1 Model for gas-liquid reactions Based on film model

\[ A(g) + \nu B(l) \rightarrow \text{Products} \]

Governing equations are as follows:

\[ D_A \frac{d^2 C_A}{dx^2} = k_2 C_A C_B \tag{1} \]

\[ D_B \frac{d^2 C_B}{dx^2} = \nu k_2 C_A C_B \tag{2} \]

Here \( x \) is the actual distance into the film with \( x = 0 \) representing the gas-liquid interface.

We now introduce the following dimensionless parameters.

\[ a = \frac{C_A}{C_A^*} \]

where \( C_A^* \) is the equilibrium solubility of gas A in the liquid corresponding to the partial pressure of A in the bulk gas.

\[ C_A^* = \frac{p_{gA}}{H_A} \]

where \( H_A \) is the Henry’s law constant for the species A.

\[ b = \frac{C_B}{C_{Bl}} \]

where \( C_{Bl} \) is bulk liquid concentration of B.

Finally let \( \zeta \) be the dimensional distance in the film (\( = x/\delta \)). With these variables, the governing equations are the following:

\[ \frac{d^2 a}{d\zeta^2} = H a^2 ab \tag{3} \]

\[ \frac{d^2 a}{d\zeta^2} = H a^2 ab/q \tag{4} \]

where \( HA \) and \( q \) are two dimensionless quantities.

\[ HA = \delta^2 \frac{k_2 C_{Bl}}{D_A} \]
and
\[ q = \frac{D_B C_B L}{\nu D_A C_A^*} \]

Noting that \( k_L = D_A / \delta \), the Hatta number can also be expressed as:
\[ Ha^2 = \frac{D_A k_2 C_B L}{k_L} \] (5)

The boundary conditions for species A are as follows:
Case 1: No gas film resistance:
At \( \zeta = 0 \), \( C_A = C_A^* \) and Hence \( a = 1 \).
At \( \zeta = 1 \), \( C_A = C_{AL} \) is some specified value depending on the bulk processes.
In other words, \( C_{AL} \) will depend on the extent of bulk reactions, convective and dispersive flow into the bulk etc. But even for moderately fast reactions, the bulk concentration of dissolved gas turns out to be zero and we take this value to be zero. Hence \( a = 0 \) at \( \zeta = 1 \) will be used as the second boundary condition. The validity of this assumption can be checked after a solution is obtained and modified if needed.

Case 2: Gas film resistance included. A balance over the gas film provides the boundary condition:
\[ k_g (p_{gA} - p_{iA}) = -D_A \frac{dC_A}{dx} \] (6)

Also note that \( p_{iA} \) the interfacial partial pressure of A is related to the interfacial concentration of A in the liquid by Henry’s law. Thus \( C_A(x = 0) = P_{ia}/H \). Using these the boundary condition can be expressed in dimensionless form as
\[ Bi_g (1 - a_{\zeta = 0}) = -\left( \frac{da}{d\zeta} \right)_{\zeta = 0} \] (7)

where \( Bi_g = k_g H / k_L \), A Biot number for gas side mass transfer. The boundary condition is now of the Robin type. The boundary condition at \( \zeta = 1 \) is the same as before. (take as \( a = 0 \) if the reactions are reasonably fast. Otherwise a need a mass balance for A in the bulk liquid as well.)

The boundary condition for species B are specified as follows:
At \( \zeta = 0 \) we use \( db/d\zeta = 0 \) since B is non-volatile and the flux is therefore zero.
At \( \zeta = 1 \), we have \( b = 1 \).
This completes the problem definition. In order to solve this using matlab, the governing (two) equations are cast as four first order differential equation. The solution vector \( \vec{y} \) is now given by:
\[ \vec{y} = \begin{pmatrix} y_1 = a \\ y_2 = da/d\zeta \\ y_3 = b \\ y_4 = db/d\zeta \end{pmatrix} \] (8)
The matlab program to do these calculations is shown below. The program structure is similar to Thiele. Note that A and B are counterdiffusing in this case and the boundary condition section reflects these changes. The program can be used to calculate the rate of absorption or to learn how the regime of absorption changes with dimensionless parameters. Thus the program is an effective learning tool. In the following sections, these features are illustrated.

```
function hatta
% program calculates the concentration profiles for gas A
% and liquid reactant B in the film.
% 11-1-03 P. A. Ramachandran
global m q bi_gas
% The dimensionless parameters are calculated in a separate function.
% m = Hatta number, q = q parameter, bi_Gas = Biot number for gas.
t = 1.0 ; % a dummy parameter
[ m , q , bi_gas ] = calculate_these ( t ) ;
% numerical solution.
nmesh = 21 % initial mesh
nplot = nmesh ; % meshes for plotting the result.
% solution block.
x = linspace ( 0, 1, nmesh ) ;
solinit = bvpinit ( x , @guess ) % trial solution generated by guess function
sol = bvp4c (@odes, @bcs, solinit) % bvp solved,
% post processing. plot concentration profiles, find eta
x = linspace ( 0, 1, nplot) ;
y = deval(sol, x) ;
y(1,:) % concentration profiles displayed
y(3,:) % concentration profile of B
plot ( x, y(1,:) ) ; hold on ; plot (x, y(3,:)) % these are plotted.
EnhanceFactor = -y(2,1)
b_interface = y(3,1)
bi = 1. + 1/q - EnhanceFactor /q
%____________________________________________________
function yinit = guess (x)
global m q bi_gas

y1= exp(-m*x)

y2= 0. * y1
yinit = [y1
 y2
 y2
 y2] ; % some arbitrary guess values here
%-------------------------------------------------------
```
function dydx = odes ( x, y )

global m q bi_gas

dydx = [ y(2)
    (m^2 * y(1)* y(3) )
    y(4)
    (m^2 * y(1)* y(3) )/q ];

%-----------------------------------------------------------
function res = bcs ( ya , yb)
% This is set up for na gas film resistance.
res = [ (ya(1) - 1)
    (ya(4))
    (yb(1) )
    (yb(3) -1) ] ;

%_______________________________________________________________
function [ m , q , bi_gas ] = calculate_these ( t )
da = 1.40e-09 ;
k2= 10.02;
db = 0.77e-09 ;
k1 = 2.2e-04;
b0 = 1000. ;
astar = 6.25 ;
msq = da* k2 * b0 / k1^2
m = msq^(0.5)
db = 0.77e-09;
z = 2 . ;
q = db * b0 / ( z * da* astar )
bi_gas = 1000.0; % assigned here.

A result of sample simulation fixing \( q \) and varying Hatta is shown in Figure 1.
The effect of large Hatta is shown in figure 2 where the reaction approaches an instantaneous asymptote.
\[ E_\infty = 1 + 1 \]

**Example; \( H_2S \) Removal**

Lo-Cat is a process for removing \( H_2S \) from refinery flue gases and uses a chelated \( Fe(3+) - EDTA \) solution. A simple representation of the reaction is:

\[ H_2S + 2Fe^{+3} \rightarrow 2H^+ + S^0 + Fe^{+2} \]

Find the rate of absorption of \( H_2S \) if the partial pressure in the gas phase is 0.05 atm and the concentration of \( Fe^{++} \) in the liquid is 60 mol/m\(^3\).
The kinetic rate constant is $9m^3/mol \cdot s$ (a second order reaction).

The diffusion coefficients in the liquid are:
- $D_A = 1.44 \times 10^{-9}m^2/s$
- $D_B = 0.54 \times 10^{-9}m^2/s$.

Henry's law coefficient is 1950 Pa/mol m$^3$

Liquid side mass transfer coefficient, $k_L = 2 \times 10^{-4}m/s$.

Solution:

The equilibrium concentration of H$2$S at the interface = $C_A^* = \frac{p_{gA}}{H} = 2.56$ mol/m$^3$. The $q$ parameter is calculated as:

$$q = \frac{D_B C_{BL}}{vD_A C_A^*} = 4.4$$

The Hatta number is calculated as:

$$Ha = \frac{\sqrt{D_A k_2 C_B l}}{k_L} = 4.4$$

Running the Matlab program Hatta.m for these parameters gives the enhancement factor as 3.12. The program also gives the complete concentration profiles for $H_2S$ and $Fe - EDTA$ complex in the film.

Using the calculated enhancement factor, the rate of absorption is calculated as:

Rate of absorption per unit interfacial area = $k_L C_A^* E = 0.0016mol/m^2s$. 

Figure 1: Concentration profiles for dissolved gas A and liquid phase reactant B for two values of Hatta number for a fixed value of $q$. Note that the species B depletes more in the film for larger value of $M = Ha$. 

Distance into film

Concentration, a or b

$M = 10; E = 6.43$

$M = 100; E = 9.9605$

Results for $q = 9$
Figure 2: Concentration profiles for dissolved gas A and liquid phase reactant B for a large values of Hatta number for a fixed value of \( q \). The reaction is now instantaneous; Note that the reaction is now confined to a narrow zone.

2 Penetration Model

Model equations are based on transient diffusion + reaction process. For species A:

\[
D_A \frac{d^2 A}{dZ^2} = \frac{dA}{dt} + k_2 AB
\]

and for species B:

\[
D_B \frac{d^2 B}{dZ^2} = \frac{dB}{dt} + \nu k_2 AB
\]

\( Z \) is the distance into the liquid starting from the interface.

Numerical solutions are needed in general but analytical solutions can be obtained for (i) Pseudo-first order reaction and (ii) instantaneous reaction.

Pseudo-first order reaction

The concentration of B is assumed to be a constant here equal to \( B_0 \) the bulk value. Defining a pseudo-first order rate constant \( k_1 = k_2 B_0 \), Eq. 9 can be expressed as:

\[
D_A \frac{d^2 A}{dZ^2} = \frac{dA}{dt} + k_1 A
\]

The solution subject to the boundary conditions of \( A^* \) at \( Z = 0 \) and zero at \( Z = \infty \) is as follows:

\[
\frac{A}{A^*} = \frac{1}{2} \exp(-Z/\sqrt{k_1/D_A}) \text{erfc} \left[ \frac{Z}{2\sqrt{D_A t}} - \sqrt{k_1 t} \right]
+ \frac{1}{2} \exp(Z/\sqrt{k_1/D_A}) \text{erfc} \left[ \frac{Z}{2\sqrt{D_A t}} + \sqrt{k_1 t} \right]
\]

(12)
The instantaneous rate of absorption is given as
\[ R_A(t) = -D_A \left( \frac{\partial A}{\partial Z} \right)_{Z=0} = A^* \sqrt{D_A k_1} \left[ \text{erf}(k_1 t) + \frac{\exp(-k_1 t)}{\sqrt{\pi k_1 t}} \right] \] (13)

The average rate of absorption given as:
\[ R_A(\text{avg}) = \frac{1}{t^*} \int_0^{t^*} R_A(t) \, dt \] (14)

and the result is:
\[ R_A(\text{avg}) = A^* \sqrt{D_A k_1} \left[ (k_1 t + 1/2)\text{erf}(\sqrt{k_1 t}) + \left( \frac{k_1 t}{\sqrt{\pi}} \right) \exp(-k_1 t) \right] \] (15)

Two limiting cases of the above expression are important:

A. \( k_1 t >> 1 \).
\[ R_A(\text{avg}) = A^* \left( D_A k_1 \right)^{1/2} \left( t + \frac{1}{2k_1} \right) \] (16)

B. \( k_1 t << 1 \).
\[ R_A(\text{avg}) = 2A^* \sqrt{D_A \pi t} \left( 1 + \frac{k_1 t}{3} \right) \] (17)

Eqs. 16 and 17 form the basis for measuring \( k_1 \) and \( D_A \) from experimental data in model contactors where the contact time \( t^* \) is precisely known. Experimental average absorption data collected for various values of the contact time can be fitted by the above models to find both the rate constant and the diffusivity. One such apparatus is the laminar jet. The mean contact time is given as:
\[ t^* = \frac{\pi d^2 h}{4Q} \] (18)

where \( d \) is the diameter of the jet, \( h \) is the length of the jet and \( Q \) is the volumetric flow rate of liquid in the jet. If one measures the total amount of gas absorbed over a time \( t^* \) denoted as \( q \) then the average rate of absorption \( R_A(\text{avg}) \) per unit interfacial area can be calculated as:
\[ q = R_A(\text{avg}) \pi dh/t^* \] (19)

Other suitable model contactors are the wetted wall column, wetted drum apparatus etc. and more details are given in the book by Danckwerts.