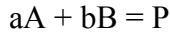


GENERAL 2ND ORDER REACTION IN TURBULENT TUBULAR REACTORS

Vassilatos & Toor, AIChEJ. 11(4), 666 (1965)

Consider the following stoichiometry:



The mass conservation law for species i yields

$$\frac{\partial C_i}{\partial t} + \nabla v C_i = \nabla \cdot D_i \nabla C_i + R_i$$

Upon representing instantaneous concentration by the sum of the time averaged and fluctuation part $C_i = \tilde{C}_i + C'_i$, we get the following equation for the time averaged concentration \tilde{C}_i .

$$\frac{\partial \tilde{C}_i}{\partial \tau} + \nabla v C_i = \nabla \cdot (D_i \nabla \tilde{C}_i - \langle v' C'_i \rangle) + \tilde{R}_i$$

In the above both \sim and $\langle \rangle$ represent ensemble (or time) averaged values.

This requires a model for the velocity concentration cross correlation and for the rate.

$$\begin{aligned} \langle v' C'_i \rangle &= -D_i \nabla \tilde{C}_i \\ \tilde{R}_A &= -k_r \langle C_A C_B \rangle = k_r \langle (C_A + C'_A)(C_B + C'_B) \rangle \\ &= -k_r [\langle \tilde{C}_A \tilde{C}_B \rangle + \langle C'_A C'_B \rangle + \langle C_A C'_B \rangle + \langle C'_A C_B \rangle] \end{aligned}$$

By definition $\langle C'_A \rangle = \langle C'_B \rangle = 0$

$$\tilde{R}_A = -k_r [\langle \tilde{C}_A \tilde{C}_B \rangle + \langle C'_A C'_B \rangle] = \frac{a \tilde{R}_B}{b}$$

$$\text{mean rate} = \left(\text{homogeneous rate at local time averaged concentration} \right) + \left(\text{cross correlation of concentration fluctuation} \right)$$

mean rate < homogeneous mean rate

As $k_r \rightarrow \infty$ $\langle C'_A C'_B \rangle \rightarrow -\tilde{C}_A \tilde{C}_B$ to keep rate finite.

Experimental verification sought on turbulence effects for:

- instantaneous
- rapid
- slow reactions

Consider that in a given system the mixing rate can be established by running instantaneous reactions at $\beta = 1$. Then

$$x_A = 1 - \frac{\Gamma^o}{\Gamma^o} \quad (1)$$

If turbulence parameters were not measured, one can determine x_A vs z i.e. (z/\bar{u}) .

Now the rate is due entirely to mixing and one can write

$$C_{Ao} \bar{u} \frac{dx_A}{dz} = R_{Am} = k_m \bar{C}_A \bar{C}_B \quad (2)$$

$$\bar{C}_A = C_{Ao} (1 - x_A) = \bar{C}_B \quad (3)$$

where \bar{C}_A is the cross-sectional average.

Thus k_m for the system can be determined over a range of Reynolds numbers.

Now the characteristic reaction number is

$$N_{RM} = \frac{k_r}{k_m} \quad (4)$$

$N_{RM} \gg 1$ instantaneous reaction

$N_{RM} > 1$ rapid reaction

$N_{RM} \ll 1$ slow reaction

The following reactions were considered:

	k_r (L/mol s) at 30°C
1. HCl + NaOH	∞ instantaneous
2. HCl + LiOH	∞ instantaneous
3. (COOH) ₂ + 2LiOH oxalic acid	10^{11}
4. HCOOH + LiOH formic acid	
5. CO ₂ + 2NaOH	1.24×10^4
6. CO ₂ + n NH ₃ (n=1-2)	5.85×10^2
7. HCOOCH ₃ + NaOH methylformate	4.7×10^1

At stoichiometric feed of reactants, $\beta = 1$, and for an instantaneous reaction (such as the first two listed above) from eq (2) it follows that

$$\bar{u} \frac{dx_A}{dz} = k_m \bar{C}_{Ao} (1 - x_A)^2 \quad (5)$$

$$z = z_o$$

$$x_A = 0 \quad (5a)$$

Integration of (5) & (5a) yields

$$\frac{1}{1 - x_A} = 1 + \frac{k_m \bar{C}_{Ao}}{\bar{u}} (z - z_o) \quad (6)$$

Experimental reactor with 100 tubes, ID = 0.052 inches (0.13 cm) 5 in long was used. Tubes were pressed into holes of a 1 1/4" diameter disk that closed the upper end of the 1 1/4" (3.175 cm) diameter

lucite tubular reactor. Reactants are fed to alternate tubes with $Re = 3,700$ in tubes and $15,000$ in the reactor. Jet velocity $= 6 \times$ mean reactor velocity. $\bar{u} \approx 15.85 \text{ in/s} = 40.26 \text{ cm/s}$.

Reactant concentration had to be monitored. Deionized water was used. Reactant carrying streams are thermostated at 29.9°C in a thermal bath. Reaction progress is monitored by adiabatic temperature rise.

$$\Delta \bar{C}_A = \frac{\rho C_p}{\Delta H_R} \Delta \bar{T} \tag{7}$$

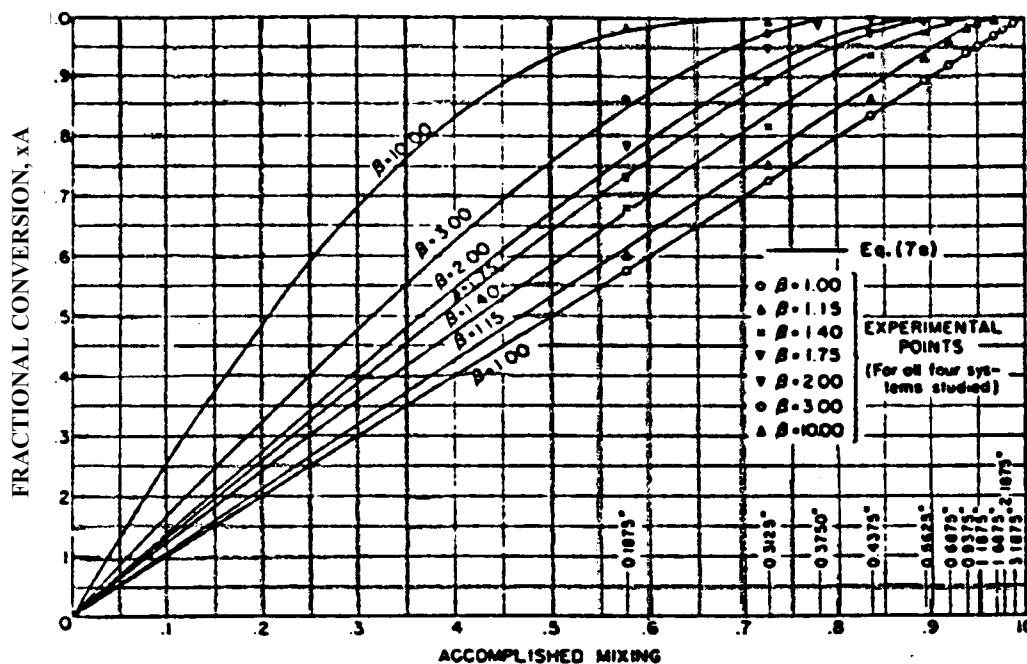
or

$$x_A = \frac{\rho C_p}{\Delta H_R} \Delta \bar{T} \tag{8}$$

$\bar{T} - \bar{T}_o$ is measured by a copper constant in glass shielded thermocouple (30 gauge) whose reference junction is in one of the feed streams just before mixing. Effective tip diameter was 0.059 in (0.15 cm). Measurements were verified with finer probes. Blind runs with pure water were also done and the signal was subtracted (heat of friction, heat losses, etc.). Measured radial T profiles were flat so \bar{T} can be measured as equal to the center line temperature.

All four very rapid reactions behaved as instantaneous and produced at fixed $\beta = 1$ the same conversion vs distance curve.

FIGURE 1: Reactant conversion for very rapid reactions as a function of distance for stoichiometric feeds ($\beta = 1$)
 [From Vassilatos and Tour, AIChE J. 11, 666 (1965)]



Least squares fit of eq (6) at $\beta = 1$ to the data gives

$$\frac{1}{1-x_A} = 1 + 19.24(z - 0.144) \quad ; \quad z > 0.144 \text{ in} \quad (9)$$

Excellent straight line is obtained when $\frac{1}{1-x_A}$ vs z is plotted except at very first few data points $z < 0.35$.

From eq (9), based on theory, we conclude that the degree of unaccomplished mixing is given by a hyperbolic decay law.

$$\frac{\Gamma^o}{\Gamma_o^o} = \frac{1}{1 + 19.24(z - 0.144)} \quad ; \quad z > 0.144 \quad (10)$$

Comparison of formula (6) and (9) yields

$$k_m = \frac{305a}{b C_{A_o}} \left(\frac{L}{mol \ s} \right) \quad (11)$$

Now for non-stoichiometric feeds the theory predicts [eq (24) and (22) of previous part]

$$x_A = 1 + (\beta - 1) \left[1 + g \left(\gamma_{to} \frac{\Gamma^o}{\Gamma_o^o} \right) \right] \quad (12)$$

where γ_{to} is given by the solution of

$$\frac{\beta}{1 - \beta} = g(\gamma_{to}) \quad (13)$$

where

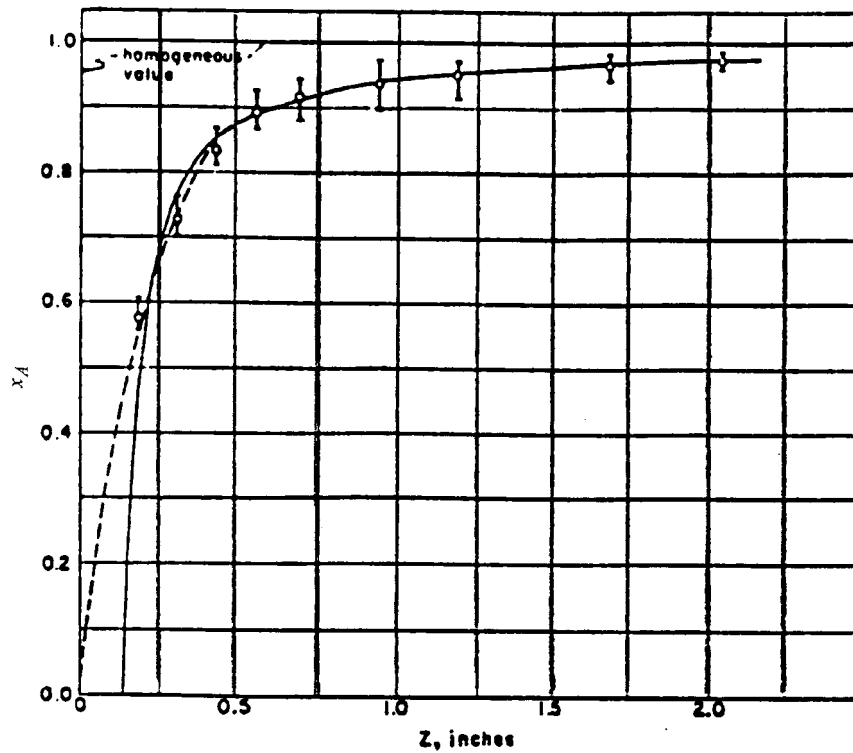
$$g(x) = \frac{x}{\sqrt{2}} \operatorname{ierfc} \left(\frac{1}{x\sqrt{2}} \right) \quad (14)$$

$$\beta = \frac{a \overline{C_{B_o}}}{b \overline{C_{A_o}}} \quad (15)$$

Now we know $\frac{\Gamma^o}{\Gamma_o^o}$ from eq (10).

Comparison of data and theoretical predictions was excellent for β in the interval (1,10).

FIGURE 2: Fractional conversion vs. accomplished mixing, very rapid reactions.



Now one tested the assumption of 2nd order mixing law at $\beta \neq 1$

For $\beta \neq 1$ eq (5) becomes

$$\bar{u} \frac{dx_A}{dz} = k'_m \frac{b}{a} \bar{C}_{Ao} (1-x_A)(\beta-x_A)$$

Upon integration this yields:

$$\ln \left(\frac{1-x_A}{\beta-x_A} \right) = -\ln \beta - (\beta-1) \frac{k'_m (b/a) \bar{C}_{Ao}}{\bar{u}} (z-z_1) \tag{17}$$

Plots of $\ln \left(\frac{1-x_A}{\beta-x_A} \right)$ vs z did yield straight lines for all instantaneous reactions. The slopes of the lines revealed

$$k'_m = \frac{305}{\frac{b}{a} \bar{C}_{Ao}} \psi(\beta) \tag{18}$$

where for $\beta = 1$, $\psi = 1$; and for $\beta = 10$, $\psi = 0.3$.

Based on these findings we see that N_{RM}

$$N_{RM} = \frac{\frac{b}{a} \bar{C}_{A_0} k_r}{305 \psi(\beta)} = \frac{k_r}{k'_m} \quad (19)$$

Since $k'_m \approx 10,000$ to $20,000$ L/mol s, indeed all of the first 4 reactions are instantaneous.

One should recall that the 2nd order decay law for $\frac{\Gamma^o}{\Gamma^o}$ is the peculiarity of the mixing device, not a general law.

NOTE: Axial dispersion effects are negligible and PFR formulas (eq 16) produce the desired result.

For the $\text{CO}_2 + 2\text{NaOH}$ reaction

$$N_{RM} = 0.5 \text{ to } 10$$

If we assume

$$\bar{R}_A = -K \bar{C}_A \bar{C}_B \quad (20)$$

Plot of $\ln\left(\frac{1-x_A}{\beta-x_A}\right)$

$$\ln\left(\frac{1-x_A}{\beta-x_A}\right) = -\ln\beta - \frac{K(\beta-1)\frac{b}{a}\bar{C}_{A_0}}{\bar{u}}(z-z_1) \quad (21)$$

yields straight lines but $K = K(\beta)$.

For this particular reaction $k_r = 12,400$ (L/mol s).

Before we found for instantaneous reactions that at $\beta = 3.88$ we have $k'_m = 9,400 \frac{\text{L}}{\text{mol s}}$.

Then,

$N_{RM} = 1.30$ for the carbon dioxide reaction with sodium hydroxide and we get $K = 2770 \left(\frac{\text{L}}{\text{mol s}}\right)$.

Similarly, at

$$\beta = 1.26, k_m = 19,700 (\text{L/mol s}), N_{RM} = 0.63 \text{ and we find } K = 3420 \left(\frac{\text{L}}{\text{mol s}}\right)$$

Thus, $K < k_r, k'_m$ or k_m

For $\text{CO}_2 + \text{NH}_3$ - the same phenomenon is observed

$$k_r = 585 \text{ (L/mol s)}$$

	$k'_m \text{ (L/mol s)}$	N_{R_m}	$K \text{ (L/mol s)}$
$\beta = 2.1$	24,500	0.024	588
$\beta = 5.75$	12,300	0.048	336

For the Methyl formate - sodium hydroxide reaction ($N_{R_M} = 10^{-3}$) and the homogeneous rate law holds with $K = k_r = 47.1 \text{ (L/mol s)}$ and $z_{10} = 0$. Homogeneous rate reaction is observed as $N_{R_M} \rightarrow 0$.

Throughout this reactor the mean rate is a fixed fraction, K/k_r , of the homogeneous mean rate even though the fluid is becoming more homogeneous as z increases.

If PFR assumptions are O.K. then these values $-\frac{\overline{C'_A C'_B}}{\overline{C'_A C'_B}} = 1 - \frac{K}{k_r}$ vary from 0.72 at $\beta = 1.26$ to 0.78 at $\beta = 3.88$ for $\text{CO}_2 + 2 \text{ NaOH}$., and are lower for $\text{CO}_2 + n\text{NH}_3$ i.e. 0 for $\beta = 2.1$ to 0.43 at $\beta = 10$.

For intermediate reactions there is no clear pattern regarding the value of the apparent rate constant K to be used.

The approximate expression $\frac{1}{K} \approx \frac{1}{k_r} + \frac{1}{k_m}$ is valid only in the two limits as

$$N_{R_M} \rightarrow \infty \text{ or } N_{R_M} \rightarrow 0$$

The actual K , K_{act} is less than K - estimated by above formula for rapid reactions. Thus

$$\frac{1}{K} = \frac{1}{k_r} \left(1 + \frac{k_r}{k_m} \right) = \frac{1}{k_r} (1 + N_{R_M})$$

$$K = \frac{k_r}{1 + N_{R_M}} > K_{act}$$