaction wrt dissolved gas
3. Constant gas-phase concentration
4. Liquid and catalyst are backmixed
5. Isothermal operation
6. Liquid is nonvolatile
7. Catalyst concentration is constant
8. Finite gas-liquid, liquid-solid, and intraparticle gradients
Gas Reactant Limiting and Backmixed Liquid

Concentration or Axial Height

Relative distance from catalyst particle

- Concentration of dissolved gas in the liquid bulk is constant \([\neq f(z)] \quad [=A_{l,0}]\)
- Concentration of liquid reactant in the liquid bulk is constant \([\neq f(z)] \quad [=B_{l,0}]\)

**A in liquid bulk**: Analysis is similar to the previous case

\[
\left( Q \frac{x^{3/4} \cdot A}{s} \cdot \text{mole A} \right) - \left( Q \cdot A_{l_0} \right) + K_{A_B} \left( A^n - A_{l_0} \right) \frac{\text{mole A}}{m^3 \cdot s} \cdot \frac{1}{s} = 0 \quad (1)
\]

**net input by flow**

input by gas-liquid transport

loss by liquid-solid transport
Gas Reactant Limiting and Backmixed Liquid

A at the catalyst surface:

\[
\frac{\rho_s \epsilon_p (A_{e0} - A_s)}{m^2 \text{mole}^{-1} \text{g}^{-1} \text{cm}^{-2} \text{s}^{-1}} = \eta_c \frac{k_1}{\epsilon_1} A_s \left[ \frac{\text{mole A}}{\text{g catalyst}} \right] w \left[ \frac{\text{g catalyst}}{\text{cm}^2} \right] \ldots \quad (2)
\]

\[
\text{net rate of} \quad \frac{(\text{rate of rxn of A})}{(\text{liquid-solid transport})} = \frac{\text{rate of rxn of A at the catalyst surface}}{c_2 (i) \text{ by } V_L (\approx V_r) \text{ and rewrite (1) & (2) -}}
\]

\[
\frac{Q_e}{\sqrt{F}} (A_{e_i} - A_{e_0}) + K_{eB} (A_c - A_{e_0}) = \rho_s \epsilon_p (A_{e_0} - A_s) \ldots \quad (1.1)
\]

\[
\rho_s \epsilon_p (A_{e_0} - A_s) = \eta_c \frac{k_1}{\epsilon_1} A_s \ldots \quad (2)
\]

For Reactant B:

\[
\left( \text{Net input by flow} \right) = \left( \text{Rate of rxn of B at the catalyst surface} \right) \quad \text{Note: No transport to gas since B is non-volatile}
\]

\[
\frac{Q_e}{\sqrt{F}} \left( B_{e_i} - B_{e_0} \right) - \left( Q_e B_{e_0} \right) = \eta_c \frac{k_1}{\epsilon_1} A_s w \left[ \frac{\text{mole B}}{\text{m}^2 \text{g}^{-1} \text{s}^{-1}} \right] \left[ \frac{\text{g mole B}}{V_L \sqrt{F}} \right] \ldots \quad (3)
\]

\[
\frac{Q_e}{\sqrt{F}} (B_{e_i} - B_{e_0}) = \nu \eta_c \frac{k_1}{\epsilon_1} w A_s \ldots \quad (4)
\]
Gas Reactant Limiting and Backmixed Liquid

Solving the Model Equations

\[
\begin{align*}
\Delta s_{ap} (A_{lo} - A_s) &= \eta_c \frac{L}{w} \Delta s \\
A_s &= \frac{\Delta s_{ap} A_{lo}}{\eta_c k_{i,w} + \Delta s_{ap}} \quad \therefore A_{lo} - A_s &= \frac{\frac{L}{w} \eta_c A_{lo}}{\eta_c k_{i,w} + \Delta s_{ap}} \\
\frac{\omega_k}{v_k} (A_{li} - A_{lo}) + K_{lqB} A^* &= \left( K_{lqB} + \frac{1}{\Delta s_{ap}} + \frac{1}{\eta_c k_{i,w}} \right) A_{lo}
\end{align*}
\]

Solve for \( A_{lo} / A^* \) to obtain

\[
\begin{align*}
A_{lo} &= \frac{A_{li} / A^* + \alpha_{ge} \beta_{es}}{1 + \alpha_{ge} + \beta_{es}} \\
\alpha_{ge} &= \frac{K_{lqB} L}{u_k} \quad \alpha_r = \frac{L}{w} \eta_c \frac{L}{u_k} \\
\beta_{es} &= \frac{\alpha_{ge} \alpha_r}{\alpha_r + \alpha_{ge}}
\end{align*}
\]

\[
X_B = \frac{Q_x (B_{li} - B_{lo})}{Q_x B_{li}} = 1 - \frac{B_{lo}}{B_{li}} \quad \text{From (4):} \quad X_B = \frac{\frac{L}{w} \eta_c k_{i,w} \Delta s_L}{u_k}
\]

Substitute for \( A_s \) & \( A_{lo} \) from above to show:

\[
X_B = g \frac{\alpha_{ge} \Delta s_L}{\alpha_r + \alpha_{ge}} \frac{A_{li} / A^* + \alpha_{ge} \beta_{es}}{1 + \alpha_{ge} + \beta_{es}} \quad \therefore g = \frac{U A^*}{B_{li}}
\]
Flow Pattern Concepts for Various Multiphase Systems

A - Single plug flow phase flow of gas or liquid with exchange between the mobile phase and stagnant phase.

*Fixed beds, Trickle-beds, packed bubble columns*

B - Single phase flow of gas or liquid with exchange between a partially backmixed stagnant phase.

*Semi-batch slurries, fluidized-beds, ebullated beds*
Flow Pattern Concepts for Various Multiphase Systems

C, D - Co current or countercurrent two-phase flow (plug flow or dispersed flow) with exchange between the phases and stagnant phase.

*Trickle-beds, packed or empty bubble columns*

E - Exchange between two flowing phases, one of which has strong internal recirculation.

*Empty bubble columns and fluidized beds*
Strategies for Multiphase Reactor Selection

- **Strategy level I: Catalyst design strategy**
  - gas-solid systems: catalyst particle size, shape, porous structure, distribution of active material
  - gas-liquid systems: choice of gas-dispersed or liquid-dispersed systems, ratio between liquid-phase bulk volume and liquid-phase diffusion layer volume

- **Strategy level II: Injection and dispersion strategies**
  - (a) reactant and energy injection: batch, continuous, pulsed, staged, flow reversal
  - (b) state of mixedness of concentrations and temperature: well-mixed or plug flow
  - (c) separation of product or energy in situ
  - (d) contacting flow pattern: co-, counter-, cross-current

- **Strategy level III: Choice of hydrodynamic flow regime**
  - e.g., packed bed, bubbly flow, churn-turbulent regime, dense-phase or dilute-phase riser transport
Strategies for Multiphase Reactor Selection

Two-Film Theory: Mass and Heat Transfer

\[ C_i^g(j), T^g(J) \]
\[ \text{Gas Bulk} \]
\[ N_{i,(j)}^f \bigg|_{X=0} \]
\[ q_{i,(j)}^f \bigg|_{X=0} \]
\[ C_i^g(j-1), T^g(J-1) \]

\[ \text{Gas Film} \]
\[ \text{Liquid Film} \]
\[ \text{Cell J}^{th} \]
\[ D_i \frac{d^2 C_i^f}{dx^2} = -\sum_{j=1}^{NR} u_{ji} R_j^f \]
\[ \kappa \frac{d^2 T^f}{dx^2} = \sum_{j=1}^{NR} R_j^f (-\Delta H_R) \]

\[ q_{i,(j)}^f \bigg|_{X=1} \]
\[ N_{i,(j)}^f \bigg|_{X=1} \]

\[ \text{Heat Film} \]
\[ \text{Liquid Bulk} \]
\[ \delta_m \]
\[ \delta_h \]
\[ C_i^L(j-1), T^L(J-1) \]
Gas-Liquid Film Model: Mass Transfer

B.C.1

\[ D_i \frac{d^2 C_i^f}{dZ^2} = -\sum_{j=1}^{NR} \nu_{ji} R_j \]

\[ \text{Bi}_{m,i} \left[ c_{g,i}^* - c_i^f \right|_{\xi = 0} = \frac{d c_i^f}{d \xi} \right|_{\xi = 0} \]

B.C.2: Dirichlet conditions

\[ C_{i,z=0}^g = H_i^f C_{i,z=0}^f \]

Solubility or Violability

\[ H_i^f = H_i^{ref} \exp \left[ -\frac{\Delta H_{si}}{R} \left( \frac{1}{T_{Z=0}^f} - \frac{1}{T_{ref}} \right) \right] = H_{ref} h(\theta_{\xi=0}^f) \]
Gas-Liquid Film Model: Heat Transfer

\[ \lambda_L \left( \frac{d^2 T^f}{dZ^2} \right) = \sum_{j=1}^{NR} (-\Delta H_{r,j})(R_j) \]

\[ -\lambda_L \left. \frac{dT^f}{dZ} \right|_{Z=0} = h_g (T_{\text{out}} - T^f_{Z=0}) + \sum_{i=1}^{NS} (-\Delta H_{s,i})(-D_i) \left. \frac{dC^f_i}{dZ} \right|_{Z=0} \]

\[ -\lambda_L \left. \frac{dT^f}{dZ} \right|_{Z=\delta_h} = -\lambda_L \left( \frac{T^L - T^f_{Z=\delta_m}}{\delta_h - \delta_m} \right) \]
Bubble Column Mixing Cell Model

- Cells arranged in different modes to simulate the averaged flow patterns
- These averaged flow patterns can be obtained from the CFD simulations

Cells in series: G and L mixed flow

Cells in series: G plug flow, L mixed flow

Cells in series-parallel combination

Prototype cell

Exchange between Upward and downward moving liquid
Prototype Gas Cell

Prototype Liquid Cell

**Novel features**

- Non-isothermal effects in the gas-liquid film and in the bulk liquid
- Effect of volatility of the liquid phase reactant on the interfacial properties
- Interfacial region modeled using film theory and solved using integral formulation of the Boundary Element Method (BEM)
- Model validity over a wide range of dimensionless numbers like Hatta, Arrhenius, solubility parameter, Biot, Damköhler
- Application to oxidation reactions like cyclohexane, p-xylene, etc. in stirred tank and stirred tank in series

*(Ruthiya et al. under progress)*

*(Kongto, Comp.&Chem.Eng., 2005)*
## Gas-Liquid Reactor Model

### Non-Dimensionalized parameters

#### Variables

\[
c_i^g = \frac{C_i^g}{C^g_{i,\text{ref}}} \quad \text{and} \quad c_i^f = \frac{C_i^f}{C^f_{i,\text{ref}}}
\]

\[
\bar{\xi} = \frac{Z}{\delta_m}
\]

\[
\Theta^g = \frac{T^g}{T_{\text{ref}}}
\]

\[
\Theta^L = \frac{T^L}{T_{\text{ref}}}
\]

\[
f^g = \frac{Q^g}{Q_{\text{ref}}}
\]

\[
\gamma_j = \frac{u^L}{u^g H_{i,\text{ref}}}
\]

### Effective G/L ratio

#### Reaction based

- **Heat of reaction parameter**
  \[
  B_j = -\frac{\Delta H_{r,j} C_{\text{ref}}}{\rho L \overline{C}^L T_{\text{ref}}}
  \]

- **Bulk reaction number**
  \[
  M_j = \frac{V_{\text{cell}} (e_L - a \delta_m)}{Q^L C_{\text{ref}}} R_j
  \]

- **Hatta number**
  \[
  H_j^2 = \frac{R_{j,\text{ref}} \delta_m^2}{D_i C_{\text{ref}}}
  \]

- **Arrhenius number**
  \[
  \gamma_j = \frac{E_{aj}}{RT_{\text{ref}}}
  \]

- **Heat of reaction parameter**
  \[
  \beta_j = \frac{(-\Delta H_{r,j}) D_{\text{ref}} C_{\text{ref}}}{\lambda L T_{\text{ref}}}
  \]

#### Mass transfer based

- **Damkohler number**
  \[
  \alpha_{gL} = \frac{a V_{\text{cell}} k_L}{u^L A_r}
  \]

- **Biot number**
  \[
  B_{iM,j} = \frac{\delta_m H_{i,\text{ref}} k_g}{D_i}
  \]

- **Diffusivities ratio**
  \[
  s_i = \frac{D_i}{D_{\text{ref}}}
  \]

#### Heat transfer based

- **Biot number**
  \[
  B_{iH} = \frac{h_g \delta_m}{\lambda_L}
  \]

- **Heat of solution parameter**
  \[
  \beta_{s,j} = \frac{(-\Delta H_{s,j}) D_i C_{i,\text{ref}}}{\lambda L T_{\text{ref}}}
  \]

- **Liquid heat transfer number**
  \[
  S^L = \frac{a_{gL} V_{\text{cell}} \lambda_i}{m_{L} \overline{C}^L \delta_m}
  \]

- **Gas heat transfer number**
  \[
  S^g = \frac{a_{gL} V_{\text{cell}} \lambda_i}{m_{g} \delta_m \overline{C}^g_{p,g}}
  \]

- **Lewis number**
  \[
  Le = \lambda_L \overline{\rho L \overline{C}^L p} D_{\text{ref}}
  \]
Studies for Complex Gas-Liquid Reactions


Types of Heat Generation

1. *Heat of solution* ($\Delta H_s$), which is generated at the gas-liquid interface due to the physical process of gas dissolution.

2. *Heat of vaporization* ($\Delta H_v$), of volatile reactants due to evaporative cooling in oxidation reaction.

3. *Heat of reaction* ($\Delta H_r$), which is generated in the film near the gas-liquid interface (for fast reactions), or in the bulk liquid (for slow reactions).

• Uncontrolled heat generation can lead to:
  1. Undesired production of by-products
  2. Thermally-induced product decomposition
  3. Increased rate of catalyst deactivation
  4. Local hot spots and excess vapor generation
  5. Reactor runaway and unsafe operation

• Modeling of simultaneous mass and heat transport effects in the film is necessary for accurate predictions.
How Heat Generation Can Affect Mass Transfer Rates in Gas-Liquid Reactions

1. Physical, transport, and thermodynamic properties of the reaction medium exhibit various degrees of temperature dependence.

2. Kinetic parameters exhibit exponential dependence on the local temperature.

3. Instabilities at the gas-liquid reaction interface that are driven by surface tension effects (Marangoni effect) and density effects.
Typical Systems with Notable Heat Effects

### A. Gas-Liquid Systems

<table>
<thead>
<tr>
<th></th>
<th>Heat of Reaction (kcal/mol)</th>
<th>Heat of Solution (kcal/mol)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Absorption of ammonia in water</td>
<td>7.6</td>
<td>Chiang and Toor (1964)</td>
</tr>
<tr>
<td>2.</td>
<td>Absorption of carbon dioxide in a solution of ammonia</td>
<td>22.2</td>
<td>Shreve (1956)</td>
</tr>
<tr>
<td>3.</td>
<td>Absorption of sulfur trioxide in water</td>
<td>31.0</td>
<td>Shreve (1956)</td>
</tr>
<tr>
<td>4.</td>
<td>Absorption of nitric oxide in water</td>
<td>10.5</td>
<td>Shreve (1956)</td>
</tr>
<tr>
<td>5.</td>
<td>Absorption of ammonia in dilute nitric acid</td>
<td>20.6</td>
<td>Shreve (1956)</td>
</tr>
<tr>
<td>6.</td>
<td>Chlorination of n-decane</td>
<td>24.0-27.0</td>
<td>Ding et al. (1974)</td>
</tr>
<tr>
<td>7.</td>
<td>Chlorination of toluene</td>
<td>30.0</td>
<td>Groggins (1952)</td>
</tr>
<tr>
<td>8.</td>
<td>Absorption of hydrochloric acid in ethylene glycol</td>
<td>18.5</td>
<td>Clegg and Kilgannon (1971)</td>
</tr>
<tr>
<td>10.</td>
<td>Absorption of chlorine in benzene</td>
<td>7.46</td>
<td>Lohse and Deckwer (1981)</td>
</tr>
<tr>
<td>11.</td>
<td>Absorption of chlorine in toluene</td>
<td>5.7</td>
<td>Lohse and Deckwer (1981)</td>
</tr>
<tr>
<td>16.</td>
<td>Chlorination of organic compounds</td>
<td>23.0-25.0</td>
<td>Groggins (1952)</td>
</tr>
</tbody>
</table>

### B. Gas-Liquid-Solid Systems

1. Reduction of nitrobenzene over iron catalyst  
   127.0 kcal/mol nitrobenzene  
   Groggins (1952)  
   Shreve (1956)
2. Acetylene from calcium carbide  
   30.0 kcal/mol acetylene  
   Shah and Paraskos (1975)
3. Residual hydrodesulfurization  
   ~ 1.8 kcal/gm of sulfur  
   Shah and Paraskos (1975)
4. Gas oil hydrocracking  
   ~ 0.14 kcal/gm oil converted  
   Shah and Paraskos (1975)
5. Shale oil dehydrogenation  
   ~ 1.9 kcal/gm of nitrogen  
   Shah and Paraskos (1975)  
   Galli and Bucey (1982)
6. Fischer-Tropsch reaction  
   ~ 48.9 kcal/mol hydrogen  
   Groggins (1952)
7. Reduction of nitroxylen over Ni catalyst  
   ~ 116.0 kcal/mol of nitroxylen  
   Groggins (1952)
8. Coal liquefaction  
   ~ 5.0-7.0 kcal/mol hydrogen consumed  
   Singh et al. (1981a)
9. Hydrocracking operation  
   ~ 533.0 kcal/m³ of hydrogen consumed  
   Lovasic and Saha (1982)
10. Fermentation of glucose  
    ~ 31.0 kcal/mol glucose  
    Shreve (1956)

## Properties and Interfacial Temperature Rise for Some Practical Systems

<table>
<thead>
<tr>
<th>Reference</th>
<th>Theoretical (T)/Experimental (E)</th>
<th>( \rho_f ) (g/m³)</th>
<th>( \Delta_p ) (cal/(g°C))</th>
<th>( D \times 10^4 ) (cm²/s)</th>
<th>( \alpha \times 10^4 ) (cm²/s)</th>
<th>( H_A ) (kcal/mol)</th>
<th>( H_R ) (kcal/mol)</th>
<th>Solubility (mol/cc)</th>
<th>Interfacial Temp. Rise (°C)</th>
<th>System</th>
</tr>
</thead>
<tbody>
<tr>
<td>Danckwerts (1970)</td>
<td>T</td>
<td>1.0</td>
<td>1.0</td>
<td>1.5</td>
<td>1.46</td>
<td>5.0</td>
<td>—</td>
<td>4 \times 10^{-5}</td>
<td>0.02</td>
<td>CO₂/water</td>
</tr>
<tr>
<td>Danckwerts (1970)</td>
<td>T</td>
<td>1.0</td>
<td>1.0</td>
<td>1.5</td>
<td>1.46</td>
<td>4.7</td>
<td>1.5</td>
<td>3 \times 10^{-3}</td>
<td>0.21</td>
<td>CO₂/NaOH (LM)</td>
</tr>
<tr>
<td>Danckwerts (1970)</td>
<td>T</td>
<td>1.0</td>
<td>1.0</td>
<td>1.8</td>
<td>1.46</td>
<td>4.75</td>
<td>6.3</td>
<td>—</td>
<td>0.615*</td>
<td>H₂S/NH₃ (soln)</td>
</tr>
<tr>
<td>Clegg et al. (1969)</td>
<td>E</td>
<td>0.866</td>
<td>0.4</td>
<td>3.40</td>
<td>1.03</td>
<td>5.5</td>
<td>30.0</td>
<td>LA**</td>
<td>7.05*</td>
<td>Cl₂/Toluene</td>
</tr>
<tr>
<td>Chiang and Toor (1964)</td>
<td>T</td>
<td>1.0</td>
<td>1.0</td>
<td>3.55</td>
<td>1.5</td>
<td>7.63</td>
<td>—</td>
<td>LA**</td>
<td>17.0</td>
<td>NH₃/Water</td>
</tr>
<tr>
<td>Clegg and Kilgannon (1971)</td>
<td>E</td>
<td>1.11</td>
<td>0.580</td>
<td>0.147</td>
<td>1.05</td>
<td>—</td>
<td>18.5</td>
<td>LA**</td>
<td>20.0</td>
<td>HCl/Ethylene Glycol</td>
</tr>
<tr>
<td>Clegg and Mann (1972)</td>
<td>E</td>
<td>1.584</td>
<td>0.192</td>
<td>2.88</td>
<td>1.32</td>
<td>5.47</td>
<td>—</td>
<td>1.85 \times 10^{-3}</td>
<td>10.0</td>
<td>Cl₂/Carbon Tetra-chloride (CCl₄)</td>
</tr>
</tbody>
</table>

*Maximum possible temperature rise.
**Linear approximation of solubility with temperature.

**Laboratory Reactors for Gas - Liquid Reaction Kinetics**

<table>
<thead>
<tr>
<th>Model</th>
<th>Laminar Jet</th>
<th>Wetted Wall Column</th>
<th>String of Disks</th>
<th>Stirred Cell</th>
<th>Rotating Drum</th>
<th>Modified Stirred Cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scheme</td>
<td></td>
<td>Cylinder</td>
<td>Sphere</td>
<td>Cone</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reference</td>
<td></td>
<td>Liquid</td>
<td>Gas</td>
<td>Liquid</td>
<td>Gas</td>
<td>Gas</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Liquid</td>
<td>Gas</td>
<td>Liquid</td>
<td>Liquid</td>
<td>Liquid</td>
</tr>
<tr>
<td>Bjerle et al.</td>
<td></td>
<td>Liquid</td>
<td>Gas</td>
<td>Liquid</td>
<td>Gas</td>
<td>Liquid</td>
</tr>
<tr>
<td>(1972)</td>
<td></td>
<td>Liquid</td>
<td>Gas</td>
<td>Liquid</td>
<td>Gas</td>
<td>Liquid</td>
</tr>
<tr>
<td>Roberts and Danckwerts</td>
<td></td>
<td>Davidson and Cullen (1957)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Danckwerts</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1975)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Danckwerts</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>and Alper (1958)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Danckwerts</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>and Kennedy</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1974)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
**Case 1: Single non-isothermal reaction**

**Reaction Scheme:** \( A + νB \rightarrow C \)

**GL second order reaction**

\[
\begin{align*}
D_A \frac{d^2 A}{dx^2} &= k_2 A B \\
D_B \frac{d^2 B}{dx^2} &= νk_2 A B
\end{align*}
\]

**Non-dimensionlizing**

\[
\begin{align*}
\frac{d^2 a}{dy^2} &= Ha^2 a \quad & \frac{d^2 b}{dy^2} &= \frac{Ha^2}{q} ab \\
\frac{d^2 a}{dy^2} &= q \frac{d^2 b}{dy^2}
\end{align*}
\]

\[
E = \frac{Ha}{\tanh(Ha)}
\]

For no depletion of \( B \) (interface concentration = bulk, first order reaction)

\[
b_i = \frac{1}{q} \left( q + 1 - \frac{Ha\sqrt{b_i}}{\tan(Ha\sqrt{b_i})} \right)
\]

\[
H_i^2 = \frac{\delta^2 k_2 B_0}{D_A}
\]

For depletion of \( B \)

\[
y = \frac{x}{\delta}
\]

\[
q = \frac{D_B B_0}{zD_A A^*}
\]

\[
H_i^2 = \frac{\delta^2 k_2 B_i}{D_A}
\]
Case 1: Single non-isothermal reaction

Reaction Scheme:
A + vB → C

Ha = 10, q = 0.05, γ = 22,
γs = -7.5, γvap = 2, βs=0.001,
βvap = -0.005, BiHg = 1

<table>
<thead>
<tr>
<th></th>
<th>Non-volatile</th>
<th>Volatile</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas (A)</td>
<td>0.70</td>
<td>0.76</td>
</tr>
<tr>
<td>Reactant (B)</td>
<td>0.58</td>
<td>0.33</td>
</tr>
<tr>
<td>Product (C)</td>
<td>0.42</td>
<td>0.31</td>
</tr>
<tr>
<td>Enhancement</td>
<td>13.0</td>
<td>6.7</td>
</tr>
</tbody>
</table>

- การกระจายของความเข้มข้นและอุณหภูมิในฟิล์มของเหลวสำหรับการถ่ายโอนมวลของปฏิกิริยาเดียวกันแบบ
- ผันแปรไม่ได้สำหรับระบบที่มีการระเหย (Bi_m=1.5) และไม่มีการระเหย (Bi_m=0)
Case 1: Single non-isothermal reaction

\[
Bi_{Hg} = \frac{\delta_m h_g}{K}
\]

\[
Ha^2 = \frac{k_{ref} \delta_m^2 C_B^b}{D_A}
\]
Case 2: Local Supersaturation in the film

Axial Dispersion Model (Single Phase)

Basis: Plug flow with superimposed "diffusional" or "eddy" transport in the direction of flow

\[
\frac{\partial C}{\partial t} = D_{ax} \frac{\partial^2 C}{\partial z^2} - u \frac{\partial C}{\partial z} + R
\]

@ \ z = 0 \quad u_0 C_0 = u C - D_{ax} \frac{\partial C}{\partial z}

@ \ z = L \quad \frac{\partial C}{\partial z} = 0

Let

\eta = \frac{z}{L} \quad Pe_{ax} = \frac{u L}{D_{ax}} \quad \tau = \frac{L}{u}

\tau \frac{\partial C}{\partial t} = \frac{1}{Pe_{ax}} \frac{\partial^2 C}{\partial \eta^2} - \frac{\partial C}{d\eta} + \tau R

@ \ \eta = 0 \quad C_0 = C - \frac{1}{Pe_{ax}} \frac{\partial C}{\partial \eta}

@ \ \eta = 1 \quad \frac{\partial C}{\partial \eta} = 0
Axial Dispersion Model

\[ \tau \frac{\partial C}{\partial t} = \frac{1}{Pe_{ax}} \frac{\partial^2 C}{\partial \eta^2} - \frac{\partial C}{d \eta} + \tau R \]

\[ @ \ \eta = 0 \quad C_0 = C - \frac{1}{Pe_{ax}} \frac{\partial C}{\partial \eta} \]

\[ @ \ \eta = 1 \quad \frac{\partial C}{\partial \eta} = 0 \]

- \( \lim \{C(\eta,t)\} \Rightarrow \) Plug-flow model "PFR"
  - \( \lim \{C(\eta,t)\} \Rightarrow \) Backmixed model "CFSTR"

For nonlinear \( R = \text{Rate} \), solve by numerical methods [spline collocation, etc.]

- Extend to multiphase systems by applying to each phase
- Extract \( T \) and \( Peax \) from tracer data \( \beta^2 = \frac{2}{Peax} \)
Axial Dispersion Model for the Liquid with Constant Gas-Phase Concentration - 1

Mass Balance of A in the liquid phase

\[
\begin{align*}
\text{(Net input by convection)} & \quad + \quad \text{(Net input by axial dispersion)} & \quad + \quad \text{(input by gas-liquid transport)} & \quad - \quad \text{(Loss by Liquid-solid Transport)} & \quad = \quad 0 \\
\end{align*}
\]

\[
<A_l> = \text{mean X-sectional area occupied by liquid at } z
\]

\[
\begin{align*}
&\left( Q_x \cdot \frac{m^3}{s} \cdot A_x \cdot \frac{\text{kmole}}{m^3 \cdot \text{H}_2 \cdot \text{s}} \right) \frac{z}{2^2 + \Delta z} - \left( Q_x \cdot A_x \right) \frac{z}{2^2 + \Delta z} + \\
&\left( -D_{ax} \cdot \frac{dA_x}{dz} \cdot \frac{\text{kmole}}{m^3 \cdot \text{H}_2 \cdot \text{s}} \right) \frac{z}{2^2 + \Delta z} - \left( -D_{ax} \cdot \frac{dA_x}{dz} \cdot <A^l> \right) \frac{z}{2^2 + \Delta z} \\
&+ K_l \cdot a_B \left( A_x - A_x \right) \frac{\text{kmole}}{m^3 \cdot \text{reactor}} \frac{z}{2^2 + \Delta z} + R_s \cdot a_p \left( A_x - A_s \right) \frac{\text{kmole}}{m^3 \cdot \text{reactor}} \frac{z}{2^2 + \Delta z} \\
&= \frac{b \cdot y_s \cdot \Delta \omega}{\Delta z} \text{ take limit as } \Delta z \to 0 \\
&- \frac{d}{dz} \left( \frac{Q_x}{A_x} \cdot A_x \right) + \frac{d}{dz} \left( D_{ax} \cdot \frac{dA_x}{dz} \cdot \frac{A_x}{\Delta \omega} \right) + K_l \cdot a_B \left( A_x - A_x \right) \\
&- R_s \cdot a_p \left( A_x - A_s \right) = 0 \quad - (1)
\end{align*}
\]
Axial Dispersion Model for the Liquid with Constant Gas-Phase Concentration - 2

\[
\frac{\Phi}{\varepsilon_A A_r} = \frac{\frac{u_d A_r}{\varepsilon_A A_r}}{u_d} = u_d \text{ (interstitial velocity)}
\]

\[
\frac{\langle A^L \rangle}{\varepsilon_A A_r} = \frac{\langle A^L \rangle A_r L}{\langle A^L \rangle L} = 1 \quad \text{where} \quad \varepsilon_A = \frac{V_L}{V_r} = \frac{\langle A^L \rangle L}{A_r L}
\]

Eq 1 becomes:

\[- \frac{d}{dz} \left( u_d A_d \right) + \frac{d}{dz} \left( D_{ax} \frac{dA_d}{dz} \right) + K_L a_b (A^* - A_d) - \Phi \frac{p}{p_s} (A_d - A_s) = 0 \]

Assume \( u_d \neq f(z) \) & \( D_{ax} \neq f(z) \) \( \Rightarrow \)

\[- D_{ax} \frac{d^2 A_d}{dz^2} - u_d \frac{dA_d}{dz} + K_L a_b (A^* - A_d) = \Phi \frac{p}{p_s} (A_d - A_s) \ldots (2) \]

Mass Balance of A at the Catalyst Surface:

\[ \Phi \frac{p}{p_s} (A_d - A_s) \left[ \frac{\text{kmole} A}{m^3 \text{liq.} \cdot s} \right] = \eta_c \Phi, \: \text{W} A_s \left[ \frac{\text{kmole} A}{m^3 \text{liq.} \cdot s} \right] \ldots (3) \]
Axial Dispersion Model for the Liquid with Constant Gas-Phase Concentration - 3

Mass Balance of B in the Liquid Phase

\[ \frac{\partial}{\partial z} \left( \frac{\partial B}{\partial z} \right) - \left( \frac{\partial B}{\partial z} \right) + \left( -D_{\text{ax}} \frac{\partial^2 B}{\partial z^2} \langle \Delta z \rangle \right) - \left( -D_{\text{ax}} \frac{\partial B}{\partial z} \langle \Delta z \rangle \right) \]

\[ - \frac{k_{\text{sp}} (B_e - B_s)}{\varepsilon_e A_r} \Delta z = 0 \]

\[ \Rightarrow \frac{\varepsilon_e A_r \Delta z \to \text{take limit as } \Delta z \to 0, \text{ and follow same assumptions to show that}}{\text{}} \]

\[ D_{\text{ax}} \frac{\partial^2 B}{\partial z^2} - u \frac{\partial B}{\partial z} = k_{\text{sp}} (B_e - B_s) \]

Mass Balance of B at the Catalyst Surface

\[ k_{\text{sp}} (B_e - B_s) = \eta \varepsilon_l w A_s = \Delta \tau_a \]
ADM Model: Boundary Conditions

\[ \text{at } z = 0 : \quad Q_k \frac{c^2 K_k}{5} A_{k_i} \frac{dA_{k_i}}{dz} = Q_k A_k - D_{ox} \frac{dA_k}{dz} \quad \langle A^k \rangle_{2 \Delta t} \]

\[ \langle \sigma = 0 \rangle \quad \text{at } z = 0^+ \quad \langle \sigma = 0 \rangle \quad \text{at } z = 0^+ \]

\[ \text{at } z = L \quad \frac{dA_k}{dz} = 0 \quad \text{(4b)} \]

\[ \therefore \text{eq. (4a) by } A_r \quad \text{to obtain} \]

\[ \left( \frac{Q_k}{A_r} \right) A_{k_i} = \left( \frac{Q_k}{A_r} \right) A_k - D_{ox} \frac{dA_k}{dz} \langle A^k \rangle \]

\[ \text{But: } \quad \frac{Q_k}{A_r} = \frac{u_{sl} A_r}{A_{kr}} = \frac{u_{sl}}{A_{kr}} \]

\[ \langle A^k \rangle = \frac{A^k}{A_r} \cdot L = \frac{V^k}{V_r} = \epsilon_x \]

\[ \therefore \text{at } z = 0 \quad \epsilon_x u_{k} A_{k_i} = \epsilon_x u_{k} A_k - D_{ox} \epsilon_x \frac{dA_k}{dz} \quad \text{(5a)} \]

\[ \text{or } \quad u_{k} A_{k_i} = u_k A_k - D_{ox} \frac{dA_k}{dz} \quad \text{-- -- --} \]

\[ \text{at } z = L \quad \frac{dA_k}{dz} = 0 \quad \text{(5b)} \]
Axial Dispersion Model - Summary

\[ D_{ax} \frac{d^2 A_l}{dz^2} - u_l \frac{dA_l}{dz} + k_l a_B \left( A^* - A_l \right) = k_s a_p \left( A_l - A_s \right) \]

\[ k_s a_p \left( A_l - A_s \right) = \eta_c k_1 w A_s \]

\[ @ z = 0 \quad u_l A_{li} = u_l A_l - D_{ax} \frac{dA_l}{dz} \]

\[ @ z = L \quad \frac{dA_l}{dz} = 0 \]
Comments regarding axial dispersion model (ADM)

- The model is very popular because it has only a single parameter, axial dispersion coefficient, $D_{ax}$, the value of which allows one to represent RTDs between that of a stirred tank and of a plug flow. The reactor model is usually written in dimensionless form where the Peclet number for axial dispersion is defined as:

$$Pe_{ax} = \frac{UL}{D_{ax}} = \frac{L^2 / D_{ax}}{L/\bar{U}} = \frac{characteristic\, axial\, dispersion\, time}{characteristic\, convection\, time}$$

$Pe_{ax} \rightarrow \infty$ plug flow

$Pe_{ax} \rightarrow 0$ complete back mixing
ADM comments continued-1

• Use of ADM was popularized by the work of Danckwerts, Levenspiel, Bischoff, j. Smith and many others in the 1960s through 1970s.

• Since $D_{ax}$ encompasses the effects of the convective flow pattern, eddy as well as molecular diffusion, prediction of the Axial Peclet Number with scale-up is extremely difficult as a theoretical basis exists only for laminar and turbulent single phase flows in pipes.

• Moreover use of ADM as a model for the reactor is only advisable for systems of Peclet larger than 5 (preferably 10).
• However, ADM leads to the boundary value problem for calculation of reactor performance with inlet boundary conditions which are needed to preserve the mass balance but unrealistic for actual systems. Since at large Peclet numbers for axial dispersion the RTD is narrow, reactor performance can be calculated more effectively by a tanks in series model or segregated flow model.
ADM comments continued -3

- ADM is not suitable for packed beds, since there is really never any dispersion upstream of the point of injection (Hiby showed this conclusively in the 1960s); a parabolic equation does not describe the physics of flow in packed beds well. A hyperbolic equation approach (wave model) should be used as shown recently by Westerterp and coworkers (AICHE Journal in the 1990s).

- ADM is not suitable for bubble column flows as the physics of flow requires at least a two dimensional convection- eddy diffusion model for both the liquid and gas phase (Degaleesan and Dudukovic, AICHEJ in 1990s).

- ADM is clearly unsuitable for multiphase stirred tanks
Final Comments

• To improve predictability of multiphase reactor models and reduce the risk of scale-up, they should be increasingly developed based on proper physical description of hydrodynamics in these systems.

• Improved reactor scale descriptions coupled with advances on molecular and single eddy (single particle) scale will facilitate the implementation of novel environmentally benign technologies by reducing the risk of such implementations.
Return to Systems Approach in selecting best reactor for the task

- Expansion in capacity of a ‘best selling’ herbicide provides an opportunity to assess the current reactor and suggest a better solution
- Detailed chemistry is kept proprietary
Reaction System

- Complex - multiple reactions
- Oxidation in aqueous solution

**SIMPLIFIED MECHANISM**

\[ A(t) + \frac{1}{2} O_2(g) \xrightarrow{C} P(t) + R(t) + CO_2(g) \]
\[ R(t) + \frac{1}{2} O_2(g) \xrightarrow{C} S(t) \]
\[ S(t) + \frac{1}{2} O_2(g) \xrightarrow{C} CO_2(g) \]
\[ P(t) \xrightarrow{R,S} U(t) \]

- Wanted product P

**Current Reaction:**

- batch stirred liquid with catalyst suspension
- continuous gas flow
- subsequent catalyst separation
- poor volumetric productivity and selectivity
Disadvantages of Semi-Batch Slurry Reactor

- Batch nature – variable product
- Low volumetric productivity (due to low catalyst loading and limited pressure)
- Pressure limitation (shaft seal)
- High power consumption
- Poor selectivity (due to high liquid to catalyst volume ratio and undesirable homogeneous reactions)
- Catalyst filtration time consuming
- Catalyst make-up required
- Oxygen mass transfer limitations
Potential Advantages of Fixed Bed System

- Continuous flow operation
- No need for catalyst separation
- Higher catalyst to liquid volume ratio
- High pressure operation
- Lower dissipated power

- Various operations (upflow, downflow)
- Various flow regimes
- Partial wetting for gas limiting reaction
- Periodic liquid feed mode
Slurry vs Fixed Bed

• With proper design of catalyst particles a packed-bed reactor with co-current down-flow of gas and liquid both in partial wetting regime and in induced pulsing regime can far surpass the volumetric productivity and selectivity of the slurry system, yet require an order of magnitude less of the active catalyst component.

• Undesirable homogenous reactions are suppressed in the fixed bed reactor due to much higher catalyst to liquid volume ratio

• Father advantage is accomplished in fixed beds by operation at higher pressure (no moving shafts to seal).

• Fixed bed operation requires long term catalyst stability or ease of in situ regeneration.
References


References


For any process chemistry involving more than one phase one should:

- Select the best reactor flow pattern based on the kinetic scheme and mass and heat transfer requirements of the system,
- Assess the magnitude of heat and mass transfer effects on the kinetic rate
- Assess whether design requirements can be met based on ideal flow assumptions
- Develop scale-up and scale-down relations
- Quantify flow field changes with scale if needed for proper assessment of reactor performance
- Couple physically based flow and phase contacting model with kinetics