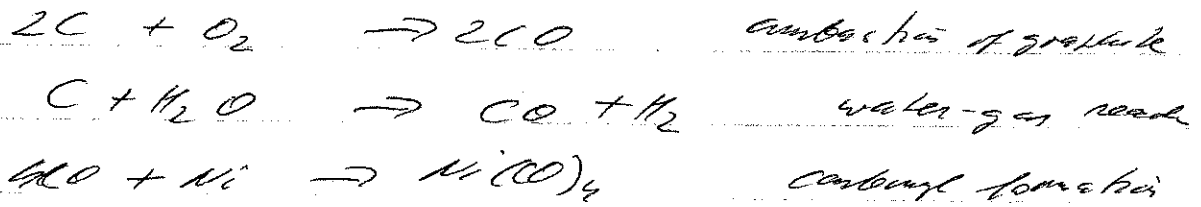


Gasification reactions



1) Negligible amounts of solid residue remain

a) Shrinking core model ^(with changing particle size) for reaction of nonporous solid or solid where rate of reaction much more rapid than diffusional transport into the solid reactant

b) DSRM models with changing solid structure

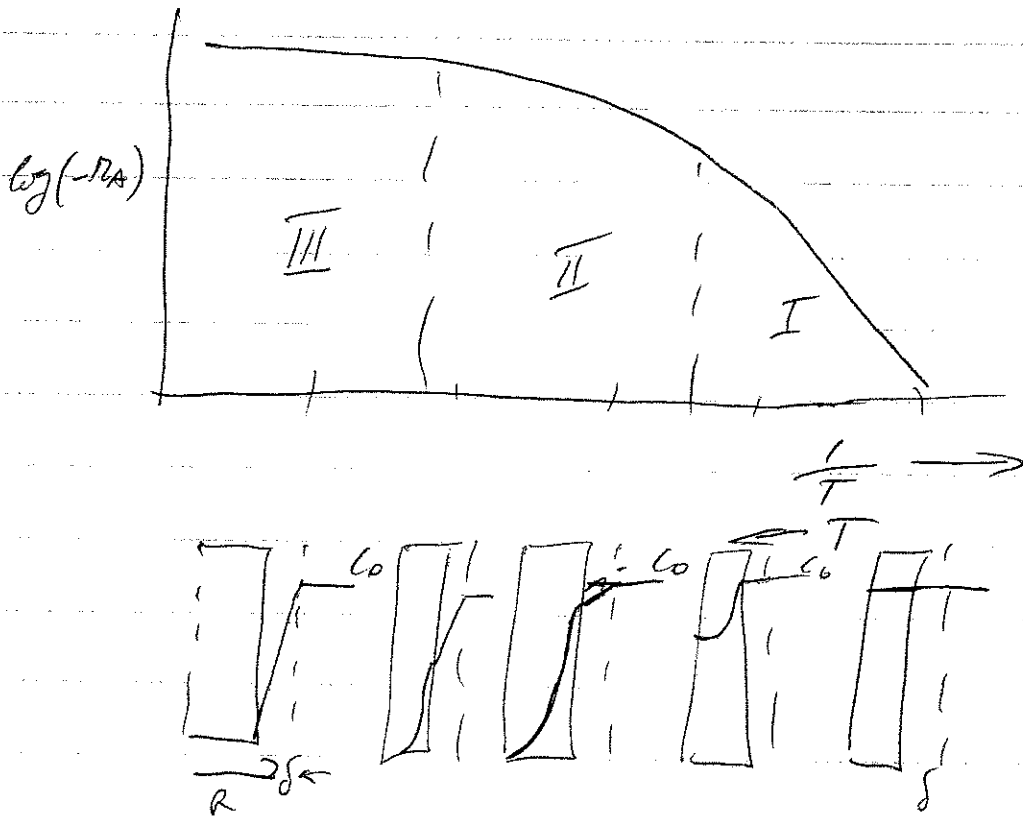
c) granular models

2) Appreciable amounts of solid residue remain.

Previous USCM & DSRM with changing solid structure.

Category I

One can qualitatively represent the gasification reactions in the following manner.



(I) Low T region kinetically controlled
 $E_{app} = E_{true}$ the whole solid reacts

(II) With increasing T the effect of internal diffusion and pore film diffusion become more & more prominent in hindering the rate
 $E_{app} \approx \frac{1}{2} E_{true}$

(III) At high T the whole process is film mass transfer controlled

Particles with Enlarging Pores (Regime I)

C_A - uniform



Solid contains uniform cylindrical pores. No additional pores created by particles

$$\frac{\text{mol}}{\text{cm}^3} \frac{\text{cm}^2 \cdot \text{cm}}{\text{cm}^3 \cdot \text{s}} \frac{P_B}{P_B} S_g \cdot \rho_{\text{pellet}} \frac{dr_{\text{pore}}}{dt} = \frac{P_B}{P_B} \frac{d\epsilon}{dt}$$

$S_g \left(\frac{\text{cm}^2}{\text{g}} \right)$ - BET area of the solid

$\rho_{\text{pellet}} \left(\frac{\text{g}}{\text{cm}^3} \right)$ density of the pellet

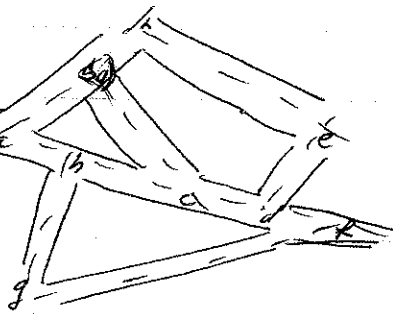
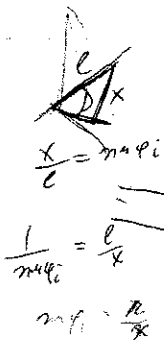
$\frac{P_B}{P_B} = C_{Bt}$ - free molar density of the fluid reactant

$$\left(\frac{\text{cm}^2}{\text{cm}^3} \right) S_v = S_g \rho_{\text{pellet}} = \frac{d\epsilon}{dr}$$

r -pore radius, uniform

Assume an empirical form for the rate

$$\frac{dr}{dt} = \left(\frac{b}{a} \right) \frac{k_a}{C_{Bt}} C_A^m$$



$L \left(\frac{\text{cm}}{\text{cm}^3} \right)$ total length of the pore system per unit volume

$$L = \bar{ab} + \bar{bc} + \bar{cd} + \bar{de} + \dots$$

$$S_v = 2\pi r \left[L - r \sum_{i=1}^m \frac{1}{\sin \phi_i} \right] - r^2 \sum_{i=1}^m \beta(\phi_i)$$

m - number of pore intersections per unit volume

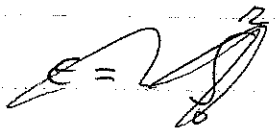
$\beta(\phi_i)$ shape factor of i -th intersection based on angle ϕ_i

$\sum_{i=1}^m \frac{1}{\sin \phi_i}$ allows for the shortening of the pore as intersections get larger

$$S_v = 2\pi RL - KR^2$$

K - a constant for a given rod

$$K = \left[2\pi \sum_{i=1}^n \frac{1}{n\varphi_i} + \sum_{i=1}^n \rho(\varphi_i) \right]$$



$$\frac{dE}{dR} = S_v = 2\pi RL - KR^2$$

$$E = \pi R^2 L - \left(\frac{K}{3}\right) R^3$$

$$E = \pi R_0^2 \xi^2 - \left(\frac{K}{3}\right) R_0^3 \xi^3$$

$$E = E_0 \xi^4 \left(\frac{G-3}{G-1}\right)$$

at $t=0$

$$E = E_0$$

$$R = R_0$$

$$\frac{dE}{dR} = \frac{dE}{d\xi} \frac{d\xi}{dR}$$

$$\textcircled{1} \quad \frac{E}{E_0} = \frac{\pi L R^2 - \left(\frac{K}{3}\right) R^3}{\pi L R_0^2 - \left(\frac{K}{3}\right) R_0^3} = \xi^2 \left(\frac{G-3}{G-1} \right)$$

$$\xi = \frac{R}{R_0}$$

$$G = 3\pi L / KR_0$$

Now G is a constant for a given rod.

To evaluate it assume that the derived equation holds up to $\xi \rightarrow 1$ (obviously the necessary over simplification)

As $\xi \rightarrow 1$

$$S_v \rightarrow 0$$

$$S_v = \frac{dE}{dR} = \frac{1}{R_0} \frac{dE}{d\xi} = \frac{E_0}{R_0} \frac{(2G-3\xi)\xi}{G-1} \quad \checkmark$$

$$S_v \rightarrow 0$$

$$\xi \rightarrow \frac{2}{3} G$$

$$\frac{4}{9} G^3 \left(1 - \frac{2}{3}\right) = G-1$$

$$\left(\frac{2}{3} G\right)^2 \left(\frac{G - \frac{2}{3} G}{G-1}\right) = \frac{1}{E_0}$$

$$\frac{4}{27} G^3 - G + 1 = 0$$

$$\frac{4}{27} E_0 G^3 - G + 1 = 0$$

measure experimentally E_0 , determine G from above

Rate of reaction per unit volume of solid

$$C_{A,t} S_V \frac{dR_{pore}}{dt} = \frac{b}{a} k C_A^m S_V$$

$$k S_V C_A^m = k \frac{\epsilon_0}{R_0} \left[\frac{(25-35)^3}{6-1} \right] C_A^m = \frac{a C_{A,t}}{b} \frac{dR}{dt}$$

$$\xi = \frac{R}{R_0} = 1 + \frac{t}{\tau_c}$$

$$\tau_c = \frac{R_0 C_{A,t}}{\left(\frac{b}{a}\right) k C_A^m}$$

Time for complete conversion
 Thus for complete conversion $X=1$

Conversion of solid

$$\frac{C_{A,0}(1-\epsilon_0) - (1-\epsilon)C_{A,0}}{(1-\epsilon_0)C_{A,0}} = X = \frac{\epsilon - \epsilon_0}{1 - \epsilon_0} = \frac{25-35}{6-1} \Rightarrow \frac{2}{3} \cdot 6 = 1 + \frac{t_{comp}}{\tau_c}$$

$$X = \frac{\epsilon_0}{1-\epsilon_0} \left[\xi^2 \left(\frac{6-\xi}{6-1} \right) - 1 \right]$$

$$t_{comp} = \tau_c \left[\frac{2}{3} \cdot 6 - 1 \right]$$

$$X = \frac{\epsilon_0}{1-\epsilon_0} \left[\left(1 + \frac{t}{\tau_c} \right)^2 \left(\frac{6-1-t/\tau_c}{6-1} \right) - 1 \right]$$

Validity only in the regime where kinetics controls

Examples: $C + CO_2 = 2CO$
 Gasification of graphite with CO_2 at $1100^\circ C$

$R_0 = 2 \mu$ $\epsilon_0 = 0.3$ $P_5 = 0.19 \frac{g}{cm^3}$
 $k = 10^{-3} \text{ cm/s}$ $C_A = 10^{-5} \text{ g mol/cm}^3$

$$\left(\frac{4}{27}\right) \epsilon_0 G^3 - G + 1 = 0$$

$$\frac{4 \times 0.3}{27} G^3 - G + 1 = 0$$

$$\frac{4}{90} G^3 - G + 1 = 0 = \phi$$

$$\frac{4}{30} G^2 - 1 = D\phi$$

$$G_n = G_{n-1} - \frac{\phi(G_{n-1})}{D\phi(G_{n-1})} \quad G = 4.1$$

Now

$$S_{V_0} = \frac{C_0}{P_0} \frac{(2G-3)}{G-1} = \frac{0.3}{2 \times 10^{-4}} \frac{2 \times 4.1 - 3}{4.1 - 1} = 2.52 \times 10^3 \frac{\text{g}}{\text{cm}^3}$$

Thus the initial rate (in absence of ~~total~~ diffusion) is:

$$k S_{V_0} C_A = 10^{-3} \times 2.52 \times 10^3 \times 10^{-5} = 2.52 \times 10^{-5} \frac{\text{g}}{\text{cm}^3 \text{ s}}$$

$$= 1.08 \frac{\text{g}}{\text{h cm}^3}$$

$$\tau_c = \frac{P_0 P_s}{\left(\frac{4}{3}\right) k C_A} = \frac{2 \times 10^{-4} \times 0.19}{10^{-3} \times 10^{-5}} = 3.8 \times 10^3 \text{ s} = \underline{1.055 \text{ h}}$$

$$f_{\text{comp}} = \left(\frac{2}{3} G - 1\right) \tau_c = 3.8 \times 10^3 \left[\frac{2 \times 4.1}{3} - 1\right] = 6.587 \times 10^3$$

$$= \underline{1.83 \text{ h}}$$

Other references: J. Gavali AICHE J vol. 1978
 excellent work Bhatia & Perlmutter AICHE J 1985

Shrinking Particles with Reaction near External Surface
 (Regime II & III)

Ass $D_c = \text{const}$ constant structure of reaction

Similar $L_p \ll L_{\text{pellet}}$

we can consider a one dimensional problem in a plate.

$$De \frac{d^2 C_A}{dr^2} - k_s v C_A^n = 0$$

$$C_A = C_{A_s} \quad r=0$$

$$C_A = \frac{dC_A}{dr} = 0 \quad r \rightarrow \infty$$

The second B.C. is satisfied when

$$N_{Th} = \frac{V_p}{A_p} \sqrt{\left(\frac{n+1}{2}\right) \frac{k_s v C_{A_s}^{n-1}}{De}} > 3$$

$$R_{A_s} = -De \left. \frac{dC_A}{dr} \right|_{r=0} = \sqrt{\frac{2}{n+1} k_s v De} C_{A_s}^{\frac{n+1}{2}} = k' C_{A_s}^{\frac{n+1}{2}}$$

Eqn 2 $\frac{1}{2}$ Eqn

$$\frac{\left(\frac{b}{a}\right) k' C_{A_s}^{\frac{n+1}{2}}}{P_b/V_b} \frac{A_p}{F_p V_p} t = 1 - (1-x)^{1/F_p}$$

Same as reaction - simplification of reaction controlled nonporous particles. $\left(\frac{b}{a}\right) \frac{k_s C_{A_s}^n A_p}{P_b/V_b F_p V_p}$
 However by applying it blindly true kinetic parameters are falsified

For nonporous particles the effect of external surface may start to contribute

$$R_{A_s} = \left(\frac{2}{n+1} k_s v De\right)^{1/2} C_{A_s}^{\frac{n+1}{2}} + k_s f C_{A_s}^n$$

f - roughness of external surface

For $n=1$

$$-\frac{a}{b} C_{B_0} \frac{drc}{dt} = \frac{C_{A_0}}{\left[\left(\frac{2}{n+1} k_s v De\right)^{1/2} + k_s f\right]^{-1} + \frac{1}{k_m}}$$

$$\frac{1}{k_m} \ll \frac{1}{k_s} \quad \text{and} \quad f \ll \left(\frac{2}{n+1} k_s v De\right)^{1/2}$$

regime II

$f \gg \left(\frac{2}{m+1} k_s S_0 D_e \right)^{1/2}$ case of numerous solid

$\frac{1}{k_m} \gg \frac{1}{k_s}$ regime III

Example gasification of graphite
 $S_0 = 2.5 \times 10^3 \frac{\text{cm}^2}{\text{cm}^2}$ mill CO_2 1100°C
 $k_s = 10^{-3} \text{ cm/s}$ $C_{A0} = 10^{-5} \text{ g/cm}^3$
 $D_e = 0.1 \text{ cm}^2/\text{s}$ $k_m = 2 \text{ cm/s}$ Assume $f=1$

Examine importance of various terms

$k_s \cdot f = 10^{-3} \text{ cm/s}$
 $\left(\frac{2}{m+1} k_s S_0 D_e \right)^{1/2} = (10^{-3} \times 2.5 \times 10^3 \times 0.1)^{1/2} = 5 \times 10^{-1} \text{ cm/s}$
 $k_m = 2 \text{ cm/s}$

Thus regime II external surface reaction is negligible

At $T = 1250^\circ\text{C}$

$k_s = 10^{-1} \text{ cm/s}$
 $\left(\frac{2}{m+1} k_s S_0 D_e \right)^{1/2} = 5 \text{ cm/s}$
 $k_m = 2 \text{ cm/s}$

External film resistance is very felt but still regime II

So different graphite with $S_0 = 250$

$k_s f = 0.1 \text{ cm/s}$ external reaction contributes negligibly
 $\left(\frac{2}{m+1} \right)^{1/2} (k_s S_0 D_e)^{1/2} = 0.5 \text{ cm/s}$
 $k_m = 2 \text{ cm/s}$ \therefore regime III

Nonisothermal Behavior

In gasification processes nonisothermal behavior often occurs especially when the particle is in regime II or III

$$\text{Lewis Number } Le_A = \frac{D_A}{\alpha} = \frac{D_A}{(k_e S / c_p)}$$

~~$Le_A = \frac{D_A}{\alpha}$~~

For most solids of interest $Le_A < 1$ thus ~~the~~ transport of heat is faster than that of mass. However there are cases where $Le \approx 1$ or > 1 .

In regime I reaction controls the rate thus both diffusion and heat fluxes are large enough to maintain T constant C_A & T .

In regime II reaction rate is faster and the diffusion flux starts hindering the rate for $Le \neq 1$ a temperature profile may develop in the pellet

$$\frac{D_A}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C_A}{\partial r} \right) - R_A = 0 \quad / \times \left(\frac{-\Delta H}{k_e} \right)$$

$$\frac{k_e}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial T}{\partial r} \right) + (-\Delta H) R_A = 0 \quad / \times \frac{1}{k_e}$$

$$r = R$$

$$C_A = C_{A_s}$$

$$T = T_s$$

$$NEO$$

$$\frac{\partial C_A}{\partial r} = \frac{\partial T}{\partial r} = 0$$

Sum

Nonisothermal Effects in Gas-Solid Noncatalytic Reactions

K. J. Cannon, K. G. Denbigh: "Studies on gas-solid reactions" I: The oxidation of zinc sulphide CES 6 (4/5), 145-154 (1957), II: Causes of thermal instability CES 6, 155-159 (1957)



First to notice nonisothermal effects in gas-solid reactions and to distinguish two basic types of thermal instabilities:

- 1) general ^{thermal} thermal instability due to unstable crossing of heat generation and heat loss lines
- 2) geometrical instability — effect of the solid reaction product which prevents the loss of heat.
- 3) sudden transition of the rate controlling steps

① Overall heat & mass balance:

$$e \frac{\partial C_A}{\partial t} = D_e \nabla^2 C_A - k_0 e^{-E/RT} f(C_A) \varphi(C_B)$$

$$\frac{\partial C_B}{\partial t} = -k_0 e^{-E/RT} f(C_A) \varphi(C_B)$$

$$\frac{\partial T}{\partial t} = \frac{k_0}{\rho C_p} \nabla^2 T + \left(\frac{-\Delta H_p}{\rho C_p} \right) k_0 e^{-E/RT} f(C_A) \varphi(C_B)$$

$$\bar{T}_p = \frac{\int_0^{V_p} T dV}{V_p}$$

$$\bar{C}_{A0} = \frac{\int_0^{V_p} C_A dV}{V_p}$$

$$f(\bar{C}_A) \approx \int \frac{f(C_A) dC_A}{V}$$

$$\tau = \frac{V_p}{S_{ex}}$$

~~$$e \frac{d\bar{C}_A}{dt} = S(C_{A0} - \bar{C}_A)$$~~

$$0 = e \frac{d\bar{C}_A}{dt} = k_m (C_{A0} - \bar{C}_A) - k_0 e^{-E/RT} f(\bar{C}_A) \varphi(\bar{C}_B)$$

solve for \bar{C}_A

$$\frac{d\bar{C}_B}{dt} = -k_0 e^{-E/RT} f(\bar{C}_A) \varphi(\bar{C}_B)$$

different time scale

$$\tau \frac{dT}{dt} = \left(\frac{h}{C_p}\right) (T_0 - T) + J_0 k_0 e^{-E/RT} f(\bar{C}_A) \varphi(\bar{C}_B) \approx 0$$

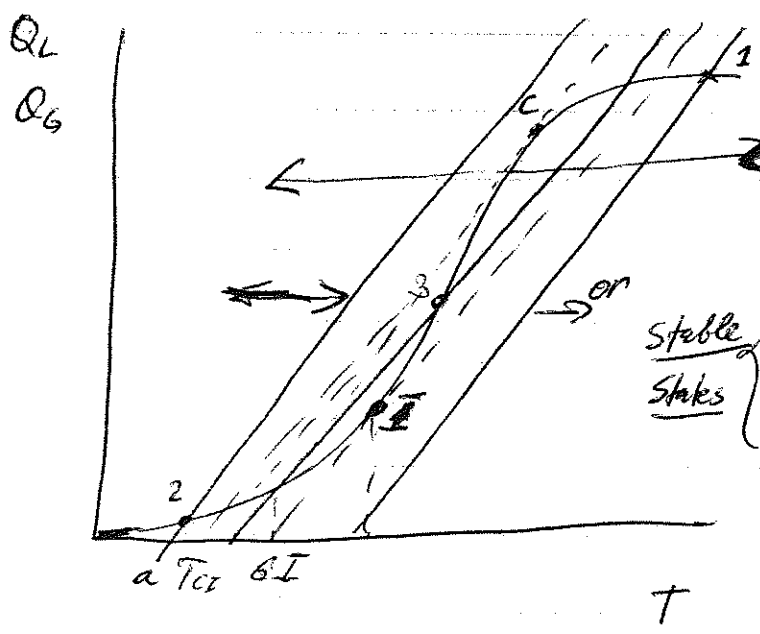
~~$$h(T_0 - T)$$~~

$$h(T - T_0) = J_0 k_0 e^{-E/RT} \varphi(\bar{C}_B) \varphi(C_A(T))$$

$\left(\begin{matrix} \text{Heat loss} \\ \text{from the solid} \\ \text{pellet} \end{matrix} \right) = \left(\begin{matrix} \text{heat generation} \\ \text{within the solid} \\ \text{pellet} \end{matrix} \right) - \left(\begin{matrix} \text{heat} \\ \text{accumulation} \\ \text{within the} \\ \text{pellet} \end{matrix} \right)$

 $Q_L = Q_G - \approx 0$

 for small heat capacity pellets



- ① High T ~~stable~~ state
diffusion limited
- ② Low T ~~stable~~ state
kinetics limited
- ③ unstable operating point
- not realizable

For an exothermic reaction if we introduce the solid at gas temperature T_I it will reach state 2 and move along the sigmoid line in kinetically controlled region until it hits point I. T_I is the minimum ignition temperature of the solid, T_{GI} is the minimum gas temperature for ignition of the cold solid. Then the reaction rapidly moves to the upper portion of the sigmoid curve into diffusion controlled region.

T_c is the minimum combustion temperature i.e. the minimum T at which the solid will react in a high rate diffusion controlled region. Notice that the gas temperature T_{GI} to sustain combustion is lower than minimum ignition T .

(2) Geometric instability - can occur in exothermic reactions why. If the product layer is less conductive than the solid reactant this may reduce the heat removal rate from the pellet thus increasing the T in some regions of the pellet. In turn this larger T may ignite inside the pellet.

overcompensate for diffusional resistance (if one is in the kinetically controlled region) and may cause a higher rate to occur in the pellet rather than in the outside layers.

This, if the pellet were then deaged the shrinking core model may cause the reaction to take off at certain centers of the core thus making the core-product interface highly irregular in shape (geometric instability)

Necessary condition for geometric instability

$\frac{dT_i}{d(R-r_c)} > 0$ $\frac{dT_i}{dT_c} < 0$ necessary condition

for a shrinking core model.

Essentially this phenomenon (independent of a model) may occur whenever:

~~$\frac{dT_i}{dT_c} > 0$~~ $\frac{dT}{dx_c} > 0$ or $\frac{d\eta}{dx_c} > 0$



pellet reaction from inside like a rotten apple.

$\eta = \frac{\text{actual overall rate}}{\text{rate obtainable when pellet is at gas } T \text{ \& } C_a}$

J. Shen & J. M. Smith "Diff. Effects in Gas-Solid
Reactions" *AIChE J* 4, 293 (1958)

C. Y. Wen & S. C. Wang "Thermal & Diff. Eff. in
Solid Gas Reaction" *IEC* 62, 30 (1970)

Add equations

valid when

$$k_e \nabla^2 T = 0 \quad r_c < R < R$$

heat capacity
is small.

$$(1) \quad R = R \quad k_e \frac{\partial T}{\partial r} = h(T_0 - T)$$

$$R = R_c \quad k_e \frac{\partial T}{\partial r} = k_s(r_c) C_{Ac} (-\Delta H_r)$$

$$k_s = k_s^0 e^{-E/RT_c}$$

$$\frac{4}{3} \pi R_c^3 \rho_c C_p \frac{\partial T_c}{\partial t} = 4 \pi R_c^2 a k_s C_{Ac} (-\Delta H_r) + 4 \pi R_c^2 k_e \frac{\partial T}{\partial r} \Big|_{r_c}$$

Added later by Wang & Wen *AIChE J* 18, 1231 (1972)

$$\frac{T_c - T_0}{\frac{1}{k_e} \left(\frac{1}{R_c} - \frac{1}{R} \right) + \frac{1}{R^2 h}} = \frac{C_{A0} (-\Delta H)}{\frac{T_c/T_0}{R_c^2 k_s^0 C_{A0}} + \frac{1}{D_e(T_0)} \left(\frac{1}{R_c} - \frac{1}{R} \right) + \frac{1}{R^2 k_m(T_0)}}$$

Heat loss Q_L

Heat generation
 Q_R

or

$$\frac{T_c}{T_0} - 1 = F_2 \frac{C_{Ac}}{C_{A0}} \exp \left[\gamma_5 \left(1 - \frac{T_0}{T_c} \right) \right] = 0$$

$$F_2 = \gamma_2 \gamma_4 \left[\gamma_3 \left(\frac{R_c}{R_0} \right)^2 + \left(\frac{R_c}{R_0} \right) \left(1 - \frac{R_c}{R_0} \right) \right] \quad \frac{R_c}{R_0} = (1-x)^{1/3}$$

$$C_{Ac} = \frac{C_{A0}}{1 + \frac{k_s R_c}{D_r} \left(1 - \frac{R_c}{R} \right) + \frac{k_s}{k_m} \left(\frac{R_c}{R} \right)^2}$$

$$y_2 = \frac{h_s R_o}{D_c} = \frac{r_D}{r_R} \quad \left| \quad y_3 = \frac{k_c}{hR} = \frac{1}{Nu} = \frac{1}{Bi_h}$$

$$y_4 = \frac{\Delta H (C_{A0}) D_c}{T_0 k_c} = -\beta$$

$$y_5 = \frac{E}{R_g T_0} = \gamma$$

Solve simultaneously with

$$1 - \frac{C_{Ac}}{C_{A0}} - F_1 \frac{C_{Ac}}{C_{A0}} \exp\left[y_5 \left(1 - \frac{T_g}{T_c}\right)\right] = 0$$

$$F_1 = y_2 \left[y_1 \left(\frac{R_c}{R_o}\right)^2 + \frac{R_c}{R_o} \left(1 - \frac{R_c}{R_o}\right) \right]$$

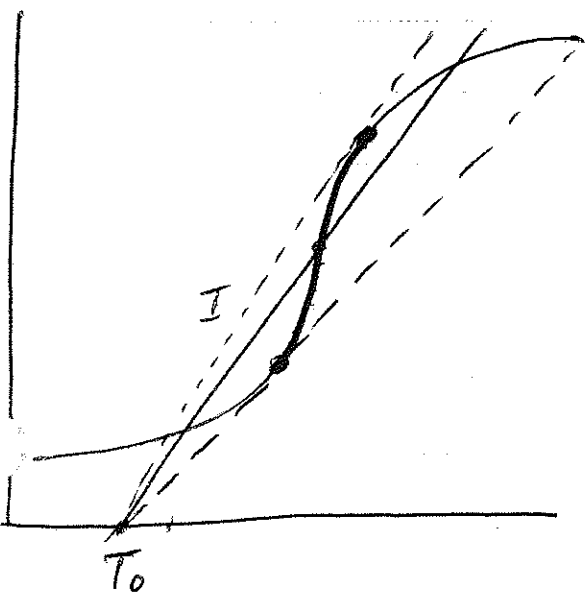
One of the real positive roots represents an unstable condition

Thermal Instability

Necessary & sufficient condition

$$\frac{\delta Q_{loss}}{\delta T_c} < \frac{\delta Q_{ov}}{\delta T_c}$$

$$\boxed{\frac{dQ_c}{dT} < \frac{dQ_o}{dT}}$$



Kinetic Region - Unstable

$$y_3 < \frac{2(R_c/R) - 1}{2(R_c/R)} < 0.5$$

For instability to occur useful criteria to decide whether minimum ignition T will be observed.