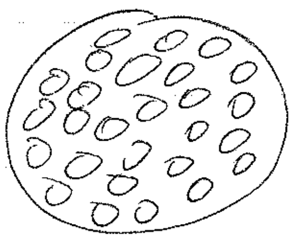
Reactions of Porous Solids

A.) Reactions of Solid Particles of Unchanging Size

B) gasification Reactions

Structural Models for Pellets of Unchanging Size



$\cancel{A + B}$ $aA(g) + bB(s) \rightarrow sS(s) + gG(g)$

A pellet is composed of uniform size grains which may be spherical, long cylinders or platelets in shape

$F_g = 1, 2, 3$ $\qquad$ $F_g = \nu_g + 1$

Every grain reacts according to the USCM since D_{eg} is very, very low thus $\phi_g >> 1$,

One can have ~~two~~ several cases:

(1) $\phi_g >> 1$, $\frac{D_{eg}}{D_{egp}} << 1$ and σ_g^2 can be anything. In this case the solid product must form a looser crystal structure with more cavities i.e. allow a more rapid transfer of gas.

(2) $\phi_g >> 1$, $D_{eg} \simeq D_{egp}$ in which case $\sigma_g^2 >> 1$ and the USCM for the grain is diffusion limited. The ~~k_s & D_{eg}~~ activation energy for the process is then small.

$$\phi_g^2 = \frac{L_g^2 \, r_{A0}}{D_{eg} \, C_{A0}} \qquad \sigma_g^2 = \frac{k_s L}{2 D_g F_g} = \frac{k_s}{2 D_{eg}} \left(\frac{V_B}{S_{oxg}} \right)$$

(3) $\phi_p^2 = \frac{L_p^2 r_{Ao}}{\mathcal{D}_{ep} C_{Ao}} << 1$. The pellet reacts uniformly i.e. every grain at any location reacts at the same rate, and for each case 1 or 2 may hold.

(4) $\phi_p^2 >> 1$, $\frac{\mathcal{D}_{ep}(\text{product})}{\mathcal{D}_{ep}^{\prime}} << 1$
and $\phi_p^2 >>$ $\mathcal{D}_{ep} \approx \text{const}$
the whole pellet reacts according to the shrinking core model.

The most comprehensive model should consider a pellet of unchanging size with grains changing in size and thus affecting the pellet diffusivity $\mathcal{D}_{ep}$.
The mass balance equations are:

$$\frac{1}{r^\nu}\frac{\partial}{\partial r}\left(r^\nu \mathcal{D}_{ep}\frac{\partial C_A}{\partial r}\right) - r_A = \frac{\partial}{\partial t}(\epsilon C_A)$$

$$\frac{\partial C_B}{\partial t} = -\left(\frac{b}{a}\right) r_A$$

$t = 0$ $\quad C_B = C_{Bo}$ $\quad C_A = 0$

$r = R$ $\quad \mathcal{D}_{ep}\frac{\partial C_A}{\partial r}\Big|_R = k_m(C_{Ao} - C_A)$

$r = 0$ $\quad \frac{\partial C_A}{\partial r}\Big|_0 = 0$

We have to relate the rate per unit volume of the pellet to rate per grain, and the change in diffusivity and porosity should be tied to local grain conversion.

The rate per unit volume of the pellet is now given by:

$$\boxed{r_{A} = n_g \, r_{A_g}}$$

where n_g - number of grains per unit volume

r_{A_g} - rate per grain

$$\boxed{n_g = \frac{N_g}{V_p} = \frac{1-\epsilon_p}{V_g}}$$

$$N_g V_g = (1-\epsilon_p) V_p$$

ϵ_p - porosity of the pellet (most likely macroporosity)

$$\boxed{r_{A_g} = \frac{a}{b} V_{g_0} C_{Bt} \frac{dx_B}{dt}}$$

$$r_A = \left(\frac{a}{b}\right)(1-\epsilon_p) C_{Bt} \frac{dx_B}{dt}$$

C_{Bt} — true molar density of the grains of B.

$$\theta_g = g_{F_g}(x) + \sigma_{g_0}^2 f_{F_g}(x)$$

$$g_{F_g}(x) = 1-(1-x)^{\frac{1}{F_g}}$$

$$f_{F_g}(x) = \frac{(F_g-2)(F_g-3)}{2} \, 2 x^2$$

$$+ (F_g-1)(3-F_g)\left\{\frac{[z+(1-z)(1-x)]\ln[z+(1-z)(1-x)]}{z-1}\right.$$

$$\left. + (1-x)\ln(1-x)\right\}$$

$$+ \frac{(F_g-1)(F_g-2)}{2}\left[1-(1-x)^{2/3} + \frac{1-[z+(1-z)(1-x)]^{2/3}}{z-1}\right]$$

$$\theta_g = \frac{\left(\frac{b}{a}\right) k_s C_{A_0}}{C_{Bt}} \left(\frac{S_{gex}}{F_g V_g}\right)_0 t \qquad \sigma_{g_0}^2 = \frac{k_s}{2 D_{eg}} \left(\frac{V_g}{S_{ex}}\right)_0$$

For <u>spherical grains</u>

$$\frac{dx}{d\theta_g} = \frac{1}{\frac{1}{3}(1-x)^{-2/3} + 2\sigma_{g0}^2\left[(1-x)^{-1/3} - [z+(1-z)(1-x)]^{-1/3}\right]}$$

$$\frac{dx}{d\theta_g} = \frac{3}{(1-x)^{-2/3} + Da_{g0}\left[(1-x)^{-1/3} - [z+(1-z)(1-x)]^{-1/3}\right]}$$

$$\frac{dx}{dt} = \frac{3\,\frac{\left(\frac{b}{a}\right) k_s C_{A0}}{C_{Bt}}\left(\frac{S_g}{F_g V_g}\right)_0}{(1-x)^{-2/3} + Da_{g0}\left[(1-x)^{-1/3} - [z+(1-z)(1-x)]^{-1/3}\right]}$$

$$r_{Ag} = \frac{3\, k_s C_{A0}\,(S_g/F_g)_0}{(1-x)^{-2/3} + Da_{g0}\left[(1-x)^{-1/3} - [z+(1-z)(1-x)]^{-1/3}\right]}$$

$$\boxed{r_A = \frac{3(1-\epsilon_p)\, k_s C_{A0}\left(\frac{S_g}{F_g V_g}\right)_0}{(1-x)^{-2/3} + Da_{g0}\left[(1-x)^{-1/3} - [z+(1-z)(1-x)]^{-1/3}\right]}} \quad F_g = 3$$

For <u>platelets</u> (slab)

$$\boxed{r_A = \frac{\text{[illegible]}(1-\epsilon_p)\, k_s C_{A0}\left(\frac{S_g}{F_g V_g}\right)_0}{1+2zX} \quad ; \quad F_g = 1}$$

$$\boxed{r_A = \left(\frac{a}{b}\right)(1-\epsilon_p)\, C_{Bt}\frac{dx_B}{dt} = (1-\epsilon_p)\, k_s C_{A0}\left(\frac{A_g}{F_g V_g}\right)_0 \frac{dx_B}{d\theta_g}}$$

$$r_A = (1-\epsilon_p)\, k_s C_A \left(\frac{A_g}{V_g}\right)\left(\frac{r_c A_g}{V_g F_g}\right)^{F_g - 1}$$

In general we have:

$$\theta_g = g_{F_g}(x) + \sigma_{g_0}^2 f_{F_g}(x)$$

$$\frac{dx}{d\theta_g} = \frac{1}{g'_{F_g}(x) + \sigma_{g_0}^2 f'_{F_g}(x)}$$

$$g_{F_g}(x) = 1 - (1-x)^{\frac{1}{F_g}}$$

$$f_{F_g}(x) = \frac{F_g}{F_g - 2}\left[1 - (1-x)^{\frac{2}{F_g}}\right] + \left(\frac{1 - \left[z + (1-z)(1-x)\right]^{\frac{2}{F_g}}}{(F_g-2)(z-1)}\right) F_g$$

$$g'_{F_g}(x) = \frac{1}{F_g}(1-x)^{\frac{1-F_g}{F_g}}$$

$$f'_{F_g}(x) = \frac{2}{(F_g-2)}\left\{(1-x)^{\frac{2-F_g}{F_g}} - \left[z + (1-z)(1-x)\right]^{\frac{2-F_g}{F_g}}\right\}$$

<u>In general</u>

$$\boxed{r_A = \frac{(1-\epsilon_p)\, k_s\, C_A \left(\frac{A_g}{V_g}\right)_0}{(1-x)^{\frac{1-F_g}{F_g}} + \frac{2\sigma_{g_0}^2 F_g}{F_g-2}\left\{(1-x)^{\frac{2-F_g}{F_g}} - \left[z + (1-z)(1-x)\right]^{\frac{2-F_g}{F_g}}\right\}}}$$

$$Da_{g_0} = 2F_g\, \sigma_{g_0}^2 = \frac{k_s \left(\frac{F_g V_g}{A_g}\right)_0}{D_{eg}}$$

$$\boxed{r_A = \frac{(1-\epsilon_p)\, k_s\, C_A \left(\frac{A_g}{V_g}\right)_0}{(1-x)^{\frac{1-F_g}{F_g}} + \frac{Da_{g_0}}{F_g-2}\left\{(1-x)^{\frac{2-F_g}{F_g}} - \left[z + (1-z)(1-x)\right]^{\frac{2-F_g}{F_g}}\right\}}}$$

Thus ϵ_p will change with time

over

For reaction control at the grain

Also

$$r_A = (1-\epsilon_p) k_s C_A \left(\frac{A_g}{V_g}\right)_0 \left(\frac{A_g}{V_g F_g}\right)_0^{F_g-1} r_c^{F_g-1}$$

$$\eta = \frac{A_g r_c}{F_g V_g}$$

$$-C_{Bt} \frac{dr_c}{dt} = \frac{b}{a} k_s C_A$$

$$\frac{1}{\xi^\nu} \frac{\partial}{\partial \xi}\left(\xi^\nu \delta \frac{\partial y}{\partial \xi}\right) - \phi^2 F_g\, y\, (1-\epsilon)'_0 \cancel{\left(\frac{A_g}{V_g F_g}\right)_0} \eta_c^{F_g-1}$$

$$= \left(\frac{b}{a}\right) \frac{\epsilon_0}{1-\epsilon_0} \phi^2 \frac{\partial}{\partial t}(\epsilon' y)$$

$$\frac{d\eta_c}{d\theta} = -y \qquad \eta_2 = 1 - y$$

reaction control at the grains

$$\phi^2 = \frac{\sigma^2}{F_g} \text{ of Szekely}$$

$$X = F_p \int_0^1 \xi^{F_p-1}(1-\eta_c^{F_g})\, d\xi \qquad \cancel{\int_0^1 \xi^{F_p-1} d\xi}$$

$$\bar{\eta} = \cancel{\frac{1}{\theta}}\, F_p \int_0^1 \xi^{F_p-1}\left(-F_g \eta_c^{F_g-1} \frac{d\eta_c}{d\theta}\right) d\xi \qquad \frac{1}{F_p}\xi^{F_p}$$

Analytical solution possible
for $F_g = 1$

$$\frac{d\eta_c}{d\theta} = -\frac{y}{1 + Da_{g_0}\left(\eta_c - \frac{\eta_c^2}{u}\right)} \quad \text{for sphere}$$

$u = Z + (1-Z)\eta_c^3$

$$\frac{1}{r^\nu}\frac{\partial}{\partial r}\left(r^\nu \frac{\partial C_A}{\partial r}\right) = 0$$

$$r = r_c \qquad \mathcal{D}_e \frac{\partial C_A}{\partial r} = k_s C_A$$

$$r = R \qquad C_A = C_{As}$$

$$r^\nu \frac{\partial C_A}{\partial r} = A$$

$$\frac{\partial C_A}{\partial r} = A r^{-\nu}$$

$$C_A = \frac{A}{1-\nu} r^{1-\nu} + B \qquad \frac{dC_A}{dr} = A r^{-\nu}$$

$$C_{As} = \frac{A}{1-\nu} R^{1-\nu} + B$$

$$\mathcal{D}_e A r_c^{-\nu} = \frac{k_s A}{1-\nu} r_c^{1-\nu} + k_s B$$

$$k_s C_{As} - \mathcal{D}_e A r_c^{-\nu} = \frac{A}{1-\nu}\left[k_s R^{1-\nu} - k_s r_c^{1-\nu}\right]$$

$$k_s C_{As} = A\left\{\mathcal{D}_e r_c^{-\nu} + \frac{k_s}{1-\nu}\left(R^{1-\nu} - \cancel{k_s}\, r_c^{1-\nu}\right)\right.$$

$$A = \frac{k_s C_{As}}{\mathcal{D}_e r_c^{-\nu} + \frac{k_s}{1-\nu}\left(R^{1-\nu} - r_c^{1-\nu}\right)}$$

$$\mathcal{D}_e \left.\frac{\partial C_A}{\partial r}\right|_{r_c} = \frac{\mathcal{D}_e k_s C_{As} r_c^{-\nu}}{\mathcal{D}_e r_c^{-\nu} + \frac{k_s}{1-\nu}\left(R^{1-\nu} - r_c^{1-\nu}\right)} =$$

$$= \frac{k_s C_{As}}{1 + \frac{k_s R}{(1-\nu)\mathcal{D}_e}\left(\frac{r_c}{R}\right)^\nu - \frac{k_s r_c}{(1-\nu)\mathcal{D}_e}} \qquad = -\left(\frac{a}{b}\right) C_{Bt} \frac{dr_c}{dt}$$

$$t = \frac{C_{Bt}}{\left(\frac{b}{a}\right) k_s C_{As}} \int_0^{R_0} \left[1 + \frac{k_s R}{(1-\nu)\mathcal{D}_e}\left(\frac{r_c}{R}\right)^\nu - \frac{k_s r_c}{(1-\nu)\mathcal{D}_e}\right] dr_c$$

$$\frac{dR_c}{dt} = -\frac{\left(\frac{b}{a}\right) k_s C_{As}}{C_{Bt}} \quad \frac{1}{1 + \frac{k_s R_o}{(1-\nu) D_e}\left(\frac{R_c}{R_o}\right)^{\nu}\left(\frac{R}{R_o}\right)^{1-\nu} - \frac{k_s R_o}{(1-\nu) D_e}\left(\frac{R_c}{R_o}\right)}$$

$$\left(\frac{R}{R_o}\right)^{\nu+1} = z + (1-z)\left(\frac{R_c}{R_o}\right)^{\nu+1}$$

$$\theta = \left(\frac{b}{a}\right) \frac{k_s C_{Ao}}{C_{Bt}} \left(\frac{A_g}{F_g V_g}\right)_o t$$

$F_g = \nu + 1$

$\nu = F_g - 1$

$\nu - 1 = F_g - 2$

$$\eta_c = \frac{R_c}{R_o} \qquad y = \frac{C_{As}}{C_{Ao}}$$

$$\frac{\partial \eta_c}{\partial \theta} = -\frac{y}{1 + \frac{Da_{g_o}}{F_g - 2}\left\{\eta_c - \eta_c^{F_g - 1}\left[z + (1-z)\eta_c^{F_g}\right]^{\frac{2-F_g}{F_g}}\right\}}$$

Point solid conversion is:

$$x = 1 - \left(\frac{R_{cg}}{R_{go}}\right)^{F_g} = 1 - \xi_g^{F_g} = 1 - \frac{V_{gc}}{V_{go}}$$

where $R_{go} = \left(\frac{F_g V_g}{A_g}\right)_0$ $\qquad R_{cg} = \left(\frac{F_g V_{gc}}{A_{gc}}\right)$

Total solid conversion is:

$$X = 1 - \frac{N_{Bp}}{N_{Bpo}} \qquad n_g V_g = (1-\epsilon_0) V_p$$

$$N_{Bpo} = n_g C_{Bt} V_g = (1-\epsilon) C_{Bt} V_p \qquad \cancel{n_g = (1-\epsilon)\frac{V_p}{V_g}}$$

$$\cancel{N_{Bp} = (1-\epsilon)\int_{V_p} C_{Bt} V_{gc} \frac{dV_p}{V_p}}$$

$$N_{Bp} = \int_{V_p} C_{Bt} V_{gc} \cdot n_g \, dV_p = \int_{V_p} (1-\epsilon) C_{Bt} \frac{V_{gc}}{V_{go}} \, dV_p$$

Thus

$$\frac{1}{\xi^{\nu}} \frac{\partial}{\partial \xi}\left(\xi^{\nu} \delta \frac{\partial y}{\partial \xi}\right) - \phi^2 \frac{F_g\, y\, (1-\epsilon)'}{(1-x)^{\frac{1-F_g}{F_g}} + \frac{Da_{go}}{F_g - 2}\left\{(1-x)^{\frac{2-F_g}{F_g}} - \left[z + (1-z)(1-x)\right]^{\frac{2-F_g}{F_g}}\right\}}$$

$$= \left(\frac{b}{a}\right) \frac{\epsilon_0}{1-\epsilon_0} \phi^2 \frac{\partial}{\partial \theta}(\epsilon' y)$$

$$\frac{\partial x}{\partial \theta} = \frac{F_g\, y}{(1-x)^{\frac{1-F_g}{F_g}} + \frac{Da_{go}}{F_g - 2}\left\{(1-x)^{\frac{2-F_g}{F_g}} - \left[z + (1-z)(1-x)\right]^{\frac{2-F_g}{F_g}}\right\}}$$

$$\phi^2 = \left(\frac{F_p V_p}{A_p}\right)^2 \frac{(1-\epsilon_{po})\, k_s \left(\frac{A_g}{F_g V_g}\right)_0}{\mathcal{D}_{epo}} \qquad \delta = \frac{\mathcal{D}_{ep}}{\mathcal{D}_{epo}}$$

$$(1-\epsilon)' = \frac{1-\epsilon_p}{1-\epsilon_{po}} = \frac{(1-\epsilon)}{(1-\epsilon_p)_0} \qquad \epsilon' = \frac{\epsilon}{\epsilon_0}$$

$$\theta = \left(\frac{b}{a}\right) \frac{k_s C_{Ao}}{\ldots} \left(\frac{A_g}{\ldots}\right) + \qquad \xi = \frac{r}{R} = \frac{r A_p}{\ldots}$$

Conversion for the pellet, x_B

$$x_B = \frac{\int_{V_p} (C_{B0} - C_B)\, dV}{C_{B0} V_p} = 1 - \frac{\int_{V_p} C_B \, dV}{C_{B0} V_p}$$

$$x_B = 1 - \frac{4\pi \int_0^R r^2 (C_B / C_{B0})\, dr}{\frac{4}{3}\pi R^3}$$

$$x_B = 1 - 3 \int_0^1 \xi^2 z \, d\xi$$

$$\boxed{x_B = 1 - (\nu + 1) \int_0^1 \xi^\nu z \, d\xi}$$

Effectiveness Factor, η

η = actual rate of reaction for the pellet / ideal rate in absence of diffusional limitations assoc. with fresh pellets

$$\boxed{\eta = \frac{\int_{V_p} r_A (C_A, C_B)\, dV}{\int_{V_p} r_A (C_{A0}, C_{B0})\, dV} = (\nu + 1) \int_0^1 \xi^\nu \bar{r}_A (y, z)\, d\xi}$$

Thus

$$\boxed{\eta = \frac{d x_B}{d\theta}}$$

$$\cancel{X = \int_0^1 \xi^\nu x \, d\xi}$$

$$X = (\nu+1)\int_0^1 \xi^\nu x \, d\xi$$

$\theta = 0 \qquad x = 0 \qquad y = 0$

$\xi = 0 \qquad \dfrac{\partial y}{\partial \xi} = 0$

$\xi = 1 \qquad \delta \dfrac{\partial y}{\partial \xi} = Bi_{mo}(1-y)$

$$Bi_{mo} = \frac{k_m}{D_{ep0}}\left(\frac{F_p V_p}{A_p}\right)$$

$$\frac{\epsilon}{\epsilon_0} = \frac{1}{\epsilon_0} - \frac{1-\epsilon_0}{\epsilon_0}\left[z + (1-z)\ldots\right.$$

Change in porosity:

$$n_g = \frac{N_g}{V_p} = \text{const} = \frac{1-\epsilon}{V_g} = \frac{1-\epsilon_0}{V_{g0}}$$

$$1-\epsilon = (1-\epsilon_0)\frac{V_g}{V_{g0}} = (1-\epsilon_0)\left[z + (1-z)(1-x)\right]$$

$$\cancel{z} + 1 - x - \cancel{z} + zx = 1 + (z-1)x$$

$$\frac{1-\epsilon}{1-\epsilon_0} = (1-\epsilon)' = z + (1-z)(1-x) = u$$

$1-\epsilon = (1-\epsilon_0)[z + (1-z)(1-x)] \qquad \epsilon = 1 - (1-\epsilon_0)[1 + (z-1)x]$

$\epsilon = 1 - (1-\epsilon_0)[z + (1-z)(1-x)]$

$U \in \left[1, \dfrac{1}{1-\epsilon_0}\right]$ for ~~decreasing~~ ~~increasing~~ decreasing porosity

$U \in [0, 1]$ for increasing porosity

$$\frac{\epsilon}{\epsilon_0} = \frac{1}{\epsilon_0} - \frac{1-\epsilon_0}{\epsilon_0}\left[1 + (z-1)x\right] \; ?$$

Maximum value of $(1-\epsilon)' = u$ for decreasing porosity is $\dfrac{1}{1-\epsilon_0}$ after which it stays at that value

$$\epsilon' = \frac{\epsilon}{\epsilon_0} = \frac{1}{\epsilon_0} - \left(\frac{1-\epsilon_0}{\epsilon_0}\right)\left[z + (1-z)(1-x)\right] = \frac{1}{\epsilon_0} - \frac{1-\epsilon_0}{\epsilon_0} u$$

$\epsilon' \in [1, 0]$ for decreasing porosity $\qquad \epsilon' \in \left[1, \dfrac{1}{\epsilon_0}\right]$ for increasing p 8

$D_{ep} = \cancel{D_{ea}}(\epsilon)^{\alpha}$

$\delta = (\epsilon')^{\alpha}$

$\delta = (\epsilon')^{\alpha} = \left[\frac{1}{\epsilon_0} - \frac{1-\epsilon_0}{\epsilon_0} u\right]^{\alpha}$

$\delta = \left[\frac{1}{\epsilon_0} - \frac{1-\epsilon_0}{\epsilon_0}[z + (1-z)(1-x)]\right]^{\alpha}$

$\delta = \left[z - \frac{1-\epsilon_0}{\epsilon_0}(1-z)(1-x)\right]^{\alpha} =$

Most often $\alpha = 1$, or $\alpha = 2$

One should solve that system of equations by orthogonal collocation or other methods.

Mr. Dewan: ~~Dt~~ ~~and~~ neglect accumulation term, $Bim \to \infty$ take $\alpha = 1$, or 2

Mr. Sizgarsam : take $\delta = 1$ and $\epsilon' = 1$ $\quad (1-\epsilon)' = 1$ and examine effect of accumulation term

Use again transformation

$$\boxed{\begin{aligned} Y &= \int_0^{\theta} y \, d\theta \\ Y &= \frac{1}{F_g} f_{Fg}(x) \end{aligned}}$$

get cap Y in all equations and then substitute $\frac{1}{F_g} f_{Fg}(x)$ solve collocation for x

For orthogonal collocation and other methods of weighted residuals see:

(1) J. V. Villadsen and W. E. Stewart, "Solution of Boundary-Value problems by Orthogonal Collocation" CES 22, 1483–1501 (1967)

(2) B. A. Finlayson, "Applications of the method of weighted residuals and variational methods", British Chem. Eng. 14(1), 53–57 (1969) 14(2), 179–182 (1969)

(3) N. B. Ferguson, B. A. Finlayson, "Transient Chemical Reaction Analysis by orthogonal collocation", The Chem. Eng. J, 1, 327–335 (1970)

(4) Finlayson, B.A. "The Method of weighted Residuals and Variational Principles" Academic Press (1972).

Consider a simple problem of solid particle: $r_A = k C_A C_B$

$$\frac{1}{\xi^\nu}\frac{\partial}{\partial \xi}\left(\xi^\nu \frac{\partial Y}{\partial \xi}\right) + \phi^2\left(e^{-Y} - 1\right) = \phi^2 \frac{\partial Y}{\partial \theta}$$

$$Y = \int_0^\theta y \, d\theta$$

$$X = \frac{\nu+1}{\phi^2}\left(\frac{\partial Y}{\partial \xi}\right)_1 - \epsilon \frac{C_{A0}}{C_{B0}} \int_0^1 (\nu+1)\, \xi^\nu \frac{\partial Y}{\partial \theta}\, d\xi$$

or $$X = 1 - (\nu+1)\int_0^1 \xi^\nu e^{-Y}\, d\xi$$

$\xi = 0 \qquad \frac{\partial Y}{\partial \xi} = 0 \qquad\qquad \theta = 0 \quad Y = 0$

$\xi = 1 \qquad Y = \theta \quad (Bi \to \infty)$

Expand y in series of known functions with arbitrary coefficients

$$y(\theta,\xi) \approx \theta + \sum_{i=1}^{m} a_i(\theta)\, P_i(\xi^2) = y^{(m)}(\xi,\theta)$$

~~These coeff~~ $\left.\frac{\partial P_i}{\partial \xi}\right|_{\xi=0} = \frac{\partial P_i}{\partial \xi^2} \cdot \left. 2\xi \right|_{\xi=0} = 0$

Other B.C is also satisfied

$$\sum_{i=1}^{m} a_i(\theta)\, P_i(1) = 0$$

$$P_i(1) = 0 \qquad \text{all } i$$

Now the coefficients a_i can be chosen according to a number of criteria.

The <u>residual</u> $R(\xi,\theta)$ is obtained by substituting the trial function into the D.E

$$\nabla^2 y^{(m)} + \phi^2\left(e^{-y^{(m)}} - 1\right) + R(\xi) = \epsilon\, \phi^2 \frac{C_{A_0}}{C_{B_0}} \frac{\partial y^{m}}{\partial \theta}$$

where $R(\xi)$ is the residual by which the trial function fails to satisfy the D.E.

In the M.W.R (method of weighted residuals) we choose a_i in such a way that the residual is forced to be approximately zero in some weighted average sense

$$(w_j, R) = \int_V w_j\, R\, dV = 0$$

The weighting functions can be chosen in several ways and each way corresponds to a different criteria in MWR

<u>Collocation method</u> $w_j = \delta(\xi - \xi_j)$

requires the residual to be <u>zero</u> at collocation points ξ_j, $j = 1, 2, \ldots n$

<u>Method of Moments</u> $w_j = x^j$ $j = 0, 1, 2 \ldots$

weighting functions are members of a complete set of functions so that any continuous function can be expanded in terms of them.

$w_j = \sin j\pi x$ $j = 1, 2, \ldots$

$w_j = \mathcal{L}_j$ (Legendre polynom

Since any function that is orthogonal to all functions of a complete set must be zero we hope that as $n \to \infty$ $R \equiv 0$.

<u>Galerkin method</u> $w_j = \varphi_j$

a sub case of the method of moments

<u>Least squares method</u> $w_j = \dfrac{\partial R}{\partial a_j}$

minimizes the mean square residual

$$\frac{\partial}{\partial a_j} \int_V R^2 \, dV = 0 \qquad \int_V \underbrace{\frac{\partial R}{\partial a_j}}_{w_j} R \, dV$$

Villadsen & Stewart have shown after ingenious work:

a) that the collocation points should be the roots of polynomial used

b) that Jacobi polynomials are to be used for $\cancel{\nabla^2}$ Laplaces and parabolic equations with 1st kind B.C.

c) that the constants a_i should be obtained by requiring that the residual be orthogonal with the polynomials used.

$$\int_0^1 \rho(\xi^2)\, P_i(\xi^2)\, P_j(\xi^2)\, \xi^\nu\, d\xi = C_i\, \delta_{ij}$$

where $\rho(\xi^2) = \begin{cases} 1-\xi^2 & \text{Jacobi} \\ 1 & \text{Legendre} \\ (1-\xi^2)^{-1/2} & \text{Chebyshev poly} \end{cases}$

C_i tabulated

d) that the trial function y^n and its derivative can be represented in terms of values at collocation points.

$$y^{(n)} = \sum_{j=1}^{n+1} D_{ij}\, y_j \qquad y_j = y(\theta, \xi_j)$$

$$\left.\frac{dy}{d\xi}\right|_{\xi_i} = \sum_{j=1}^{n+1} A_{ij}\, y_j \qquad \int_0^1 f(\xi)\, \xi^{\nu-1} d\xi = \sum_{j=1}^{n+1} w_j f(\xi_j)$$

$$\cancel{\nabla^2} \left[\frac{1}{\xi^\nu} \frac{d}{d\xi}\left(\xi^\nu \frac{\partial y}{\partial \xi}\right)\right]_{\xi_i} = \sum_{j=1}^{n+1} B_{ij}\, y_j$$

Now our equation can be written as:

$$\sum_{j=1}^{n+1} B_{ij} y_j + \phi^2 (e^{-y_i} - 1) = \epsilon \phi^2 \frac{C_{A_0}}{C_{B_0}} \frac{\partial y_i}{\partial \theta}$$

$$y_{n+1} = \theta$$

Simple system of O.D.E to solve for PSSA:

$$\sum_{j=1}^{n+1} B_{ij} y_j + \phi^2 (e^{-y_i} - 1) = 0$$

set of algebraic equations by [illegible]

Easier to solve DE's

$$\sum_{j=1}^{n+1} B_{ij} \frac{d y_j}{d\theta} - \phi^2 e^{-y_i} \frac{d y_i}{d\theta} = 0$$

$$\frac{d y_{n+1}}{d\theta} = 1$$

$\theta = 0 \qquad y_j = 0 \qquad j = 1, 2, \ldots n, n+1$

$$X = \frac{\nu+1}{\phi^2} \sum_{j=1}^{n+1} A_{n+1j}\, y_j = 1 - (\nu+1) \sum_{j=1}^{n+1} w_j\, e^{-y_j}$$

1 collocation point

$$\cancel{B_{11} \frac{d y_1}{d\theta} - \phi^2 e^{-y_i} \frac{d y_1}{d\theta} = 0}$$

$$B_{11} \frac{d y_1}{d\theta} + B_{12} \frac{d y_2}{d\theta} - \phi^2 e^{-y_1} \frac{d y_1}{d\theta} = 0$$

$$\frac{d y_2}{d\theta} = 1 \qquad y_2 = \theta$$

$$B_{11} \frac{d y_1}{d\theta} + B_{12} - \phi^2 e^{-y_1} \frac{d y_1}{d\theta} = 0$$

$$\left(B_{11} - \phi^2 e^{-y_1}\right) \frac{d y_1}{d\theta} = -B_{12}$$

$$\boxed{B_{11} y_1 + \phi^2 (e^{-y_1} - 1) = -B_{12}\, \theta}$$

$$X = \frac{\nu+1}{\phi^2}\left[A_{21} y_1 + A_{22}\theta\right] = 1-(\nu+1)\left[w_1 e^{-y_1} + w_2 e^{-y_2}\right]$$

$\nu = 2$, where.

$w_1 = \frac{7}{30}$ $\qquad w_2 = 0.233333$

$A_{21} = -2.29129$ $\qquad A_{22} = 2.29129$

$B_{11} = -\frac{21}{2}$ $\qquad B_{12} = \frac{21}{2}$

$$-\frac{21}{2} y_1 + \phi^2(e^{-y_1} - 1) = -\frac{21}{2}\theta$$

$$X = \frac{3}{\phi^2}\left[-2.29129\, y_1 + 2.29129\,\theta\right] = 1 - 3\left[\frac{7}{30}e^{-y_1} + 0.23333 e^{-\theta}\right]$$

$$\boxed{\begin{gathered} X = \frac{6.87387}{\phi^2}(\theta - y_1) = 1 - 0.7e^{-y_1} - 0.699999\, e^{-\theta} \\ 10.5(\theta - y_1) = \phi^2(1 - e^{-y_1}) \end{gathered}}$$

The two limiting cases of structural models are $\Phi_p \to 0$ $\Phi_p \to \infty$

In the first case the reaction ~~progresses~~ ~~gradually~~ uniformly in all grains

$$\theta_g = g_{F_g}(X) + \sigma_g^2\, p_{F_g}(X)$$

$$\theta_g = \frac{(b/a)\, k_s\, C_{A0}}{C_{B0}} \left(\frac{A_g}{F_g V_g}\right) t$$

Conversion versus time curves look like if the other the OSCM but one would not find any dependence on the radius of the pellet.

For $\Phi_p \to \infty$

$$\tilde{\theta} = p_{F_p}(X)$$

$$\tilde{\theta} = \frac{\left(\frac{b}{a}\right) 2\, D_e\, F_p\, C_{A0}}{(1-\epsilon)\, C_{Bt}} \left(\frac{A_p}{F_p V_p}\right)^2 t = \frac{\theta}{\phi^2} \cdot 2F_p$$

Now the time required to obtain a certain conversion is proportional to the square of the characteristic dimension of the pellet.

Szekely suggested the following ~~dimensionless~~ normalized modulus:

$$\hat{\sigma} = \frac{V_p}{A_p} \sqrt{\frac{(1-\epsilon)\, k_s\, F_p}{2\, D_e} \left(\frac{A_g}{F_g V_g}\right)} \qquad \hat{\sigma}^2 = \left(\frac{V_p F_p}{A_p}\right)^2 \frac{(1-\epsilon)\, k_s}{2\, F_p D_e} \left(\frac{A_g}{F_g V_g}\right)$$

$$\theta^* = g_{F_g}(X) \qquad \theta = \theta^* = \frac{\left(\frac{b}{a}\right) k_s\, C_{A0}}{C_{Bt}} \left(\frac{A_g}{F_g V_g}\right) t$$

$$\frac{\theta^*}{\hat{\sigma}^2} = p_{F_p}(X)$$

Important reminder — when solving structural models which base the grain reaction on the USCM a two-stage problem or moving boundary problem always arises. When the grains on the outside solid surface are entirely reacted two zones exist (like in the Ishida & Wen model): in the outer zone diffusion only occurs, in the inner zone diffusion and reaction take place simultaneously, and the boundary between the two zones moves as reaction progresses and additional grains get reacted.

Szekely showed that grain reaction control appropriate for

$$\hat{\sigma} < 0.3 \quad (\hat{\sigma}^2 < 0.1)$$

$\sigma_g^2 < 0.1$ — grain reaction controlled

$\sigma_g^2 > 10$ — intragrain diffusion control

Linear relationship between $g_{F_g}(x)$ & θ obtained does not necessarily mean reaction control. Even for $\hat{\sigma}^2 > 2.0$ one obtains linear relationship

For Reversible reactions $C_A \Rightarrow C_A - \frac{C_B}{K}$

The other asymptotic behavior of $\phi_p \to \infty$ is approached for $\hat{\sigma} > 3$ ($\hat{\sigma}^2 > 10$)

Approximate solutions

Szekely showed an approximate solution valid for all grains and better shapes:

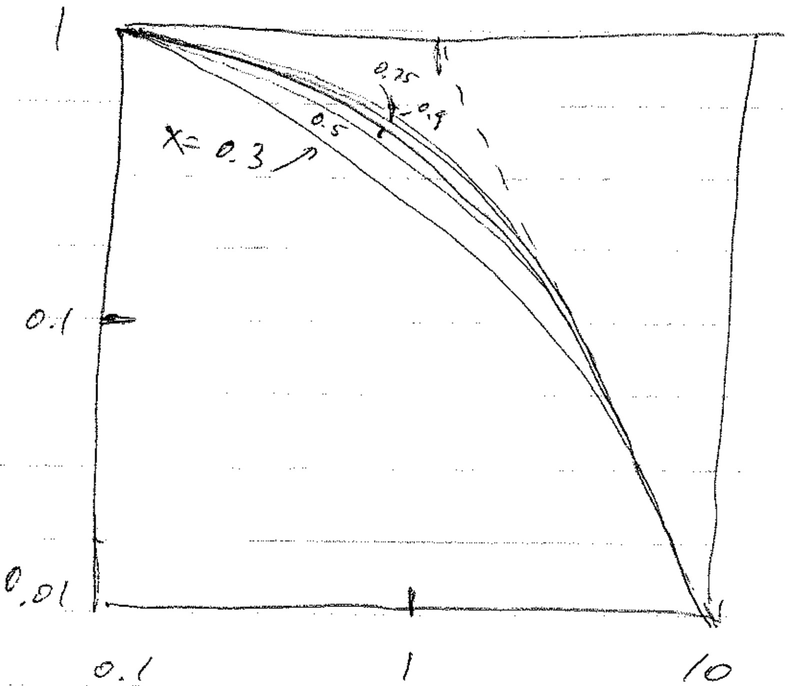
$$\theta = g_{Fg}(X) + \hat{\sigma}^2 p_{Fp}(X)$$

$$\sigma = \frac{\frac{b}{a} k_s C_{An} (1-\epsilon)_0}{C_{Bt}} \left(\frac{A_g}{F_g V_g}\right) t$$

This says that time required to reach certain conversion is

$$\theta(X) = g_{Fg}(X) + \hat{\sigma}^2 p_{Fp}(X)$$

$$= \theta(X)\Big|_{\hat{\sigma}=0} + \hat{\sigma}^2 \tilde{\theta}(X)\Big|_{\hat{\sigma}\to\infty}$$



$$\frac{\theta}{\theta\big|_{\hat{\sigma}=0}} \simeq 1 + \hat{\sigma}^2 \frac{p_{Fp}(X)}{g_{Fg}(X)}$$

Approximate solution

$$\theta(X) = g_{Fg}(X) + \hat{\sigma}^2 \left[p_{Fp}(X) + \frac{2}{Bi_m} X \right]$$

Same form of approximate solution can then be used to account for <u>intra grain diffusion</u>

$$\theta(x) = g_{Fg}(x) + \sigma_g^2 P_{Fg}(x) + \hat{\sigma}^2\left[P_{Fp}(x) + \frac{2}{Bi_m} x\right]$$

$$\sigma_g^2 = \frac{V_g}{2 D_{eg}}\left(\frac{V_g}{S_{ex}}\right)_0$$

$\boxed{\text{Examples}}$ $\quad FeO + H_2 \underset{500°C}{\rightarrow} Fe + H_2O$

(1) 1^{st} order reaction $\quad K_E = 0.5$

$$\frac{A_g}{F_g V_g} = 5\times10^{4}\ cm^{-1} \quad (R_0 = 2\times10^{-5}\ cm = 2\times10^{-4}\ mm = 0.2\ \mu)$$

$k_s = 10^{-4}$ cm/s $\qquad D_e = 0.8$ cm²/s $\qquad \epsilon = 0.3$

Estimate the largest allowable pellet size for which diffusional resistance is negligible

We want $\quad \hat{\sigma} < 0.3$

$$0.3 > \frac{V_p}{A_p}\sqrt{\frac{(1-\epsilon) k_s F_p}{2 D_e}\left(\frac{A_g}{F_g V_g}\right)\left(1+\frac{1}{K_E}\right)} = \frac{F_p V_p}{A_p}\sqrt{\frac{(1-\epsilon) k_s \frac{A_g}{F_g V_g}(1+\dots)}{2 F_p D_e}}$$

$$> \left(\frac{F_p V_p}{A_p}\right)\sqrt{\frac{(1-0.3)\ 10^{-4}\times\cancel{3}\times 5\times10^{4}(1+2)}{\cancel{3}\quad 2\times0.8}}$$

$0.3 > 1.979\ R_p \qquad \boxed{R_p < 2.028\ cm}$

(2) Same reaction

$F_g = 3 \qquad \frac{F_g V_g}{A_g} = 2\times10^{-4}$ cm

$D_e = 0.8$ cm²/s $\qquad \epsilon = 0.35$

$k_s = 5\times10^{-4}$ cm/s $\qquad C_{Bt} = 0.0794$ gmol/cm³

$Bi_m = 10 \qquad K_E = 0.5$

Calculate time for ~~complete~~ conversion of 0.9 for spherical pellets 0.2, 2 & 4 cm in dia

$$\theta = g_{Fg}(X) + \bar{\sigma}^2 \left[p_{Fp}(X) + \frac{2X}{Bi_m} \right]$$

$$g_{Fg} = 1 - (1-X)^{\frac{1}{3}} = 1 - (1-X)^{1/3}$$

$$p_{Fp=3} = 1 - 3(1-X)^{2/3} + 2(1-X)$$

$$g_{Fg}(X = 0.9) = 0.5358$$

$$p_{Fp}(0.9) = 0.5538$$

$$\bar{\sigma}^2 = R_0^2 \left[\frac{(1-0.35)\, 5\times10^{-4} \times 3 \times (\cancel{2})}{3 \times 2 \times 0.8 \times 2\times10^{-4}} \right]$$

$$\bar{\sigma}^2 = R_0^2 \times \cancel{}\ 1.015 \qquad R_0 = 0.1,\ 1,\ 2$$

$R_0 = 0.1$ $\quad \bar{\sigma}^2 = \cancel{0.0024}\ 0.0102$

$R_0 = 1.$ $\quad \bar{\sigma}^2 = \cancel{}\ 1.02$

$R_0 = 2$ $\quad \bar{\sigma}^2 = 4.08$

$$\theta = 0.5358 + \bar{\sigma}^2 \left[0.5538 + 0.18 \right]$$

$$= 0.5358 + \bar{\sigma}^2 \times 0.7338$$

$R_0 = 0.1$	$\theta = 0.5433$	$t = 1622\,s$
1.0	1.2892	3929 s
2.0	3.5293	10 799 s

$$\theta = (b/a) \frac{k_s}{C_{Bt}} \frac{A_g}{F_g V_g}\, t \left(C_{Ao} - \frac{C_{Bo}}{K_E} \right)$$

$$C_{Ao} = \frac{1}{82.1 \times (900+273)} = 1.038\times10^{-5}\ \frac{\text{gmole}}{\text{cm}^3}$$

$$b/a = 1$$

$$t = \frac{C_{Bt}\left(\frac{F_g V_g}{A_g}\right)}{k_s C_{Ao}}\, \theta = \underbrace{\frac{0.0799 \times 2\times10^{-4}}{5\times10^{-4} \times 1.038\times10^{-5}}}_{3\ 079.7}\, \theta$$

(3) Same reaction. Spherical grains

$F_g = 3$ 800°C

solid state diffusion

Formed product is nonporous

$\frac{F_g V_g}{A_g} = 2\times10^{-4}$ cm $k_s = 5\times10^{-3}$ cm/s

a) $D_g = 1\times10^{-5}$ cm²/s

b) $D_g = 10^{-7}$

$$\sigma_g^2 = \frac{k_s}{2D_g}\left(\frac{V_g}{A_g}\right)\left(1+\frac{1}{K_e}\right)$$

a) $\sigma_g^2 = \frac{5\times10^{-3}}{2\times10^{-5}} \; \frac{2\times10^{-4}}{3} \; 3 = 5\times10^{-2} = 0.05$

b) $\sigma_g^2 = \frac{5\times10^{-3}}{2\times10^{-7}} \; \frac{2\times10^{-4}}{3} \; 3 = 5$

a) grain diffusion can be neglected

b) grain diffusion has to be accounted for but is not controlling