Treatment of Very Rapid Reactions - Summary of Basic Concepts

We have so far considered only the situations where the characteristic reaction time is much larger than the mixing time, $\tau_R \gg \tau_{mix}$. Now let us look at the other extreme when $\tau_R \ll \tau_{mix}$ so that the reactants cannot coexist but the reaction interface divides the space into zones that have either reactant A or reactant B present but not both.

We will consider <u>dilute</u> systems in the sense that

a)   fluxes of A and B do not affect the velocity profiles in a given flow field
b)   fluxes of A and B are linearly related to the driving force for that component alone
        <u>i.e</u> there are no coupling effects.
c)   the diffusivities of the two components A and B in the solvent are equal.

Two situations should be considered:

a)   laminar flow
b)   turbulent flow

We first look at systems without mechanical mixing where there is a distinct coordinate z_1 pointing in the direction of the main flow. This is the case in pipe, film like, flat plate like configurations and flows.

Assume the reaction stoichiometry is:

$$aA + bB = pP \tag{1}$$

and the reaction rate is <u>instantaneous</u> on the time scale of diffusion or mixing. [In principle $\tau_R = f(C_A, C_B, T)$ and has a limiting step that depends only on changes in electron density and configuration, it is not a function of any linear dimension while τ_{mix} is a function of the segregation of flow and some characteristic distance that separates A from B. Ultimately the limiting step in mixing is diffusion $\tau_D = \lambda^2 / D$. Instantaneous reactions are those for which a λ small enough cannot be reached to make $\tau_D < \tau_R$ <u>i.e</u> reaction is never limiting].

<u>Laminar Systems</u>

The problem can now be described by the general convection-diffusion equation in region D of interest

$$\frac{\partial c_i}{dt} + v \cdot \nabla c_i = D\nabla^2 c_i - R_{i-} \; ; \quad i = A, B \tag{2}$$

where the velocity field $\underset{\sim}{v}$ is known as a function of position (and time) from the solution of the Navier Stokes equations with appropriate boundary conditions.

Initial and boundary conditions are prescribed:

$$t = 0, c_i = c_{io} \quad (3a)$$
$$on \ \partial D, c_i = c_{is} \quad (3b)$$

The boundary ∂D engulfs the whole region D of interest.

Two typical types of problems arise:

1.   <u>Open steady state flow systems</u>

Here the boundary can typically be divided into two or more segments, e.g.

$$\partial D = \partial D_1 + \partial D_2 + \partial D_3$$

Say reactant A is fed through some inlet ports, ∂D_1, and reactant B through some other ones, ∂D_2, while the rest of the boundary ∂D_3 is impermeable to either A or B. Then:

$$on \ \partial D_1 \qquad C_A = C_{Ao}$$
$$on \ \partial D_2 \qquad C_B = C_{Bo}$$
$$on \ \partial D_3 \qquad \frac{\partial C_A}{\partial n} = \frac{\partial C_B}{\partial n} = O$$

In case of an instantaneous reaction, since A and B cannot coexist, reaction surface ∂D_R then separates the region D_A containing A from the region D_B containing B. Such a reaction surface (interface) must exist since A and B cannot coexist.

2.   <u>Closed (with or without flow) systems in transient operation</u>

An example is *region D containing at* $t = 0, C_B = C_{Bo}$ *and with* $\frac{\partial C_A}{\partial n} = 0$ *on* ∂D which is suddenly exposed to concentration C_{Ai} on ∂D or portion thereof. A "reaction surface" ∂D_R evolves that separates A and B and moves inward until all B is reacted.

Usually we want to know how long in the direction of flow should system 1 be to react A or B completely, or how long a time it will take to react system 2 completely.

<u>For nonturbulent (laminar flow and/or diffusion only) systems we can show:</u>

that by defining

$$C_t = bC_A - a \ C_B \qquad\qquad\qquad\qquad\qquad (4)$$

The position of the <u>reaction interface</u> is given by

$$\frac{\beta}{\beta+1} = f(z_1, z_2, \ldots z_n) \tag{5}$$

where

$$\beta = \frac{aC_{Bo}}{bC_{Ai}} \tag{6}$$

and we had the following boundary conditions

$$BCO: C_B = C_{Bo}, C_A = 0 \tag{7a}$$

$$BCI: C_B = 0, C_A = C_{Ai} \tag{7b}$$

Here $f(z_1, z_2 \ldots z_n)$ is the solution

$$\frac{C^o - C_o^o}{C_1^o - C_o^o} = f(z_1, z_2 \ldots z_n) \tag{8}$$

(with z_1 being either time or the spatial variable in the direction of main flow and other z_k being spatial coordinates) for the concentration of a nonreacting dilute species in the same flow field and satisfying equivalent BCs (or ICs) i.e C^o satisfies:

$$\frac{\partial C^o}{\partial t} + \underline{v}\nabla C^o = D\nabla^2 C^o \tag{9}$$

with

$$BCO: \quad C^o = -aC_{Bo} \tag{10a}$$
$$BCI: \quad C^o = bC_{Ai} \tag{10b}$$

By flow averaging (or cross-sectional averaging) of the result (8) over all coordinates except z_1, and by using the analogy between the reactive and nonreactive case, one obtains a profile of average concentrations of A and B as a function of z_1.

$$\frac{\dfrac{\overline{C_A}}{C_{Ai}} - \beta\dfrac{\overline{C_B}}{C_{Bo}} + \beta}{\beta+1} = \int\limits_{z_2} \ldots \int\limits_{z_n} w\, f\, dz_2 \ldots dz_n = \overline{f}(z_1) \tag{11}$$

Here w is the appropriate geometric weighting function needed to achieve the proper average. The position (or time in a transient closed system) z_{1f} required to achieve

complete reaction of one of the reactants (say B) can be obtained either from eq (5) by mapping the reaction surface and finding the distance (time) z_{1f} of furthest penetration of B or from eq (11) by setting $\overline{C_B} = 0$ and $\overline{C_A} = C_{Ai}$ so $that$ $1 = \overline{f}\left(z_{1f}\right) \Rightarrow z_{1f} = \overline{f}^{-1}(1)$. Clearly inversion of the function $\overline{f}$ is required.

Turbulent Systems

In turbulent flow fields it is impractical to attempt to compute instantaneous concentrations C°, C_A, C_B or $C_t = bC_A-aC_B$. Instead one introduces the ensemble average concentrations, $<C^\circ>, \hat{C}_A, \hat{C}_B, \hat{C}_t$ etc. and fluctuating concentrations so that the instantaneous concentration is given by the sum of the ensemble average and fluctuating component.

One cannot now obtain the time averaged behavior of the system with instantaneous reaction considering only the time average concentration of the nonreacting system because $\hat{C}_t = 0$ does not any more describe the reaction interface but a surface of time averaged stoichiometric ratio around which reaction takes place.

An estimate of the length (or time) needed to accomplish complete reaction can still be obtained from the requirement that the spatial average of the time averaged "concentration" $\overline{\hat{C}}_t$ be zero leading to:

$$\frac{\beta}{\beta+1} = \overline{f_T}\left(z_{1f}\right) \tag{12}$$

Define root mean square concentration fluctuations (RMSCF) in the same turbulent field with reaction

$$\Gamma_t = \sqrt{\hat{c}_t^2} \tag{13a}$$

and without reaction

$$\Gamma^o = \sqrt{\hat{c}^{o2}} \tag{13b}$$

where

$$C_t = bC_{Ai} - aC_{Bo} = \hat{C}_t + c_t \tag{14a}$$
$$C^o = \hat{C}^o + c^o \tag{14b}$$

The relationship between Γ_t and Γ^o is then given by:

$$\frac{\Gamma_t}{\Gamma^o} = \left(\frac{C_{ti} - C_{to}}{C_i^o - C_o^o}\right) \tag{15}$$

where i, o indicate the values at the two boundaries where boundary conditions BCO and BCI are specified.

The relative concentration fluctuations are:

$$\gamma_t = \frac{\Gamma_t}{\hat{C}_t} \quad (16a) \qquad ; \qquad \gamma^o = \frac{\Gamma^o}{\hat{C}^o} \tag{16b}$$

and their relationship can be shown to be:

$$\gamma_t = \gamma^o \frac{f_T(z_1, z_2 \ldots)}{f_T(z_1, z_2 \ldots) - \dfrac{\beta}{1+\beta}} \tag{17}$$

where

$$\frac{\hat{C}^o - C_o^o}{C_i^o - C_o^o} = \frac{\hat{C}_t - C_{to}}{C_{ti} - C_{to}} = f_T(z_1, z_2 \ldots z_n) \tag{18}$$

In case of <u>isotropic</u> turbulence (independent in all directions except z_1) one can show:

<u>for stoichiometric mixture $\beta = 1$</u>

$$x_A = x_B = 1 - \frac{\Gamma^o}{\Gamma_o^o} \tag{19}$$

where Γ_o^o is determined at a plane z_{10} where the mixture coarseness has been uniformized.

<u>For nonstoichiometric mixture $\beta \neq 1$</u>

$$x_A = 1 + (\beta - 1)(1 + g(\gamma_t)) \; ; \quad \beta > 1 \tag{20a}$$

$$x_B = 1 + \frac{\beta - 1}{\beta} g(\gamma_t) \; ; \quad \beta < 1 \tag{20b}$$

with

$$g(\gamma_t) = \frac{\gamma_t}{\sqrt{2}} \, ierfc\left(\frac{1}{\gamma_t \sqrt{2}}\right) \tag{21}$$

and $\gamma_t = \gamma_{to} \dfrac{\Gamma^o}{\Gamma_o^o}$

One needs to know the reactants feed ratio and reaction stoichiometry to get β. Then one needs to measure Γ_o^o and Γ^o in absence of reaction in the same flow field and calculate γ_{to} from $\dfrac{\beta}{1-\beta} = g(\gamma_{to})$.

Working at $\beta \neq 1$ dramatically reduces the distance required for conversion of limiting reactant.

The main message of the theory is as follows. If we can determine the function f_T that defines the ensemble average concentration profiles in the nonreacting system (eq (18)), and we measure the RMSCF γ^o in the nonreactive system under the identical hydrodynamic conditions encountered in the system with instantaneous reactions, then the conversions in such reacting system can be determined by eq (19) for stoichiometric reactant feed ratio and by eq (20) for nonstoichiometric feeds.