IDEAL REACTORS

(CHE 471)

M.P. Dudukovic

Chemical Reaction Engineering Laboratory

(CREL),

Washington University, St. Louis, MO

IDEAL REACTORS

One of the key goals of chemical reaction engineering is to quantify the relationship between production rate, reactor size, reaction kinetics and selected operating conditions. This requires a mathematical model of the system, which in turn rests on application of conservation laws to a well-defined control volume of the reaction system and on use of appropriate constitutive expressions for the reaction rates. The concepts of <u>ideal</u> reactors allow us to quantify reactor performance as a function of its size and selected operating conditions.

To illustrate this useful concept we deal here with a single, homogeneous phase, single reaction at constant temperature. We introduce then the ideal batch reactor, and two ideal continuous flow reactors. In each case we apply the conservation of species mass principle which states

(Rate of Accumulation) = (Rate of Input) − (Rate of Output) + (Rate of Generation)   (2-1)

Equation (2-1) is applied to an appropriately selected control volume, the largest arbitrarily selected volume of the system in which there are no gradients in composition.

2.1   Batch Reactor

The ideal batch reactor is assumed to be perfectly mixed. This implies that at a given moment in time the concentration is uniform throughout the vessel. The volume, V in the development below is assumed equal to the volume of the reaction mixture. This is then equal to the reactor volume V_R in case of gas phase reaction but not in case of liquids ($V < V_R$, then). The batch reactor can be an autoclave of V = const (Figure 2.1-a) and a constant pressure, P = const) (Figure 2.1-b) vessel. The former is almost always encountered in practice.

Our goal is:

a)   To find a relationship between species concentration (reactant conversion) and time on stream.

b)   To relate reactor size and production rate.

Let us consider a single irreversible reaction $A \rightarrow P$ with an n-th order irreversible rate of reaction
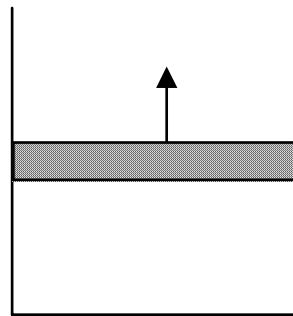
$$-R_A = kC_A^n \tag{2-2}$$

At $t = 0$ a batch of volume V is filled with fluid of concentration C_{Ao}. Reaction is started ($n_{Ao} = C_{Ao}V_o$). Find how reactant conversion depends on reaction time? Also determine the production rate as a function of reaction time.

We apply (eq 2-1) to reactant A:

$$0 - 0 + (R_A V) = \frac{dn_A}{dt} = \frac{d(VC_A)}{dt} \tag{2-3}$$
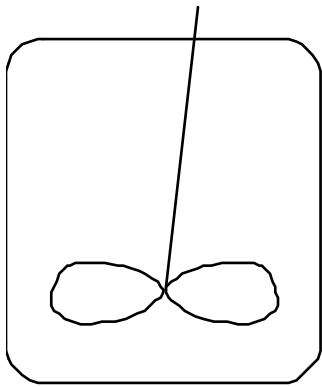
a) V = const   b) P = const

FIGURE 2-1: Schematic of Batch Reactors

In our case due to the fact that $\sum_{j=1}^{2} \upsilon_j = 0$, V= const irrespective of the batch reactor type, so that eq (2-3) becomes

$$\frac{dC_A}{dt} = R_A \tag{2-4}$$

$$-\frac{dC_A}{dt} = (-R_A) = kC_A^n; \quad t = 0 \quad C_A = C_{Ao} \tag{2-5}$$

Separation of variables and integration yields:

$$\int_o^t dt = -\int_{C_{A_0}}^{C_A} \frac{dC_A}{kC_A^n} = \frac{1}{k} \int_{C_A}^{C_{Ao}} \frac{dC_A}{C_A^n} \tag{2-6}$$

$$t\Big|_o^t = \frac{1}{k}\frac{C_A^{1-n}}{1-n}\Bigg|_{C_A}^{C_{Ao}}$$

(2-7)

$$t - 0 = \frac{1}{k(1-n)}\left[C_{Ao}^{1-n} - C_A^{1-n}\right]$$

$$t = \frac{C_{Ao}^{1-n}}{k(1-n)}\left[1 - (1-x_A)^{1-n}\right]$$

(2-8a)

or

$$t = \frac{1}{k(n-1)C_{Ao}^{n-1}}\left[(1-x_A)^{1-n} - 1\right]$$

(2-8b)

Once order of reaction, n, is specified (as shown below for n=0, 1, 2, 1.5), the relation between t and x_A is readily found

$$\begin{array}{ccc} n=0 & n=1 & n=2 \\ t=\dfrac{C_{Ao}x_A}{k} & t=\dfrac{1}{k}\ell n\dfrac{1}{1-x_A} & t=\dfrac{1}{kC_{Ao}}\left[\dfrac{1}{1-x_A}-1\right] \end{array}$$

(2-9)

$$n=1.5; \quad t=\frac{1}{0.5k\sqrt{C_{Ao}}}\left[\frac{1}{(1-x_A)^{0.5}}-1\right]$$

Production Rate of Product P can be related by stoichiometry to he consumption rate of A as

$$F_P\left(\frac{mol}{S}\right) = \frac{F_{Ao}x_A}{1}$$

The production rate of P is given by:

$$F_P = \frac{(\text{moles of P processed per batch})}{(\text{reaction time} + \text{shut down time per batch})}$$

(2-10)

$$F_P = \frac{C_{Ao}V\,x_A}{t+t_s} = \frac{C_{Ao}V\,x_A}{\dfrac{1}{k(n-1)C_{Ao}^{n-1}}\left[(1-x_A)^{1-n}\right]+t_s}$$

(2-11)

NOTA BENE: Equation (2-11) is valid only for systems of constant density. Thus, it is valid for all systems, gas or liquid, conducted in an autoclave at V = const (see Figure 2-1a). It is also valid for gaseous systems with no change in the

number of moles $\left(\sum v_j = 0\right)$ conducted in P = const. system at T = const (Figure 2-1b).

The first equality in equation (2-11) gives the general result, the second equality presents the result for an n-th order irreversible reaction with resect to reactant A.

To use this equation the shut down time, i.e. the time needed between batches, t_s, must be known. Consider now the following second order reaction with stoichiometry A = P.

$$-R_A = 0.1 C_A^2 \left(\frac{mol}{L\,min}\right)$$

a)   Find the batch reactor volume needed to produce F_P = 38 kmol/min if reactor shut down time is 60 minutes and the desired conversion is 0.95. Initial reactant concentration is $C_{Ao} = 1$ (mol L).

Using the right form of equation (2-9) for n = 2 we get the reaction time.

$$t = \frac{1}{0.1 * 1}\left[\frac{1}{1-0.95} - 1\right] = \frac{1}{1-0.95} = 190.0(min)$$

Then, solving equation (2-11) for the volume we get

$$V = \frac{F_P(t+t_s)}{C_{Ao}x_A} = \frac{1.38(190+60)}{1x0.95} = 10,000L = 10m^3$$

b)   What is the maximum production rate, F_P, achievable in the above batch reactor of volume V=10m^3 if t_s, T, C_{Ao} all are fixed at previous values.

Consider eq (2-11) for production rate as a function of conversion

$$F_P = \frac{C_{Ao}V x_A}{\frac{1}{kC_{Ao}}\left[\frac{x_A}{1-x_A}\right]+t_s} = \frac{10^4 x_A}{10\frac{x_A}{1-x_A}+60} = \frac{10^3 x_A}{\frac{x_A}{1-x_A}+6}$$

$$F_P = 10^3 \frac{x_A(1-x_A)}{x_A+6(1-x_A)} = 10^3 \frac{x_A-x_A^2}{6-5x_A}$$

4

This expression has a maximum which we can locate by differentiation

$$\frac{dF_P}{dx_A} = 0 \Rightarrow (1 - 2x_A)(6 - 5x_A) + 5(x_A - x_A^2) = 0$$

$$6 - 5x_A - 12x_A + 10x_A^2 + 5x_A - 5x_A^2 = 0$$

$$6 - 12x_A + 5x_A^2 = 0$$

$$x_{A_{12}} = \frac{6 \pm \sqrt{36 - 30}}{5} = \frac{6 - \sqrt{6}}{5} = 0.710$$

Clearly, the positive sign is not permissible as conversion cannot exceed unity. We need to check whether the answer is a maximum or a minimum.

$$\frac{dF_P}{dx_A} > 0 \ for \ x_A < 0.710$$

$$\frac{dF_P}{dx_A} < 0 \ for \ x_A > 0.710$$

Maximum at $x_A = 0.710$.

$$F_{P_{max}} = 10^3 \frac{0.710 - 0.710^2}{6 - 5x0.710} = 84.0 \frac{mol}{min}$$

An increase in productivity of $\frac{84 - 38}{38} x100 = 121\%$ can be achieved at the expense of more unreacted A to be recycled.

One must include the cost of separation into the real economic optimization.

2.2   Continuous Flow Reactors (Steady State)

2.2.1 <u>Continuous Flow Stirred Tank Reactor (CFSTR or CSTR or STR)</u>

The CSTR is assumed perfectly mixed, which implies that there are no spatial gradients of composition throughout the reactor. Since the reactor operates at steady state, this implies that a single value of species concentration is found in each point of the reactor at all times and this is

equal to the value in the outflow. The outflow stream is a true representative of the reaction mixture in the reactor.
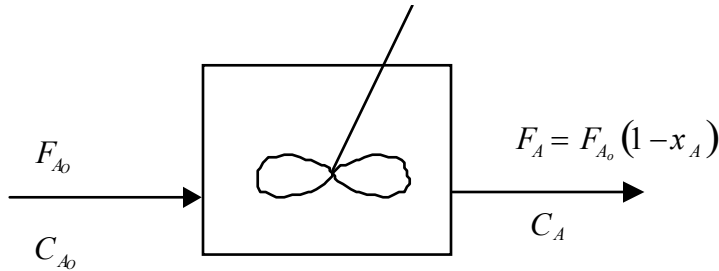
FIGURE 2-2: Schematic of a Continuous Flow Stirred Tank Reactor (CSTR)

What does the above idealization of the mixing pattern in a CSTR imply? It postulates that the rate of mixing is "instantaneous" so that the feed looses its identify instantly and all the reaction mixture is at the composition of the outlet. Practically this implies that the rate of mixing from macroscopic level down to a molecular scale is orders of magnitude faster than the reaction rate and is so fast in every point of the vessel.

Then the mass balance of eq (2-1) can be applied to the whole volume of the reactor recognizing that at steady state the accumulation term is identically zero. Again, taking a simple example of an irreversible reaction A $\rightarrow$ P application of eq (2-1) to reactant A yields:

$$F_{Ao} - F_A + ((R_A)V = 0 \tag{2-12}$$

Molar flow rate of unreacted A in the outflow by definition is given by $F_A = F_{Ao}(1 - x_A) = Q\, C_{Ao}(1 - x_A)$. The production rate of P is given by

$$F_P = (-R_A)V = (R_P)V \tag{2-13}$$

Reactor volume is given by eq (2-12)

$$V = \frac{F_{Ao} x_A}{(-R_A)} = \frac{Q_o C_{Ao} x_A}{(-R_A)} \tag{2-14}$$

Reactor space time is defined by

$$\tau = \frac{V}{Q_o} = \frac{C_{Ao}x_A}{(-R_A)} \qquad (2\text{-}15)$$

Using stoichiometry we readily develop the relation between production rate, F_P, and reactor volume, V.

Let us consider again the example of our 2nd order reaction, A = P, with the rate below:

$$-R_A = kC_A^n = 0.1C_A^2 \left(\frac{mol}{L\,min}\right)$$

Find CSTR volume needed to process $F_P = 38$ mol/min. Suppose we choose again $x_A = 0.95$ for our exit conversion.

From eq (2-13) we get

$F_P = 0.1\ C_{Ao}^2\ (1\text{-}x_A)^2\ V$

And solving for volume V

$$V = \frac{F_P}{0.1C_{Ao}^2(1-x_A)^2} = \frac{38}{0.1x1(1-0.95)^2} = 152,000L = 152m^3$$

If we consider eq (2-13) it is clear that now the maximum production rate is obtained when the reaction rate is the highest. That for n-th order reactions is at zero conversion. So the maximum F_P from $V_{CSTR} = 12,000$ L is obtainable at $x_A = 0$.

$F_{P_{max}} = 0.1$ x 1 x 152,000 = 15,200 mol/min.

The penalty or this enormous production rate is that the product is at "zero" purity. Hence, the separation costs would be enormous. The average rate in a CSTR is equal to the rate at exit conditions.
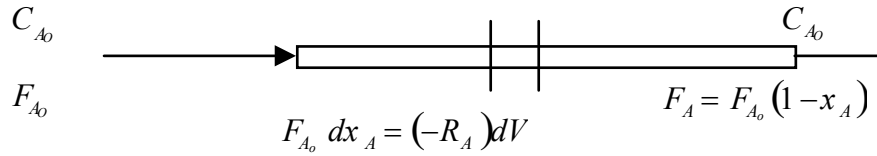
$$(-\overline{R_A}) = (-R_A)_{exit} = 0.1C_{Ao}^2(1-x_A)_{exit}^2 = 0.1x1(1-0.95)^2 = 2.5x10^{-4}(mol/L\,min)$$

2.2.2 Plug Flow Reactor (PFR)

The main assumptions of the plug flow reactor are: i) perfect instantaneous mixing perpendicular to flow, ii) no mixing in direction of flow

This implies piston like flow with the reaction rate and concentration that vary along reactor

FIGURE 2-3: Schematic of a Plug Flow Reactor (PFR)

Since there are now composition gradients in the direction of flow, the control volume is a differential volume ΔV to which eq (2-1) is applied. Let us again use the mass balance on reactant A

$$F_A\big|_V - F_A\big|_{V+\Delta V} + R_A \Delta V = 0 \tag{2-16}$$

$$-\Delta F_A + R_A \Delta V = 0$$

$$-\lim_{\Delta V \to 0} \frac{\Delta F_A}{\Delta V} = (\lim_{\Delta V \to 0})(-R_A)$$

$$-\frac{dF_A}{dV} = (-R_A) \tag{2-17}$$

Since $F_A = F_{Ao}(1 - x_A)$ then $dF_A = -F_{Ao}dx_A$

so that

$$F_{Ao} \frac{dx_A}{dV} = (-R_A) \tag{2-18}$$

With initial conditions:

$$V = 0 \quad x_A = 0 \tag{2-19}$$

Upon separation of variables in (eq 2-18) and integration:

$$\int_o^V dV = F_{Ao} \int_o^{x_A} \frac{dx_A}{(-R_A)} \qquad (2\text{-}20)$$

For an n-th order reaction (with $\varepsilon_A = 0$) we get

$$V = \frac{F_{Ao}}{kC_{Ao}^n} \int_o^{x_A} \frac{dx_A}{(1-x_A)^n} = \frac{Q_o}{kC_{Ao}^{n-1}} \frac{\left[(1-x_A)^{1-n}-1\right]}{(n-1)} \qquad (2\text{-}21)$$

The expression for the PFR space time

$$\tau = \frac{V}{Q_o} = \frac{1}{kC_{Ao}^{n-1}(n-1)}\left[(1-x_A)^{1-n}-1\right] \qquad (2\text{-}22)$$

is now identical to the expression for reaction time t in the batch reactor.

For the example of the second order reaction used earlier we get

$$V = F_{Ao}\int_o^{x_A} \frac{dx_A}{kC_{Ao}^2(1-x_A)^2} = \frac{F_{Ao}}{kC_{Ao}^2}\left[\frac{1}{1-x_A}\right]_o^{x_A}$$

$$V = \frac{F_{Ao}}{kC_{Ao}^2}\left[\frac{1}{1-x_A}-1\right] = \frac{F_{Ao}}{kC_{Ao}^2}\left[\frac{x_A}{1-x_A}\right]$$

$F_{Ao} = Q_o C_{Ao}$

$$\tau = \frac{V}{Q_o} = \frac{1}{kC_{Ao}}\frac{x_A}{1-x_A} \qquad \text{(Same as the expression for reaction time } t \text{ in the batch reactor)}$$

Let us consider our example of the second order reaction and find the PFR volume needed to produce $F_P = 38$ mol/min

$$(-R_A) = 0.1C_A^2\left(\frac{mol}{L\,min}\right)$$

when $C_{Ao} = 1\left(\frac{mol}{L}\right)$ and desired conversion $x_A = 0.95$.

From stoichiometry it follows that

$$F_{Ao}x_A = F_P \qquad F_{Ao} = \frac{F_P}{x_A}$$

Substitution in the expression for reactor volume (eq (2-21)) we get:

$$V = \frac{F_P}{kC_{Ao}^2 x_A}\left[\frac{x_A}{1-x_A}\right] = \frac{F_P}{kC_{Ao}^2(1-x_A)}$$

$$V = \frac{38}{0.1 x 1(1-0.95)} = 7,600 L = 7.6 m^3$$

The maximum production rate from that volume can be obtained at zero conversion

$$F_P = kC_{Ao}^2(1-x_A)V$$

$$F_{P_{max}} = 0.1 x 1 x 7600 = 760 mol/min$$

Average rate in PFR $-\overline{R_A} = \frac{F_{Ao}x_A}{V} = \frac{F_P}{V} = \frac{38}{7,600} = 5.0 x 10^{-3} \frac{mol}{min}$

$$(-R_A)_{entrance} = 0.1 C_{Ao}^2 = 0.1 = 10^{-1}\left(\frac{mol}{L\,min}\right)$$

$$(-R_A)_{exit} = 0.1 C_{Ao}^2(1-0.95)^2 = 2.5 x 10^{-4}\left(\frac{mol}{L\,min}\right)$$

Clearly there is a big variation in the reaction rate between the entrance and exit of the plug flow reactor (PFR).

2.3 STY – Space Time Yield

Volumetric Reactor Productivity - RVP

Reactor volumetric productivity (RVP) is defined by:

$$\overline{R_P} = \frac{F_P}{V} \tag{2-23}$$

For our 2nd order reaction example of stoichiometry A=P, RVP for the two continuous flow reactors is:

CSTR $\overline{R_P} = (R_P)_{exit} = (-R_A)_{exit} = kC_{Ao}^2(1-x_A)^2$ $\tag{2-24a}$

PFR $\overline{R_P} = \frac{F_P}{V} = kC_{Ao}^2(1-x_A)$ $\tag{2-24b}$

For the same exit conversion

$$\frac{\overline{(R_P)_{PFR}}}{(R_P)_{CSTR}} = \frac{kC_{Ao}^2(1-x_A)}{kC_{Ao}^2} = \frac{1}{(1-x_A)}$$

At $x_A = 0.95$

$$\frac{\overline{(R_P)_{PFR}}}{(R_P)_{CSTR}} = 20$$

Indeed 20 x 7,600 L = 152,000 L

This is why higher CSTR volume is needed.

At $x_A = 0$ $\qquad (\overline{R_P})_{PFR} = (\overline{R_P})_{CSTR}$

There is no difference!

Let us consider another example to illustrate some important points.

Ex: $\quad$ 2A + 3B = P + S – stoichiometry

$r = 0.1C_A C_B^2 \left(\dfrac{mol}{L\ min}\right)$ - rate of reaction

$C_{Ao} = 2\left(\dfrac{mol}{L}\right)$ and $\quad x_A = 0.95$ - are the feed reactant concentration and desired conversion

$F_P = 10$ mol/min is the desired production rate

Assume first that we will operate at stoichiometric ratio so that $C_{Bo} = 3$ (mol/L). The reaction occurs in the liquid phase so that $\varepsilon_A = 0$. Find the needed reactor volume.

a) $\quad$ <u>Batch ($t_s = 60$ min)</u>

$$-R_A = 0.2\,C_{Ao}(1-x_A)\left(C_{Bo} - \frac{b}{a}C_{Ao}x_A\right)^2$$

$$-R_A = 0.2\,C_{Ao}^3(1-x_A)\left(\frac{3}{2}\right)^2(1-x_A)^2$$

$$-R_A = 0.2\,C_{Ao}^3(1-x_A)^3\left(\frac{3}{2}\right)^2$$

11

Reaction time is:

$$t = \frac{1}{0.2C_{Ao}^2 \left(\frac{3}{2}\right)^2} \int_o^{x_A} \frac{dx_A}{(1-x_A)^3}$$

$$t = \frac{1}{0.2x2^2} \frac{g}{a} \int_o^{x} \frac{dx}{(1-x)^3} = \frac{1}{1.8} \frac{1}{2} \frac{1}{(1-x)^2} \bigg|_o^{x_A}$$

$$t = \frac{1}{3.6} \left[\frac{1}{(1-x_A)^2} - 1 \right] = \frac{1}{36} \left[\frac{1}{(1-0.95)^3} - 1 \right]$$

t = 110.83 min

$$F_P = \frac{\frac{1}{2}C_{Ao}x_A V}{t+t_s} = \frac{0.95xV}{110.83+60} = 10$$

$$V = \frac{170.83x10}{0.95} = 1,798 \, L = 1.8m^3$$

b) <u>CSTR</u>

$$\frac{F_{Ao}}{2} = \frac{F_P}{1} \text{ - from stoichiometry}$$

$$\frac{V}{F_{Ao}} = \frac{x_A}{-R_A} \text{ - basic design equation (2-14)}$$

$$V = \frac{F_{Ao}x_A}{-R_A} = \frac{2F_P}{(-R_A)} = \frac{2F_P}{0.2C_A C_B^2}$$

$$V = \frac{F_P}{0.1C_{Ao}^3(1-x_A)\left(\frac{C_{Bo}}{C_{Ao}} - \frac{3}{2}x_A\right)^2} = \frac{F_P}{0.1C_{Ao}^3 \left(\frac{3}{2}\right)^2 (1-x_A)^3}$$

$$V = \frac{10}{0.1 \times 2 \times 9(1-0.95)^3} = \frac{10}{1.8} \frac{1}{0.05^3} = 4,444 \,(L) = 44.4m^3$$

$$(-\overline{R_A}) = (-R_A)_{exit} = 0.2xC_{Ao}^3 \left(\frac{3}{2}\right)^2 (1-x_A)^3_{exit}$$

$$= 0.2x2x9(1-0.95)^3 = 4.5 \times 10^{-4} \, (mol/L \, min)$$

c)   PFR

$$F_{Ao} = \frac{2F_P}{x_A} \quad \text{- from stoichiometry}$$

Basic design equation (2-21)

$$V = F_{Ao} \int_o^{x_f} \frac{dx_A}{-R_A} = F_{Ao} \int_o^{x_f} \frac{dx}{0.2C_{Ao}^3 (1-x)\left(\frac{3}{2}\right)^2 (1-x)^2}$$

$$V = \frac{2F_P}{0.2C_{Ao}^3 \left(\frac{3}{2}\right)^2 x_A} \int_o^{x_f} \frac{dx}{(1-x)^3} = \frac{100}{18 x 0.95} \int_o^{x_f} \frac{dx}{(1-x)^3}$$

$$V = \frac{100}{18 x 0.95} \frac{1}{2} \left[\frac{1}{(1-x_A)^2} - 1 \right]$$

$$= \frac{50}{10 \times 0.95} \left[\frac{1}{(1-0.95)^2} - 1 \right] = 1,167(L) = 1.17\,m^3$$

Now the rate, at stoichiometric feed ratio, along the PFR as a function of conversion is

$$-R_A = 0.2C_{Ao}^3 \left(\frac{3}{2}\right)^2 (1-x_A)^3 = 3.6(1-x_A)^3$$

PFR reactor volume as function of conversion at stoichiometric feed ratio is

$$V = \frac{2F_P}{3.6x_A} \int_o^{x_A} \frac{dx}{(1-x)^3} = \frac{F_P}{1.8x_A} \int_o^{x_A} \frac{dx}{(1-x)^3}$$

Hence, the production rate from a given PFR volume as a function of conversion (at stoichiometric feed rate) is

$$F_{P_{stoich}} = \frac{1.8x_A V}{\int_o^{x_f} \frac{dx}{(1-x)^3}} = \frac{3.6x_A V}{\frac{1}{(1-x_A)^2} - 1}$$

How much can we increase the production rate by doubling C_{Bo} to $C_{Bo} = 6$ (mol/L), i.e. by using B in excess?

Now the rate as a function of conversion is:

$$-R_A = 0.2C_{Ao}^3(1-x_A)\left(\left(\frac{C_{Bo}}{C_{Ao}}\right) - \frac{3}{2}x_A\right)^2 = 0.2x2^3x\left(\frac{3}{2}\right)^2(1-x)(2-x_A)^2$$

$$-R_A = 3.6(1-x_A)(2-x_A)^2$$

a) Batch

$$t = C_{Ao}\int_o^{x_A}\frac{dx_A}{(-R_A)} = \frac{2}{3.6}\int_o^{x_A}\frac{dx}{(1-x)(2-x)^2}$$

To integrate use partial fractions:

$$\frac{A}{1-x} + \frac{B+Cx}{(2-x)^2} = \frac{A(2-x)^2 + (B+Cx)(1-x)}{(1-x)(2-x)^2}$$

$$4A - \underline{4Ax} + Ax^2 + B - \underline{Bx} + \underline{Cx - Cx^2} = 1$$

4A+B=1	4A-3A=1	A=1	
-4A-B+C=0	-3A-B-0	B=-3A	B=-3
A-C=0	C=A = 1		

$$\int\frac{dx}{(1-x)(2-x)^2} = \int\frac{dx}{1-x} + \frac{x-3}{(2-x)^2}dx$$

$$= \int_o^{x_A}\left(\frac{dx}{1-x} - \frac{2-x}{(2-x)^2}dx - \frac{1}{(2-x)^2}dx\right)$$

$$= \left(-\ell n(1-x) + \ell n(2-x) - \frac{1}{2-x}\right)_o^{x_A}$$

$$= -\ell n(1-x_A) + 0 + \ell n(2-x_A) - \ell n2 - \frac{1}{2-x_A} + \frac{1}{2}$$

$$= \ell n\frac{2-x_A}{2(1-x_A)} + \frac{1}{2}\left[1 - \frac{2}{2-x_A}\right] = \ell n\left[\frac{2-x_A}{2(1-x_A)}\right] - \frac{x_A}{2(2-x_A)}$$

$$t = \frac{1}{1.8}\left[\ell n\left(\frac{2-x_A}{2(1-x_A)}\right) - \frac{x_A}{2(2-x_A)}\right]_{x_A=0.95}$$

$$t = \frac{1}{1.8}\left[\ell n\frac{1.05}{2x0.05} - \frac{0.95}{2x1.05}\right] = \frac{1}{1.8}\left(\ell n10.5 - \frac{0.95}{2.1}\right)$$

t = 1.055 min   Batch ill advised at these conditions since $t_s \gg t$!

$$F_{P_{new}} = \frac{\frac{1}{2}C_{Ao}x_A V}{t + t_s} = \frac{0.95 x 1,798}{1.06 + 60} = 27.97 \frac{mol}{min}$$

$$\frac{\Delta F_P}{F_{P_{old}}} \times 100 = \frac{27.97 - 10}{10} \times 100 = 179.7\%$$

By operating at double the stoichiometric requirement of B we increase, at same x_A, the production rate of the batch reactor by 180%.

b)   <u>CSTR</u>

$$-R_A = 3.6(1 - x_A)(2 - x_A)^2 - 3.6(1 - 0.95)(2 - 0.95)^2$$

$$-R_A = 3.6x0.05x1.05^2 = 0.19845 \left(\frac{mol}{L\, min} \right)$$

$$F_{P_{new}} = R_P V = \left(\frac{-R_A}{2} \right) V = \frac{0.19845}{2} \times 44,494 = 4,410 \frac{mol}{min}$$

$$\frac{\Delta F_P}{F_{P_{old}}} \times 100 = \frac{4,410 - 10}{10} x100 = 44,000\%$$

In a CSTR we increase the production rate by 44,000%!

c)   <u>PFR</u>

$$V = F_{Ao} \int_o^{x_A} \frac{dx}{3.6(1 - x)(2 - x)^2}$$

$$F_{P_{new}} \frac{V x_A}{\frac{2}{3.6} \int_o^{x_A} \frac{dx}{(1 - x)(-x)^3}} = \frac{1.8 x_A V}{\int_o^{x_A} \frac{dx}{(1 - x)(2 - x)^3}}$$

$$F_{P_{new}} = \frac{1.8 x_A V}{\left[\ell n \left(\frac{2 - x_A}{2(1 - x_A)} \right) - \frac{x_A}{2(2 - x_A)} \right]}$$

$$F_{P_{new}} = \frac{1.8x0.95x1,167}{\ell n \frac{2 - 0.95}{2(1 - 0.95)} - \frac{0.95}{2(2 - 0.95)}} = \frac{1.8x0.95x1,167}{\ell n \frac{1.05}{0.1} - \frac{0.95}{2.10}}$$

$$F_{P_{new}} = 1,051\, mol\,/\,min$$

$$\frac{\Delta F_P}{F_{P_{old}}} x100 = \frac{1,051 - 10}{10} x100 = 10,419\%$$

In a PFR over 10,000% increase in F_P is obtained.

We present below these ratios of production rate obtainable at nonstoichiometric ratio of $C_{Bo}/C_{Ao} = 2 \left(C_{Bo}/C_{Ao}\right)_{stoich}$ and at stoichiometric ratio of $C_{Bo}/C_{Ao} = 3/2$ for our example reaction.

This ratio is:

For a PFR:

$$\frac{F_{P_{(non-stoich)}}}{F_{P_{(stoich)}}} = \frac{\dfrac{1.8 x_A V}{\ell n\left(\dfrac{2 - x_A}{2(1 - x_A)} - \dfrac{x_A}{2(2 - x_A V)}\right)}}{\dfrac{3.6 x_A}{\dfrac{1}{(1 - x_A)^2} - 1}} = \frac{\dfrac{1}{(1 - x_A)^2} - 1}{2\left[\ell n\left(\dfrac{2 - x_A}{2(1 - x_A)}\right) - \dfrac{x_A}{2(2 - x_A)}\right]}$$

Specifically for $x_A = 0.95$ we get

$$\frac{F_{P_{(non-stoich)}}}{F_{P_{(stoich)}}} = \frac{\dfrac{1}{0.05^2} - 1}{2\left[\ell n\dfrac{1.05}{2x0.05} - \dfrac{0.95}{2x1.05}\right]2\left(\ell n10.5 - \dfrac{0.75}{2.10}\right)} = \frac{199.5}{\ell n10.5 - 0.45228045} = 105.0$$

For a CSTR

$$\frac{F_{P_{(non-stoich)}}}{F_{P_{(stoich)}}} = \frac{3.6(1 - x_A)(2 - x_A)^2}{3.6(1 - x_A)^3} = \frac{(2 - x_A)^2}{(1 - x_A)^2} =$$

$$\left(\frac{2 - 0.98}{1 - 0.98}\right)^2 \frac{F_{P_{(non-stoich)}}}{F_{P_{(stoich)}}} = \left(\frac{1.05}{0.05}\right)^2 = 21^2 = 441$$

Let us examine the situation when the reaction just considered occurs at P = const, T = const in the gaseous phase. Then due to stoichiometry we have

2B + 3B = P + S
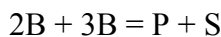
$$\sum \upsilon_j = 1 + 1 - 2 - 3 = -3$$

Consider stoichiometric feed of reactants at $C_{Bo}/C_{Ao} = 3/2$.

$$y_{Ao} = \frac{2}{5} = 0.4 \quad (-\upsilon_A) = 2$$

$$\varepsilon_A = y_{Ao} \frac{\sum \upsilon_j}{(-\upsilon_A)} = \frac{0.4 \; ^{(-3)}}{2} = -0.6$$

$$C_A = C_{Ao} \frac{1-x_A}{1-0.6x_A} \qquad C_B = C_{Ao} \frac{\dfrac{C_{Bo}}{C_{Ao}} - \dfrac{3}{2} x_A}{1-0.6x_A}$$

$$-R_A = 0.2 x C_{Ao}^3 \left(\frac{3}{2}\right)^2 \frac{(1-x_A)^3}{(1-0.6x_A)^3} = 3.6 \frac{(1-x_A)^3}{(1-0.6x_A)^3}$$

CSTR

$$F_P = \frac{(-R_A)}{2} V$$

$$V = \frac{2F_P}{-R_A} = \frac{2 x 10(1-0.6 x 0.95)^3}{3.6(1-0.95)^3}$$

$$V = \frac{10}{1.8} \frac{(1-0.57)^3}{0.05^3} = 44,444 x 0.43^3 = 3,534(L)$$

Tremendous reduction in required volume compared to the $\varepsilon_A = 0$ case occurs!

PFR

$$V = F_{Ao} \int_o^{x_A} \frac{dx_A}{-R_A} = \frac{2F_P}{x_A} \int_o^{x_A} \frac{(1-0.6x)^3 \, dx}{3.6(1-x)^3}$$

$$V = \frac{F_P}{1.8 x_A} \int_0^{x_A=0.95} \frac{(1-0.6x)^3}{(1-x)^3} \, dx = \frac{10}{1.8 x 0.95} \int_0^{0.95} \left(\frac{1-06x)}{1-x}\right)^3 dx$$

$$V = 125.6(L)$$

Again a significant reduction in PFR reactor volume requirement is observed. Why?

2.4 Graphic Comparison of PFR and CSTR

$$\left(\frac{V}{F_{Ao}}\right)_{CSTR} = \frac{x_A}{(-R_A)_{exit}}$$

$$\left(\frac{V}{F_{Ao}}\right)_{PFR} = \int_{o}^{x_{Ao}} \frac{dx_A}{-R_A}$$

The graphic representation of the above two design equations is represented below for an n-th order reaction. Clearly, for fixed feed conditions and feed rate and for chosen desired conversion the volume of the CSTR will always be larger than or equal to the PFR volume.

$\left(\dfrac{V}{F_{A_o}}\right)_{CSTR}$ = area of box

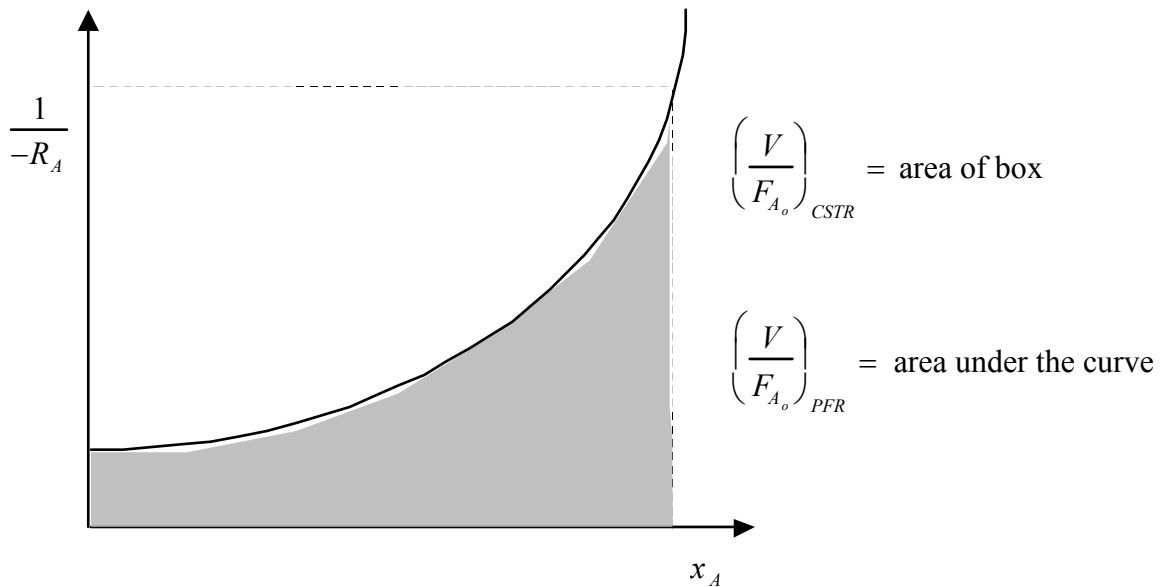$\left(\dfrac{V}{F_{A_o}}\right)_{PFR}$ = area under the curve

FIGURE 2-4: Graphical Comparison of CSTR and PFR

Ideal Reactors and Multiple Reactions

Isothermal Operation

(CHE 471)

M.P. Dudukovic

Chemical Reaction Engineering Laboratory

(CREL),

Washington University, St. Louis, MO

Ideal Reactors and Multiple Reactions
Isothermal Operation

Selection of a proper flow pattern is the key factor in achieving desired selectivities and yields in multiple reactions. For every multiple reaction system of known stoichiometry it is possible to determine "a priori" which limiting flow pattern – complete backmixing (CSTR) or no mixing (PFR) will yield superior yields or selectivities. The consideration of yields often is more important than reactor size in choosing the preferred reactor flow pattern.

From Lecture 1 we know that all multiple reaction systems can be represented by a set of R independent reactions among the S chemical species present in the system:

$$\sum_{j=1}^{S} \upsilon_{ij} A_j = 0 \quad for \quad i = 1,2,3...R \tag{1*}$$
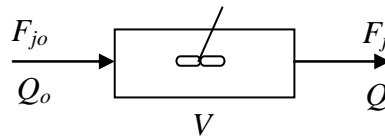
These stoichiometric relationships allow one to relate moles produced (or depleted) of each species to the molar extents of the R reactions:

$$F_j = F_{jo} + \sum_{i=1}^{R} \upsilon_{ij} \dot{X}_i \tag{1}$$

The rate of reaction of each species is given through the rates of the R independent reactions, r_i, i = 1,2,…R.

$$R_j = \sum_{i=1}^{R} \upsilon_{ij} r_i \tag{2}$$

CSTR – Ideal Stirred Tank Continuous Flow Reactor

The design equation (i.e., the mass balance for species j) can be written for R species, j = 1,2,3…R:

$$F_{jo} - F_j + \sum_{i=1}^{R} \upsilon_{ij} r_i V = 0 \tag{3}$$

for j = 1, 2,...R

If the reaction rate r_i for each independent reaction i can be represented by an n-th order form, of eq (4a)

$$r_i = k_i \prod_{j=1}^{S} C_j^{\alpha_{ij}} \tag{4a}$$

then at P = const, T = const, the rate of the i-th reaction, r_i, can be represented in terms of molar extents $\dot{X}_i$ of the reactions by:

$$r_i = k_i \prod_{j=1}^{S} C_{tot,o}^{\sum \alpha_{ij}} \left(\frac{F_{jo} + \sum_{i=1}^{R} \upsilon_{ij} \dot{X}_i}{F_{tot,o} + \sum_{j=1}^{S} \sum_{i=1}^{R} \upsilon_{ij} \dot{X}_i} \right)^{\alpha_{ij}} \tag{4b}$$

where α_{ij} is the reaction order of reaction i with respect to species j, $F_{tot,o}$ is the total initial molar flow rate.

Substitution of equations (2) and (4b) into (3) results in set of R nonlinear equations in $\dot{X}_i$. Three types of problems described below arise:

a)   Given the feed flow rates, reactor size V and rate forms for all reactions one can calculate all the reaction extents $\dot{X}_i's$ and from equation (1) get the composition of the outlet stream.

In addition, from Lecture 1, at P = const, T = const:

$$Q = Q_o \left(1 + \sum_{i=1}^{R} \sum_{j=1}^{S} \upsilon_{ij} \dot{X}_i \Big/ F_{tot,o} \right) \tag{5}$$

The exit volumetric flow rate can be computed and effluent concentrations calculated

$$C_j = \frac{F_j}{Q} \tag{6}$$

b)   Given the feed molar flow rates and composition, and the desired partial composition of the outflow, as well as the reaction rates, one can calculate the reactor size from equation (3) and the composition of other species in the outflow.

c)   Given molar feed rates and outflow molar flow rates for a given reactor size the rate of reaction for each species can be found from equation (3).

PFR – Plug Flow Reactor
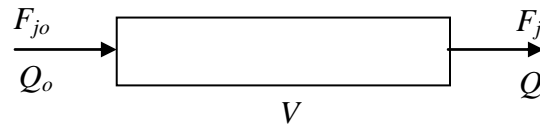
The design equation (i.e. the differential mass balance for species j) can be written for R species

$$\frac{dF_j}{dV} = \sum_{i=1}^{R} \upsilon_{ij} r_i \qquad (7)$$
$$j = 1, 2, ...R$$

The initial conditions are

$$V = 0 \qquad F_j = F_{jo} \qquad (7a)$$

Using equations (1) and (4b) the above set of R first order differential equations can be integrated simultaneously and solved for $\dot{X}_i's$ as functions of V.

a)   Given the feed flow rate and composition, and the form of the reaction rates, one could determine what volume V is required to attain the desired product distribution.

b)   Given the feed and reactor volume and reaction rate forms, one can determine the exit product distribution.

Batch Reactor – Autoclave of Constant Volume
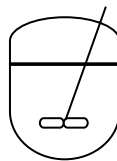
The R species (for j=1, 2, 3..R) mass balances yield:

$$\frac{dn_j}{dt} = \sum_{i=1}^{R} \upsilon_{ij} r_i \qquad (8)$$

Initial conditions are:

$$t = 0 \qquad n_j = n_{jo} \qquad (8a)$$

Moles and extents are related by:

$$n_j = n_{jo} + \sum_{i=1}^{R} \upsilon_{ij} X_i \tag{9}$$

For j = 1, 2, 3…S

The rate form as a function of extents is given by

$$r_i = k_i \prod_{j=1}^{s} C_{jo}^{\alpha_{ij}} \left(1 + \frac{\sum_{i=1}^{R} \upsilon_{ij} X_i}{n_{jo}} \right)^{\alpha_{ij}} \tag{10}$$

$$r_i = k_i \prod_{j=1}^{s} \left(C_{jo} + \sum_{i=1}^{R} \upsilon_{ij} \xi_i \right)^{\alpha_{ij}} \tag{10a}$$
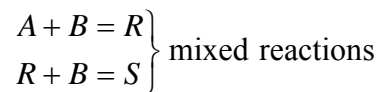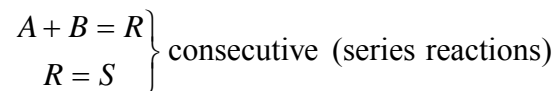
where $\xi_i = \dfrac{X_i}{V}$ $\qquad$ (10b)

One can solve the set of R first order differential equations to calculate the product distribution in time, or the desired time needed for a prescribed product distribution.

The above approach, while well suited for the computer, does not provide us with the insight as to which flow pattern is better in a given process until we actually compute the answers for both limiting cases.

In order to get better insight in the role of the flow pattern in product distribution in multiple reactions we will consider some simple systems and use the notions of yields and selectivity.

Classification of Multiple Reactions

$$\left. \begin{array}{l} A + B = R \\ C + D = P \end{array} \right\} \text{parallel}$$

$$\left. \begin{array}{l} A + B = R \\ A + 2B = S \end{array} \right\} \text{competitive}$$

$$\left. \begin{array}{l} A + B = R \\ \quad R = S \end{array} \right\} \text{consecutive (series reactions)}$$

$$\left. \begin{array}{l} A + B = R \\ R + B = S \end{array} \right\} \text{mixed reactions}$$
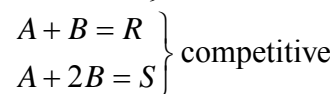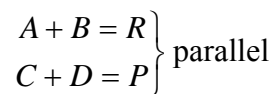
In Lecture 1 we have defined the various yields

$$y\left(\frac{P}{A}\right) = \frac{R_p}{-R_A} = \frac{\sum\limits_{i=1}^{R} \upsilon_{ip} r_i}{-\sum\limits_{i=1}^{R} \upsilon_{iA} r_i} \quad \{\text{point (relative) yield}$$

Point (relative) yield measures the ratio of the production rate of a desired product P and the rate of disappearance of the key reactant A. Point yield is a function of composition and this varies along a PFR reactor, varies in time in a batch reactor, and is a constant number in a CSTR.

$$Y\left(\frac{P}{A}\right) = \frac{F_P - F_{Po}}{F_{Ao} - F_A} \quad \{\text{overall (relative) yield}$$

Overall (relative) yield gives the ratio of the overall product P produced and the total consumption of reactant A.

In a <u>CSTR</u> the overall and point yield are identical.

$$Y(\frac{P}{A}) = y\left(\frac{P}{A}\right)$$

In a <u>PFR</u> the overall yield is the integral average of the point yield:

$$Y\left(\frac{P}{A}\right) = \frac{1}{F_{Ao} - F_A} \int\limits_{F_A}^{F_{Ao}} y\left(\frac{P}{A}\right) dF_A$$

Overall operational yield is also often used, defined as the number of moles of the desired product produced per mole of key reactant fed to the system.

$$\maltese\left(\frac{P}{A}\right) = \frac{F_P - F_{Po}}{F_{Ao}}$$

The relationship to overall relative yield is obvious

$$\maltese\left(\frac{P}{A}\right) = Y\left(\frac{P}{A}\right) x_A$$

where x_A is the overall conversion of A

$$x_A = \frac{F_{Ao} - F_A}{F_{AO}}$$

None of the above yields has been normalized, i.e., their maximum theoretical value may be more or less than one as dictated by stoichiometric coefficients.

A normalized yield can be introduced by

$$\bar{y}\left(\frac{P}{A}\right) = \frac{y\left(\frac{P}{A}\right)}{y_{max}\left(\frac{P}{A}\right)}$$

where $y_{max}\left(\dfrac{P}{A}\right)$ is obtained by assuming that only the reactions leading from A to R occur.

Point selectivity and overall selectivity measure the ratio of formation of the desired product and one or more of the unwanted products, e.g.

$$s\left(\frac{P}{U}\right) = \frac{R_p}{R_u} \qquad S = \frac{F_p - F_{po}}{F_u - F_{uo}}$$

A general rule:

If $\dfrac{dy\left(\dfrac{P}{A}\right)}{dC_A} > 0$ PFR produces more P.

If $\dfrac{dy\left(\dfrac{P}{A}\right)}{dC_A} < 0$ CSTR produces more P

If $y\left(\dfrac{P}{A}\right)$ is not a monotonic function of C_A either reactor type may produce more P depending on operating conditions. The case of monotonic point yield is illustrated below for the case with $\varepsilon_A = 0$.
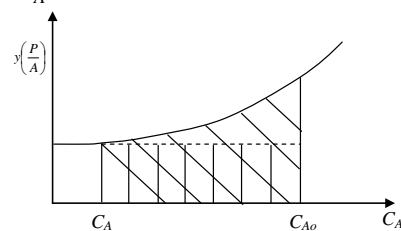
\ \ \ Area = Cp in PFR

| | | Area = Cp in CSTR

I. <u>Liquid Systems or Gases With $\displaystyle\sum_{i=1}^{R}\sum_{j=1}^{S} v_{ij} = 0$</u>

<u>Competitive Reactions</u>

$a_1A + b_1B = p_1P$
$a_2A + b_2B = s_2S$
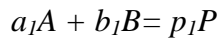
Given the rate
$$r_1 = k_1 C_A^{\alpha_{1A}} C_B^{\alpha_{1B}}$$
$$r_2 = k_2 C_A^{\alpha_{2A}} C_B^{\alpha_{2B}}$$

Point yield then is:

$$y\left(\frac{P}{A}\right) = \frac{R_p}{-R_A} = \frac{p_1 r_1}{a_1 r_1 + a_2 r_2} = \frac{\dfrac{p_1}{a_1}}{1 + \dfrac{a_2\, r_2}{a_1\, r_1}}$$
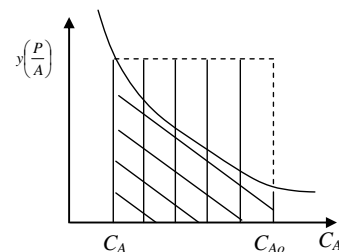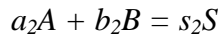
$$y\left(\frac{P}{A}\right) = \frac{\dfrac{p_1}{a_1}}{1 + \dfrac{a_2 k_2}{a_1 k_1} C_A^{(\alpha_{2A}-\alpha_{1A})} C_B^{(\alpha_{2B}-\alpha_{1B})}}$$

$$y_{max}\left(\frac{P}{A}\right) = \frac{p_1}{a_1}$$

$$\bar{y}\left(\frac{P}{A}\right) = \frac{1}{1 + \dfrac{a_2 k_2}{a_1 k_1} C_A^{(\alpha_{2A}-\alpha_{1A})} C_B^{(\alpha_{2B}-\alpha_{1B})}}$$

We want $\bar{y}\left(\dfrac{P}{A}\right)$ to be as high as possible. This implies:

i) $if \; \alpha_{2A} < \alpha_{1A}, \alpha_{2B} < \alpha_{1B}$, keep C_A and C_B as high as possible. PFR is better than CSTR.

ii) $if \; \alpha_{2A} = \alpha_{1A}, \alpha_{2B} < \alpha_{1B}$, keep C_B as high as possible. PFR is better than CSTR.

iii) $if \; \alpha_{2A} = \alpha_{1A}, \alpha_{2B} > \alpha_{1B}$, keep C_B as low as possible. CSTR is better than PFR. Try for yourself other combinations.

Example 1

$$A = P \qquad R_P = 1.0 \, C_A \, (kmol/m^3 s)$$
$$2A = S \qquad R_S = 0.5 \, C_A^2 \, (kmol/m^3 s)$$

Determine C_p in a) CSTR, b) PFR. The feed contains $C_{Ao} = 1$ $(kmol/ms)$, $C_{po} = 0$. Conversion of 98% is desired.

$$y\left(\frac{P}{A}\right) = \frac{R_p}{-R_A} = \frac{R_p}{R_p + 2R_s} = \frac{1}{1 + C_A}$$

$$y_{max}\left(\frac{P}{A}\right) = 1 \qquad \bar{y}\left(\frac{P}{A}\right) = y\left(\frac{P}{A}\right)$$

To keep point yield as high as possible, it is necessary to keep C_A low everywhere. CSTR will be better than PFR. Let us show this quantitatively.

---

a) CSTR

By setting the overall yield equal to the point yield we can solve for the exit concentration of product P.

$$Y\left(\frac{P}{A}\right) = \frac{C_p}{C_{Ao} - C_A} = y\left(\frac{P}{A}\right) = \frac{1}{1 + C_A}$$

$$C_p = \frac{C_{Ao} - C_A}{1 + C_A} = \frac{C_{Ao} x_A}{1 + C_{Ao}(1 - x_A)} = \frac{1 x 0.98}{1 + 1 - 0.98} = 0.961 \left(kmol / m^3\right)$$

Overall yield $\qquad\qquad Y\left(\frac{P}{A}\right) = \frac{C_p}{C_{Ao} - C_A} = 0.980$

Overall operational yield $\quad ⚹\left(\frac{P}{A}\right) = 0.961$

Required reactor size (space time)

$$\tau = \frac{C_{Ao} - C_A}{-R_A} = \frac{C_{Ao} x_A}{C_{Ao}(1 - x_A) + C_{Ao}^2 (1 - x_A)^2} = \underline{48.0(s)}$$

b) PFR

Product concentration is obtained by integration of the point yield

$$C_p = \int\limits_{C_A}^{C_{Ao}} y\left(\frac{P}{A}\right) dC_A = \int\limits_{C_A}^{C_{Ao}} \frac{dC_A}{1+C_A}$$

$$C_p = \ell n\left(\frac{1+C_{Ao}}{1+C_A}\right) = \ell n\left(\frac{1+1}{1+1-0.98}\right) = 0.673 (kmol/m^3)$$

Overall yield $Y\left(\dfrac{P}{A}\right) = 0.687$

Overall operational yield $✡\left(\dfrac{P}{A}\right) = 0.673$

Required reactor size $\qquad \tau = \int\limits_{C_A}^{C_{Ao}} \dfrac{dC_A}{-R_A} = \int\limits_{C_A}^{C_{Ao}} \dfrac{dC_A}{C_A(1+C_A)}$

$$\tau = \ell n\left(\frac{C_{Ao}(1+C_A)}{C_A(1+C_A)}\right) = \ell n\left[\frac{1+1-0.98}{(1-0.98)(1+1)}\right] = \underline{3.2(s)}$$

Plug flow reactor is considerably smaller but CSTR gives a better yield and higher concentration of the desired product.

Example 2

$$\begin{array}{ll} A + B = P & R_p = 1.0\ C_A C_B\ (kmol/m^3 s) \\ A + A = S & R_s = 0.5\ C_A^2\ (kmol/m^3 s) \end{array}$$
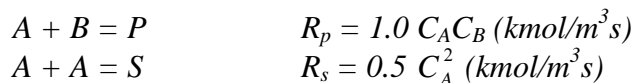
Given $F_{Ao} = F_{Bo} = 1$ (kmol/s; $C_{Ao} = C_{Bo} = 1$ (kmol/m³) $C_{Po} = C_{So} = 0$ and desired conversion $x_A = 0.98$, determine $C_p, Y\left(\dfrac{P}{A}\right), ✡\left(\dfrac{P}{A}\right), S\left(\dfrac{P}{S}\right)$ and required reactor space time for a) CSTR, b) PFR.

$$y\left(\frac{P}{A}\right) = \frac{R_p}{-R_A} = \frac{R_p}{R_p + 2R_s} = \frac{C_B}{C_B + C_A} = \frac{1}{1 + \dfrac{C_A}{C_B}}$$

To maximize point yield one should keep the reactant concentration ratio C_A/C_B as low as possible everywhere.

Eliminate C_B in terms of C_p and C_A using $C_j = C_{jo} + \sum\limits_{i=1}^{R} \upsilon_{ij} \xi_i \qquad i = 1, R$

$$C_A = C_{Ao} - \xi_1 - 2\xi_2$$
$$C_P = C_{Po} + \xi_1$$

$$\xi_1 = C_P - C_{Po} \quad \xi_2 = \frac{1}{2}\left[C_{Ao} - C_A - C_P \right]$$

Now:

$$C_B = C_{Ao} - \xi_1 = C_{Bo} - C_p$$

$$C_S = C_{So} + \xi_2 = 0 + \frac{1}{2}\left[C_{Ao} - C_A - C_p \right]$$
$$= \frac{1}{2}\left[C_{Ao} - C_A - C_{Bo} + C_B \right]$$

a) <u>CSTR</u>

$$Y\left(\frac{P}{A}\right) = \frac{C_p}{C_{Ao} - C_A} = y\left(\frac{P}{A}\right) = \frac{C_{Ao} - C_p}{C_{Ao} - C_p + C_A}$$

Solve for C_p

$$C_p^2 - (C_{Ao} - C_{Bo})C_p + C_{Bo}(C_{Ao} - C_A) = 0$$
$$C_{Ao} = C_{Bo} = 1; \quad C_A = C_{Ao}(1 - x_A) = 1 - 0.98$$
$$C_p^2 - 2C_p + 0.98 = 0$$

$$C_p = 1 - \sqrt{1 - 0.98} = 0.859 (kmol/m^3)$$
$$C_A = 0.02 \, kmol/m^3$$
$$C_B = 0.141 \, kmol/m^3 \quad \Big\} \text{exit stream composition}$$
$$C_S = 0.061 \, kmol/m^3$$

Overall yield $Y\left(\dfrac{P}{A}\right) = 0.877$

Overall operational yield $\maltese\left(\dfrac{P}{A}\right) = 0.859$

Overall selectivity $S\left(\dfrac{P}{S}\right) = \dfrac{C_p}{C_s} = 14.2$

Required Reactor Size

$$\tau = \frac{C_{Bo} - C_B}{-R_B} = \frac{C_{Ao} - C_B}{C_A C_B} = \frac{1 - 0.141}{0.02 x 0.141} = 306(s)$$

b) <u>PFR</u>

$$\frac{dF_P}{dF_A} = \frac{R_P}{R_A} = -y\left(\frac{P}{A}\right)$$

Since $F_j = QC_j$ and $Q = const$

$$\frac{dC_p}{dC_A} = -\frac{C_{Bo} - C_p}{C_{Bo} - C_p + C_A}$$

$$at C_A = C_{Ao}, C_p = 0$$

Rearrange:

$$\frac{dC_A}{dC_p} + \frac{C_A}{C_{Bo} - C_p} = -1$$

$$\frac{d}{dC_p}\left(\frac{C_A}{C_{Bo} - C_p}\right) = \frac{-1}{C_{Bo} - C_p}$$

at $C_p = 0$ $C_A = C_{Ao}$

Integrate from the indicated initial condition:

$$\frac{C_A}{C_{Ao} - C_p} - \frac{C_{Ao}}{C_{Bo}} = \ell n\left(\frac{C_{Bo} - C_p}{C_{Bo}}\right)$$

$$\frac{C_A}{1 - C_p} = 1 + \ell n\left(1 - C_p\right)(*)$$

Substitute known quantities:

$$C_A = C_{Ao}\,(1\text{-}x_A) = 1\text{-}0.98 = 0.02\ (kmol/m^3)$$

Solve for C_p by trial and error:

$$\phi(C_p) = C_p - 0.98 - (1 - C_p)\ell n(1 - C_p) = 0$$
$$D\phi(C_p) = 2 + \ell n(1 - C_p)$$
$$C_p^{n+1} = C_p^n - \frac{\phi(C_p^n)}{D\phi(C_p^n)} \qquad \text{Newton-Raphson Algorithm}$$

This yields:

$$\left. \begin{array}{l} C_p = 0.613 \ kmol/m^3 \\ C_A = 0.02 \ kmol/m^3 \\ C_B = 0.387 \ kmol/m^3 \\ C_s = 0.184 \ kmol/m^3 \end{array} \right\} \text{Exit stream composition}$$

The last two concentrations above are evaluated using the stoichiometric relationship.

Overall yield $\qquad Y\left(\dfrac{P}{A}\right) = 0.626$

Overall operational yield $\quad \maltese\left(\dfrac{P}{A}\right) = 0.613$

Overall selectivity $\ S\left(\dfrac{P}{S}\right) = 3.33$

Required reactor space time:

$$\tau = \int_{C_B}^{C_{Bo}} \frac{dC_B}{-R_B} = \int_{C_B=0.387}^{C_{Bo}=1} \frac{dC_B}{C_A C_B}$$

From (*)

$$C_A = (1 - C_p)\left[1 + \ell n(1 - C_p)\right]$$

From stoichiometry

$$C_B = C_{Bo} - C_p = 1 - C_p$$

Thus

$$C_A = C_B(1 + \ell n C_B)$$

$$\tau = \int_{C_{B=0.387}}^{C_{Bo}=1} \frac{dC_B}{C_B^2(1+\ell n C_B)} = e \int_{1+\ell n C_B}^{1+\ell n C_{Bo}} \frac{e^{-u}}{u} du$$

$$\tau = e\{E_1(1+\ell n C_B) - E_1(1+\ell n C_{Bo})\} = e\{E_1(0.05) - E_1(1)\}$$
$$= 2.71\{2.4679 - 0.2194\} = \underline{6.1(s)}$$

where

$$E_1(z) = \int_z^\infty \frac{e^{-u}}{u}\, du \quad \text{exponential integral}$$

$E_1(z)$ values tabulated in M. Abramowitz & A. Stegun "Handbook of Mathematical Functions", Dover Press, N.Y. 1964.

Comparison of CSTR & PFR

Reaction System: A + B = P (desired)
                            A + A = S

Decision variables: $x_A = 0.98$

$$M_{B/A} = \frac{F_{Bo}}{F_{Ao}} = 1$$

Rate Form: $r_1 = 10\, C_A C_B\,(\text{kmol/m}^3\text{s})$
                            $r_2 = 0.5\, C_A^2\,(\text{kmol/m}^3\text{s})$

	CSTR	PFR	Optimal Ideal Reactor
Operational yield	0.859	0.613	0.950
Overall selectivity	14.2	3.3	63.0
Reactor space time	306 (s)	6.1 (s)	150 (s)

The last column of the above Table was computed based on an ideal reactor model shown below. We have B entering a plug flow reactor while F_{Ao} is distributed from the side stream into the reactor in such a manner that $C_A = 0.02$ kmol/m^3 everywhere in the reactor.
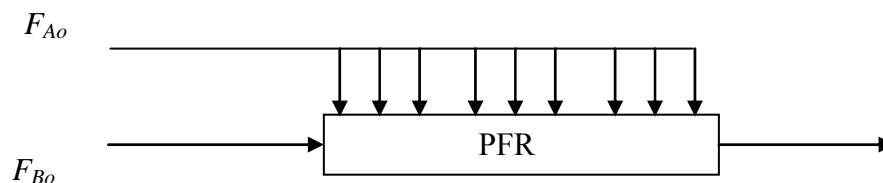
From the expression for the point yield

$$y\left(\frac{P}{A}\right) = \frac{C_B}{C_B + C_A} = \frac{1}{1 + \dfrac{C_A}{C_B}}$$

it is clear that one needs to keep C_A low and C_B high. With the constraint of $F_{Ao} = F_{Bo}$ the above ideal reactor accomplishes that requirement in an optimal manner.

Could such a "porous wall" reactor with plug flow be constructed? It depends on the nature of the reaction mixture.

However, we learn from the above that with our choice of decision variables maximum selectivity is 63, we can never do better than that! We also learn that a good reactor set up is a cascade of CSTR's.

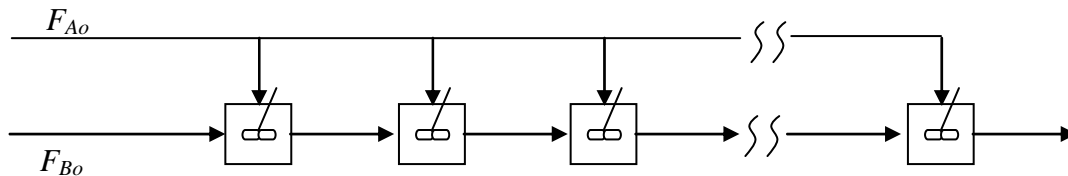The total number of reactors used will depend on economics With 2 reactors we get selectivity of over 20, with five we are close to optimum.

Examining the effect of decision variables we see that C_p increases with increased conversion of A. For conversions larger than 0.98 the reactor volume becomes excessive.

If we took $M_{B/A} > 1$ that would improve the yield and selectivity but at the expense of having to recycle more unreacted B.

Let us ask the following question. How much excess B would we have to use in a PFR in order to bring its overall selectivity to the level of a single CSTR i.e., $S = \dfrac{C_p}{C_s} = 14.2$ at $C_{Ao} = 1$ (kmol/m^3) and $x_A = 0.98$. So the goal is to choose C_{Bo} in order to get at the exit of plug flow:

$$\frac{C_p}{C_s} = 14.2$$

From stoichiometry:

$$C_s = \frac{1}{2}\left[C_{Ao} - C_A - C_p\right] = \frac{1}{2}\left[C_{Ao}x_A - C_p\right] = \frac{1}{2}\left[0.98 - C_p\right]$$

The prescribed desired selectivity is:

$$\frac{2C_p}{0.98 - C_p} = 14.2 \Rightarrow C_p = 0.859 (kmol/m^3)$$

$$C_s = 0.061 (kmol/m^3)$$

The integrated equation for PFR is:

$$\frac{C_A}{C_{Bo} - C_p} - \frac{C_{Ao}}{C_{Bo}} = \ell n \left(1 - \frac{C_p}{C_{Ao}} \right)$$

The initial concentration of B is now the only unknown. Evaluate it by trial & error.

$$\frac{0.02}{C_{Bo} - 0.859} - \frac{1}{C_{Bo}} = \ell n \left(1 - \frac{0.859}{C_{Bo}} \right) \text{ gives}$$

$$C_{Bo} = 3.79 \frac{kmol}{m^3}$$

Since $C_{Ao} = 1$ (kmol/m^3), $M_{B/A} = 3.79$ – almost four times more B than A should be introduced in the feed to get the selectivity in a PFR to the level of a CSTR.

A great excess of unreacted B has to be separated in the effluent:

$$C_B = C_{Bo} - C_p = 3.790\text{-}0.859 = 2.931 \text{ (kmol/m}^3)$$

Consecutive Reactions

$$aA = p_1 P$$
$$p_2 P = s\, S$$
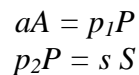
Two basic problems arise:

a) conduct the reaction to completion,
b) promote production of the intermediate.

The first problem is trivial and can be reduced to a single reaction problem. Use the slowest reaction in the sequence to design the reactor.

In order to maximize the production of intermediates PFR flow pattern is always superior to a CSTR flow pattern.

$$y\left(\frac{P}{A}\right) = \frac{R_p}{-R_A} = \frac{p_1 r_1 - p_2 r_2}{a r_1} = \frac{p_1}{a} - \frac{p_2}{a}\frac{r_2}{r_1}$$

$$y_{max}\left(\frac{P}{A}\right) = \frac{p_1}{a}$$

$$\bar{y}\left(\frac{P}{A}\right) = 1 - \frac{p_2}{p_1}\frac{r_2}{r_1} = 1 - \frac{p_2 k_2 C_P^\beta}{p_1 k_1 C_A^\alpha}$$

One needs to keep C_A high and C_p/C_A low which is best accomplished in a PFR.

Example 1

A = P	$r_1 = 1.0\ C_A$ (kmol/m³s) $\alpha = 1$
P = S	$r_2 = 0.5\ C_P$ (kmol/m³s) $\beta = 1$

Starting with $C_{Ao} = 1$ (kmol/m³) and $C_{Po} = C_{so} = 0$ find the maximum attainable C_P in
a) CSTR, b) PFR.

We could continue to use the point yield approach.

CSTR Stirred Tank Reactor

$$C_P = y\left(\frac{P}{A}\right)(C_{Ao} - C_A) = \frac{C_A - 0.5 C_P}{C_A}(C_{Ao} - C_A)$$

Solve for C_P

$$C_P = \frac{C_A(C_{Ao} - C_A)}{0.5(C_{Ao} + C_A)}$$

Find optimal C_A at which the CSTR should operate.

$$\frac{dC_P}{dC_A} = 0 \Rightarrow (C_{Ao} - 2C_A)(C_{Ao} + C_A) - C_A(C_{Ao} - C_A) = 0$$

$$C_A^2 + 2C_{Ao}C_A - C_{Ao}^2 = 0$$

$$C_{A_{opt}} = C_{Ao}\left[\sqrt{2} - 1\right] = \underline{0.414(kmol/m^3)}$$

$$C_{P_{max}} = \frac{0.414(1 - 0.414)}{0.5(1 + 0.414)} = \underline{0.343(kmol/m^3)}$$

$$C_S = C_{Ao} - C_A - C_P = \underline{0.243 kmol/m^3}$$

Overall yield $\qquad\qquad\qquad Y\left(\frac{P}{A}\right) = 0.585$

Operational yield $\qquad \qquad \qquad \maltese\left(\dfrac{P}{A}\right) = 0.343$

Overall selectivity $\qquad \qquad \quad S\left(\dfrac{P}{S}\right) = 1.4$

Required reactor space time:

$$\tau = \frac{C_{Ao} - C_{A_{opt}}}{-R_A} = \frac{C_{Ao} - C_{A_{opt}}}{C_{A_{opt}}} \cdot \frac{1 - 0.414}{0.414} = \underline{1.4(s)}$$

---

b)   <u>PFR</u>   <u>Plug Flow Reactor</u>

$$\frac{dC_P}{dC_A} = -y\left(\frac{P}{A}\right) = \frac{0.5C_P - C_A}{C_A}$$

at $C_A = C_{Ao}, \quad C_P = 0$

$$\frac{dC_P}{dC_A} - \frac{0.5\,C_P}{C_A} = -1$$

$$\frac{d}{dC_A}\left[\frac{C_P}{\sqrt{C_A}}\right] = = -\frac{1}{\sqrt{C_A}}$$

$$\frac{C_P}{\sqrt{C_A}} = 2\left[\sqrt{C_{Ao}} - \sqrt{C_A}\right]$$

$$C_P = 2\sqrt{C_A}\left[\sqrt{C_{Ao}} - \sqrt{C_A}\right]$$

Find C_A at the reactor exit by

$$\frac{dC_P}{dC_A} = 0 \Rightarrow \sqrt{C_{Ao}} - 2\sqrt{C_A} = 0$$

$$C_{A_{opt}} = \frac{C_{Ao}}{4}$$

$$C_{A_{opt}} = 0.25(kmol/m^3)$$

$$C_{P_{max}} = 2\sqrt{0.25}\left[1 - \sqrt{0.25}\right] = \underline{0.5(kmol/m^3)}$$

$$C_s = 1 - 0.5 - 0.25 = \underline{0.25(kmol/m^3)}$$

Overall yield $\qquad \qquad Y\left(\dfrac{P}{A}\right) = \dfrac{2}{3} = 0.667$

Operational yield $\qquad \quad \maltese\left(\dfrac{P}{A}\right) = 0.5$

Overall selectivity　　$S\left(\dfrac{P}{A}\right) = 2.0$

Required space time:

$$\tau = \int_{C_{A_{opt}}}^{C_{Ao}} \frac{dC_A}{C_A} = \ell n \frac{C_{Ao}}{C_{A_{opt}}} = \ell n 4 = 2\ell n 2 = 1.39(s)$$

The same results can be obtained by using the design equations (i.e. mass balance) for P & A.

CSTR

$$\tau = \frac{C_{Ao} - C_A}{C_A} \qquad\qquad C_A = \frac{C_{Ao}}{1 + \tau}$$

$$\tau = \frac{C_P}{C_A - 0.5C_P} \qquad C_P = \frac{C_A \tau}{1 + 0.5\tau} = \frac{C_{Ao}\tau}{(1+\tau)(1+0.5\tau)}$$

$$\frac{dC_p}{d\tau} = 0 \Rightarrow \text{ gives } \tau_{opt} = 1.4(s), \text{ etc.}$$

PFR

$$\frac{dC_A}{d\tau} = -C_A \quad C_A = C_{Ao}e^{-\tau}$$

$$\tau = 0, \quad C_A = C_{Ao} = 1$$

$$\frac{dC_P}{d\tau} = C_A - 0.5C_P$$

$$\tau = 0 \quad\quad C_P = 0$$

$$\frac{d}{d\tau}(e^{0.5\tau}C_P) = C_{Ao}e^{-\tau}e^{0.5\tau} = C_{Ao}e^{-0.5\tau}$$

$$C_P = 2(e^{-0.5\tau} - e^{-\tau})$$

$$\frac{dC_P}{d\tau} = 0 \Rightarrow \tau_{opt} = 2\ell n 2, \text{ etc.}$$

Mixed Reactions

This is the most frequently encountered type of multiple reactions which can be viewed as a combination of competitive and consecutive reactions. We can solve the problems involving these reactions either by setting R design equations for R components or by utilizing the concept of the point yield in simpler reaction schemes.

Example 1

$$2A + B = R \qquad\qquad -R_A = 2k_1\, C_A\, C_B \text{ (kmol/m}^3\text{min)}$$

$$2B + R = S \qquad\qquad R_S = k_2\, C_B\, C_R \text{ (kmol/m}^3\text{min)}$$

$k_1 = 10$ $k_2 = 1$ (m^3/kmol min). R is the desired product. Find C_R in a) CSTR, b) PFR, when $C_{Ro} = C_{so} = 0$. Decision variable $C_{Ao} = C_{Bo} = 1$ (kmol/m^3).

We can write two point yields:

$$y\left(\frac{R}{A}\right) = \frac{R_R}{-R_A} = \frac{k_1 C_A C_B - k_2 C_B C_R}{2k_1 C_A C_B} = \frac{1}{2}\left[1 - \frac{k_2}{k_1}\frac{C_R}{C_A}\right]$$

$$y\left(\frac{R}{B}\right) = \frac{R_R}{-R_B} = \frac{k_1 C_A C_B - k_2 C_B C_R}{k_1 C_A C_B + 2k_2 C_B C_R} = \frac{C_A - \dfrac{k_2}{k_1}C_R}{C_A + \dfrac{2k_2}{k_1}C_R}$$

The point yield $y\left(\dfrac{R}{A}\right)$ depends only on C_R and C_A and is simpler to use.

a)   <u>CSTR</u>   <u>Stirred Tank Reactor</u>

$$C_R = y\left(\frac{R}{A}\right)(C_{Ao} - C_A) = \frac{C_A - \dfrac{k_2}{k_1}C_R}{2C_A}(C_{Ao} - C_A)$$

$$C_R = \frac{C_A(C_{Ao} - C_A)}{\left(2 - \dfrac{k_2}{k_1}\right)C_A + \dfrac{k_2}{k_1}C_{Ao}} = \frac{C_A(C_{Ao} - C_A)}{1.9C_A + 0.1C_{Ao}}$$

Find optimum C_A in a CSTR.

$$\frac{dC_R}{dC_A} = 0 \Rightarrow \left(2 - \frac{k_2}{k_1}\right)C_A^2 + 2\frac{k_2}{k_1}C_{Ao}C_A - \frac{k_2}{k_1}C_{Ao}^2 = 0$$

$$C_{A_{opt}} = \frac{C_{Ao}}{\sqrt{2\frac{k_1}{k_2}+1}}$$

$$C_{A_{opt}} = \frac{1}{\sqrt{2x10+1}} = \underline{0.183(kmol/m^3)}$$

$$C_{R_{max}} = \frac{0.183(1-0.183)}{1.9x0.183+0.1} = \underline{0.334\ (kmol/m^3)}$$

From stoichiometry

$$C_B - C_{Bo} - \frac{3}{2}(C_{Ao} - C_A) + 2C_R = 1 - \frac{3}{2}(1-0.183) + 2x0.334$$

$$C_S = \frac{1}{2}(C_{Ao} - C_A) - C_R = \frac{1}{2}(1-0183) - 0.334$$

$$C_B = 0.443(kmol/m^3);\ C_S = 0.0745(kmol/m^3)$$

Overall yield $\qquad\qquad Y\left(\frac{R}{A}\right) = 0.409;\quad Y\left(\frac{R}{B}\right) = 0.600$

Operational yield $\qquad ✡\left(\frac{R}{A}\right) = 0.334;\quad ✡\left(\frac{R}{B}\right) = 0.334$

Overall selectivity $\qquad S\left(\frac{R}{S}\right) = 4.48 = 4.5$

Required reactor space time:

$$\tau = \frac{C_{Ao} - C_A}{2k_1 C_A C_B} = \frac{1-0.183}{2x1x0.183x0.443} = \underline{5.0(min)}$$

b) $\quad$ <u>PFR</u> $\qquad\qquad$ <u>Plug Flow Reactor</u>

$$\frac{dC_R}{dC_A} = -y\left(\frac{R}{A}\right) = -\frac{1}{2} + \frac{k_2}{2k_1}\frac{C_R}{C_A}$$

$$C_A = C_{Ao}, C_R = 0$$

$$\frac{d}{dC_A}\left(C_A^{-\frac{k_2}{2k_1}} C_R\right) = -\frac{1}{2} C_A^{-\frac{k_2}{2k_1}}$$

$$C_R = \frac{C_{Ao}^{\left(1-\frac{k_2}{2k_1}\right)} C_A^{\frac{k_2}{2k_1}} - C_A}{\left(2-\frac{k_2}{k_1}\right)} = \frac{C_{Ao}^{0.95} C_A^{0.05} - C_A}{1.9}$$

For optimal C_A at reactor exit:

$$\frac{dC_R}{dC_A} = 0 \Rightarrow C_{A_{opt}} = \left(\frac{k_2}{2k_1}\right)^{\left(\frac{1}{1-\frac{k_2}{2k_1}}\right)}$$

$$C_{A_{opt}} = (0.05)^{\frac{1}{0.95}} = \underline{0.0427(kmol/m^3)}$$

$$C_{R_{max}} = \frac{1^{0.95} x 0.0427^{0.05} - 0.0427}{1.9} = \underline{0.427(kmol/m^3)}$$

$$C_B = 1 - \frac{3}{2}(1 - 0.0427) + 2x0.427 = \underline{0.418(kmol/m^3)}$$

$$C_S = \frac{1}{2}(1 - 0.0427) - 0.427 = 0.0517(\underline{kmol/m^3})$$

Overall yield $Y\left(\frac{R}{A}\right) = 0.446; \quad Y\left(\frac{R}{B}\right) = 0.734$

Operational yield $\maltese\left(\frac{R}{A}\right) = 0.427; \quad \maltese\left(\frac{R}{B}\right) = 0.427$

Overall selectivity $S\left(\frac{R}{S}\right) = 8.27 = 8.3$

Reactor space time:

$$\tau = \int_{C_A}^{C_{Ao}} \frac{dC_A}{2C_A C_{B.}}$$

From stoichiometry

$$C_B = C_{Bo} - \frac{3}{2}\left(C_{Ao} - C_A\right) + 2C_R$$

but all along the PFR

$$C_R = \frac{C_A^{0.05} - C_A}{1.9}$$

$$C_B = C_{Bo} - \frac{3}{2}(C_{Ao} - C_A) + \frac{2}{1.9}\left(C_A^{0.05} - C_A\right)$$

$$C_B = \left(1.5 - \frac{2}{1.9}\right)C_A + \frac{2}{1.9}C_A^{0.05} - 0.5$$

$$C_B = 0.447C_A + 1.05C_A^{0.05} - 0.5$$

$$\tau = 0.5 \int_{0.0427}^{1} \frac{dC_A}{0.447C_A^2 + 1.05C_A^{1.05} - 0.5C_A} \quad \text{integrate numerically } (2.759 \text{ min})$$

Caution must be exercised when using the point yield concept and finding maximum concentrations in mixed reactions. Sometimes formal answers will lie outside the physically permissible range if the other reactant is rate limiting.

For example in Example 1 if we take

$$C_{Ao} = 2\left(\frac{kmol}{m^3}\right) \quad ; \quad C_{Bo} = 1\left(\frac{kmol}{m^3}\right)$$

We are feeding the reactants in stoichiometric ratio for reaction 1.

Following the above described procedure in a CSTR we would find

$$C_{A\,opt} = \frac{C_{Ao}}{\sqrt{2x10 + 1}} = 0.366(kmol/m^3)$$

$$C_{R\max} = \frac{0.366(2 - 0.366)}{1.9x0.366 + 0.2} = 0.668(kmol/m^3)$$

However these values are not attainable since from stoichiometry it follows that:

$$C_B = 1 - \frac{3}{2}(2 - 0.366) + 2x0.668 = -0.115 < 0$$

This indicates that B is not introduced in sufficient amount to allow the reactions to proceed to that point.

If $C_{Bo} = 1.115$ (kmol/m^3) then the above $C_{R\max}$ can be obtained (theoretically) at $C_B = 0$ and that would require an infinitely large reactor.

Thus the maximum reactor size that is allowed would determine $C_{B\min}$. Say $C_{B\min} = 0.01$ (kmol/m^3) (99% conversion of B).

Calculate the resulting C_A and C_R from

$$C_A = C_{Ao} - \frac{4}{3}C_R - \frac{2}{3}(C_{Bo} - C_{B_{min}})$$

$$C_R = \frac{C_A(C_{Ao} - C_A)}{1.9C_A + 0.1C_{Ao}}$$

$$C_A = 0.461(kmol/m^3)$$

That yields: $C_R = 0.660(kmol/m^3)$

$$C_S = 0.110(kmol/m^3)$$

Overall yield $Y\left(\dfrac{R}{A}\right) = 0.429; \quad Y\left(\dfrac{R}{B}\right) = 0.667$

Operational yield $✡\left(\dfrac{R}{A}\right) = 0.330; \quad ✡\left(\dfrac{R}{B}\right) = 0.660$

Overall selectivity $S\left(\dfrac{R}{S}\right) = 6.0$

Reactor space time:

$$\tau = \frac{2 - 0.461}{2x1x0.461x0.01} = 170\text{min}$$

II.   Systems with change in total volumetric flow rate $(\varepsilon_A \neq 0)\underline{\underline{gases}}$

Same approach may be used but one needs to deal with $\dot{X}_i$ extents rather than concentrations. Use relationships from Lecture 1.

Summary

PFR promotes more reactions of higher order with respect to reactions of lower order.

CSTR favors reactions of lower order with respect to those of higher order.

In consecutive reactions better yields are achieved <u>always</u> in PFR than in a CSTR for an intermediate product.

Select judiciously the objective function to be optimized.

Remember: Optimizing overall yield does not necessarily lead to the same result as maximizing the production rate (or concentration) of the desired product or as maximizing selectivity.

Be aware of the relationship of the design equations and reaction stoichiometry.

NONISOTHERMAL OPERATION OF
IDEAL REACTORS

Continuous Flow Stirred Tank Reactor

(CSTR)

(CHE 471)

M.P. Dudukovic

Chemical Reaction Engineering Laboratory

(CREL),

Washington University, St. Louis, MO

NONISOTHERMAL OPERATION OF IDEAL REACTORS
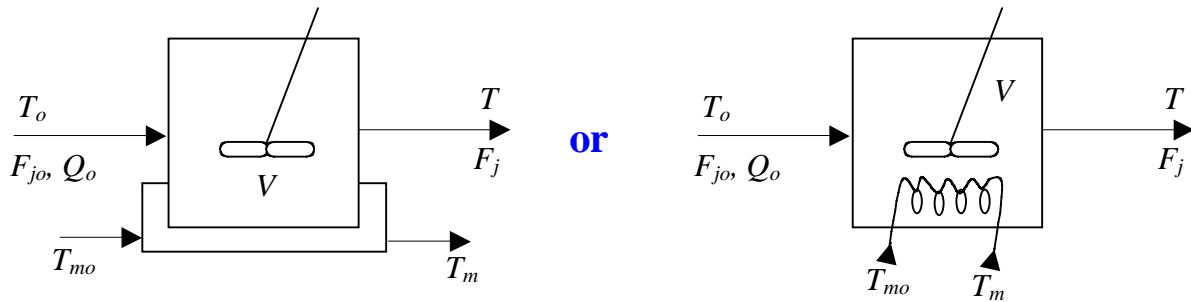### Continuous Flow Stirred Tank Reactor (CSTR)

Figure 1:   Schematic of CSTR with jacket and coil

Assumptions:

Homogeneous system

a) Single Reaction $\sum_{j=1}^{s} \upsilon_j A_j = 0$

b) Steady state

A CSTR is always assumed perfectly mixed so that the concentration of every species is uniform throughout the reactor and equal to the concentration in the outflow. Due to assumption of perfect mixing the temperature, T, throughout the reactor is uniform and equal to the temperature of the outflow. The only difference between an "isothermal" CSTR treated previously and the general case treated now, is that now we do not necessarily assume that reactor temperature, T, and feed temperature, T_o, are equal.

A CSTR can be jacketed or equipped with a cooling (heating) coil.

Two basic types of problems arise:

1. Given feed composition and temperature, rate form and desired exit conversion and temperature find the necessary reactor size to get the desired production rate and find the necessary heat duty for the reactor.

2. Given feed conditions and flow rate and reactor size together with cooling or heating rates, determine the composition and temperature of the effluent stream.

To solve either of the above two problems we need to use both a species mass balance on the system and the energy balance.

Consider a **single reaction**

$$\sum_{j=1}^{s} \upsilon_j A_j = 0 \tag{1}$$

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

Suppose the reaction is practically irreversible and the rate of reaction, which is a function of composition and temperature is given by:

$$r = \underbrace{k_o e^{-E/RT}} \underbrace{C_A^\alpha C_B^\beta} \left(\frac{kmol}{m^3 s} \right) \tag{2}$$

Arrhenius	concentration dependence
Temperature	n-th order reaction $n = \alpha + \beta$
Dependence of the rate	

For a single reaction we can always eliminate all concentrations in terms of conversion of the limiting reactant A (Lecture 1).

For liquids

$$C_j = C_{Ao} \left(M_{j/A} - \frac{\upsilon_j}{\upsilon_A} x_A \right); M_{j/A} = \frac{C_{jo}}{C_{Ao}}$$

For gases

$$C_j = C_{Ao} \left(\frac{M_{j/A} - \frac{\upsilon_j}{\upsilon_A} x_A}{1 + \varepsilon_A x_A} \right) \frac{T_o P}{T P_o}$$

where

$$\varepsilon_A = y_{Ao} \frac{\sum \upsilon_j}{(-\upsilon_A)}$$

In a CSTR we assume $P_o = P = const$ i.e constant pressure.

The rate now becomes:

For liquids

$$r = k_o e^{-E/RT} C_{Ao}^{(\alpha+\beta)} (1 - x_A)^\alpha \left(M_{B/A} - \frac{b}{a} x_A \right)^\beta \tag{3a}$$

For gases

$$r = k_o e^{-E/RT} \left(\frac{T_o}{T} \right) C_{Ao}^{\alpha+\beta} (\alpha+\beta) \frac{(1-x_A)^\alpha \left(M_{B/A} - \frac{b}{a} x_A \right)^\beta}{(1 + \varepsilon_A x_A)^{\alpha+\beta}} \tag{3b}$$

Recall that at steady state the basic conservation equation is:

$$\left(\text{Rate of input} \right) - \left(\text{Rate of output} \right) + \left(\text{Rate of generation by reaction} \right) = 0 \tag{4}$$

2

Apply equation (4) to mass of species A: (or to any species j)

$$F_{Ao} - F_A + \upsilon_A rV = 0; \qquad F_{jo} - F_j + \upsilon_j rV = 0$$

$$F_{Ao} x_A = arV = 0$$

$$C_{Ao} x_A = ar\tau \tag{5}$$

$$\dot{X} = rV \tag{5a}$$

where

$$\tau = \frac{V}{Q_o}$$

The energy balance of course cannot contain a generation term (in absence of nuclear reactions) and hence can be written as:

$$\sum_{j=1}^{s} F_{jo} \tilde{H}_{jo} - \sum_{j=1}^{s} F_j \tilde{H}_j + \dot{q} = 0 \tag{6}$$

$F_{jo} \left(\dfrac{kmol\ j}{s} \right)$ - molar flow rate of species j in the feed

$F_j \left(\dfrac{kmol\ j}{s} \right)$ - molar flow rate of species j in the outflow

$\tilde{H}_j \left(\dfrac{J}{kmol\ j} \right)$ - virtual partial molal enthalpy of species j in the outflow mixture

$\tilde{H}_{jo} \left(\dfrac{J}{kmol\ j} \right)$ - virtual partial molal enthalpy of species j in the feed

$\dot{q} \left(\dfrac{J}{s} \right)$ - rate of heat addition from the surroundings i.e from the jacket or coil to the

        reaction mixture in the reactor

The energy balance given by equation (6) is not general in the sense that the following assumptions have already been made in order to present it in that form:

Assumptions involved in deriving eq (6):

1. Potential energy changes are negligible with respect to internal energy changes.
2. Kinetic energy changes are negligible with respect to internal energy changes.
3. There is no shaft work involved i.e the only work term is the expansion (flow) work.

The virtual partial molal enthalpy, $\tilde{H}_j \left(\dfrac{J}{mol\ j} \right)$, is defined by:

$$\dot{m}_{tot} \underline{H} = \sum_{j=1}^{s} F_j \tilde{H}_j$$

$\dot{m}_{tot} \left(\dfrac{kg}{s} \right)$ - mass flow rate of the mixture

$\underline{H} \left(\dfrac{J}{kg} \right)$ - enthalpy per unit mass of the mixture

In principle the virtual partial molal enthalpy can be evaluated by the following procedure (for gases):

$$\tilde{H}_j \left(T, P, y_j \right) = \Delta H_{fj}^\circ + \int_{T_*^\circ}^{T} C_{\underset{\sim}{p_j^*}} dT + [H_{\underset{\sim}{j}}(T,P) - H_{\underset{\sim}{j}}^* T, P] + [H_{\underset{\sim}{j}}(T,P,y_j) - H_{\underset{\sim}{j}}(T,P)]$$

$\Delta H_{\underset{\sim}{f_j^\circ}}$ - standard enthalpy of formation for species j at the pressure P^o of standard state and temperature T^o (enthalpy of 1 kmole of pure j at T^o, P^o)

$\int_{T^o}^{T} C_{\underset{\sim}{f_j^*}} dT$ - change in enthalpy of species j, if it behaved as an ideal gas, due to change in temperature from standard state temperature T^o to the temperature of interest T. $C_{\underset{\sim}{p_j^*}}$ is the specific heat of j in ideal gas state. In reality C_{pj}^o data for real gases obtained at atmospheric or lower pressures can be used.

$\Delta H_{\underset{\sim}{f_j^\circ}} + \int_{T^o}^{T} C_{f_j^*} dT = H_{\underset{\sim}{j}}^*(T, P^\circ)$ enthalpy per mol of j for pure j, if it behaved like an ideal gas, at T and P^o. Since enthalpy of an ideal gas does not depend on pressure this is also the enthalpy per kmol of j, if it were an ideal gas, at T and P, $H_{\underset{\sim}{j}}^*(T,P)$.

$H_{\underset{\sim}{j}}(T,P) - H_{\underset{\sim}{j}}^*(T,P)$ = pressure correction factor i.e the difference between the enthalpy of j being a real gas at T, P, $(H_{\underset{\sim}{j}}(T,P)$ and enthalpy of j being an ideal gas at T, P ($H_{\underset{\sim}{j}}^*(T,P)$).

Frequently the pressure correction is read off appropriate charts and is given by:

$$\underset{\sim}{H}_{j}(T,P) - \underset{\sim}{H}_{j}^{*}(T,P) = -T_{cj} \left(\frac{\underset{\sim}{H}_{j}^{*} - \underset{\sim}{H}_{j}}{T_{cj}} \right)_{T_r, P_r}$$

Where

T_{cj} – critical temperature of species j.

$\left(\dfrac{\underset{\sim}{H}_{j}^{*} - \underset{\sim}{H}_{j}}{T_{cj}} \right)$ is the correction read off the charts at appropriate reduced temperature $T_r = \dfrac{T}{T_{cj}}$ and

reduced pressure $P_r = \dfrac{P}{p_{cj}}$

P_{cj} – critical pressure of species j.

Finally

$\underset{\sim}{H}_{j}(T,P,y_j) - \underset{\sim}{H}_{j}(T,P) = \pi_j$ is the correction factor which accounts for the nonideality of the mixture.

_____

For liquids (in a first approximation)

$$\widetilde{H}_{j} = \Delta \underset{\sim}{H}_{f_j^{\circ}} + \int_{T^o}^{T} C_{pj} dT + \pi_j$$

Here we will assume:

Gases:

a.   ideal mixtures $\pi_j = 0$
b.   ideal gas behavior $\underset{\sim}{H} = \underset{\sim}{H}_{j}^{*}$

Liquids:

a.   ideal mixture $\pi_j = 0$

Now the energy balance of eq (6) based on the above assumption can be written as

$$\sum_{j=1}^{s} F_{jo} \int_{T_o}^{T} C_{\underset{\sim}{p}_j} dT + \Delta H_{r_T} \dot{X} = \dot{q} \tag{7a}$$

$$\sum_{j=1}^{s} F_{j} \int_{T_o}^{T} C_{\underset{\sim}{p}_j} dT + \Delta H_{r_{T_o}} \dot{X} = \dot{q} \tag{7b}$$

where

$$\Delta H_{r_T} = \sum_{j=1}^{s} \upsilon_j \Delta H_{\underset{\sim}{f}_j^o} + \sum_{j=1}^{s} \upsilon_j \int_{T^o}^{T} C_{p_j} dT$$

is the heat of reaction at temperature T.

Finally, in preliminary reactor design we assume that the heat of reaction does not vary much with temperature

$$\Delta H_{r} \approx const \approx \Delta H_{r_{T_o}} \approx \Delta H_{r_T}$$

and that some mean value of the specific heat can be used

$$\int_{T_o}^{T} C_{\underset{\sim}{p}_j} dT = \overline{C}_{\underset{\sim}{p}_j}(T - T_o)$$

Equations (7) can then be written as:

$$\sum_{j=1}^{s} F_{jo} \overline{C}_{\underset{\sim}{p}_j}(T - T_o) + \Delta H_r \dot{X} = \dot{q}$$

or

$$\rho \underline{C}_p Q(T_o - T) + (-\Delta H_r)\dot{X} + \dot{q} = 0 \tag{8}$$

where

$$\dot{X} = \frac{F_{Ao} x_A}{(-\upsilon_A)} = \frac{C_{Ao} Q_o x_A}{(-\upsilon_A)}$$

$$\Delta H_{r_A} = \frac{\Delta H_r}{(-\upsilon_A)}$$

ΔH_r - heat of reaction for the stoichiometry as written

ΔH_{r_A} - heat of reaction per mole of A.

$$\rho \underline{C}_p Q(T_o - T) + (-\Delta H_{r_A})C_{Ao} Q_o x_A + \dot{q} = 0 \tag{9}$$

or

$$\rho \underline{C}_p Q(T_o - T) + (-\Delta H_r)rV + \dot{q} = 0 \tag{9a}$$

This final form of the energy balance resulting from all of the above assumptions can be interpreted as a "heat balance" i.e as rate of input of sensible heat by the flowing stream minus rate of output of sensible heat by exit stream plus heat generated by reaction plus heat added from the surroundings must add to zero.

In addition we now need an energy balance on the jacket or coil and a constitutive relationship for heat transfer rate, $\dot{q}$.

For a jacket at steady state (assuming that the jacket is well mixed too)

$$\rho_m Q_m \underline{C}_{p_m}(T_{m_o} - T_m) - \dot{q} = 0 \tag{10}$$

$\rho_m, Q_m \underline{C}_{p_m}$ - are density, volumetric flow rate and mean specific heat of the fluid flowing through the jacket.

T_{m_o} - inlet jacket temperature.
T_m – exit jacket temperature.

Let
$$\dot{q} = UA(T_m - T) \tag{11}$$

$$U\left(\frac{J}{m^{3o}Cs}\right)$$ - overall heat transfer coefficient.

A (m^2) – area for heat transfer between reactor and jacket.

From eq (10)

$$T_m = \frac{T_{m_o} + \kappa_m T}{1 + \kappa_m} \tag{12}$$

where
$$\kappa_m = \frac{UA}{\rho_m \underline{C}_{p_m} Q_m}$$

For a coil with plug flow of heating/cooling medium:
$$\frac{dT_m}{dz} = \kappa_m(T - T_m) \tag{13}$$

$$z = 0 \quad T_m = T_{m_o} \tag{13a}$$

z = fractional length of the coil.

$$T_m(z) = T + e^{-\kappa_m z}(T_{m_o} - T) \tag{14}$$

For an n-th order irreversible reaction G(T) always has a sigmoidal shape and at high temperatures tends to a horizontal asymptote C_{Ao}.

Finally, in dimensionalized form the two equations that have to be solved simultaneously are:

$$C_{Ao} x_A = ar\tau \tag{15}$$

$$T_o - T + \tilde{\beta}_A ar\tau - \omega(T - T_{mo}) = 0 \tag{16}$$

where r is given by equation (3) and

$$\tilde{\beta}_A = \left(\frac{-\Delta H_{r_A}}{\rho \underline{C}_p} \right)$$

$$\omega = \frac{\kappa}{1 + \kappa_m} = \frac{UA}{\rho_m \underline{C}_{p_m} Q_m + UA} \frac{\rho_m \underline{C}_{p_m} Q_m}{\rho \underline{C}_p Q} \qquad \text{for a jacketed reactor}$$

$$\omega = \frac{\kappa}{\kappa_m}\left(1 - e^{-\kappa_m}\right) \qquad \text{for a reactor with coil}$$

$$\kappa_m = \frac{UA}{\rho_m \underline{C}_{p_m} Q_m} \qquad \kappa = \frac{UA}{\rho \underline{C}_p Q}$$

When we deal with problems of type 1, to find reactor size for given feed and product stream conditions we use directly eq (15).

$$\tau = \frac{V}{Q_o} = \frac{C_{Ao} x_A}{ar} = \frac{C_{Ao} x_A}{-R_A}$$

Then calculate the desired heating or cooling rate from eq (16)

$$-\dot{q} = \rho \underline{C}_p Q(T_o - T) + \left(-\Delta H_{r_A}\right) arV$$

When we deal with problems of type 2 and try to find the operating conditions for a given reactor, then we must solve eqs (15) and (16) simultaneously by trial and error for x_A and T.

Sometimes we can solve explicitly for x_A from eq (15) in terms of temperature $x_A = x_A(T)$.

Substituting this relationship into eq (16) we get

$$T_o - T + \overline{\beta}_A a r_T \tau - \omega(T - T_{m_o}) = 0$$

r_T indicates that the rate is now a function of temperature only since $r(x_A,T) = r(x_A(T),T)$

$$\underbrace{\frac{1+\omega}{\tilde{\beta}_A} T - \frac{T_o + \omega T_{m_o}}{\tilde{\beta}_A}}_{L(T)} = \underbrace{a r_T \tau}_{G(T)} = C_{Ao} x_A \tag{15}$$

Reactor operating temperature is given by the intersection of the straight line L(T) and curvilinear function G(T).

For an n-th order irreversible reaction G(T) always has a sigmoidal shape and at high temperatures tends to a horizontal asymptote C_{Ao}.

For an endothermic reaction $\Delta H_r > 0 \Rightarrow \tilde{\beta}_A < 0$ and line L has a negative slope.
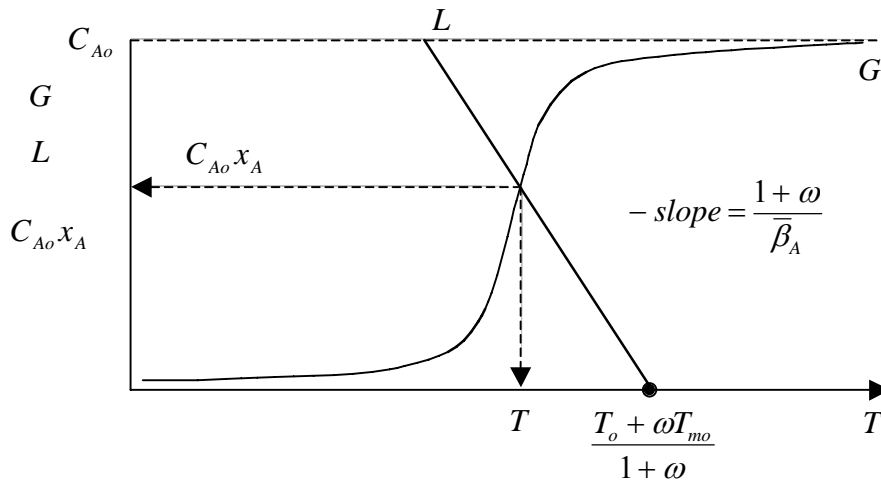

Figure 2:   Operating point for an endothermic reaction in a CSTR.

Several conclusions can be reached for endothermic reactions:

i)   L & G can intersect at most once and for a given set of parameters only one steady state exists.

ii)   For a given reactor and flow rate, fixed τ, given feed, T_o' and heating medium feed temperature, T_{m_o}, and given heat transfer properties, ω, the more endothermic the reaction, the larger $\left|\tilde{\beta}_A\right|$ and the smaller the slope of the L line, therefore the lower the operating temperature and conversion.

iii)   For a fixed reaction, feed flow rate and composition and given reactor, fixed G curve, an increase in feed temperature moves the L-line to the right while its slope remains unchanged. Hence, the operating T and x_A are increased.

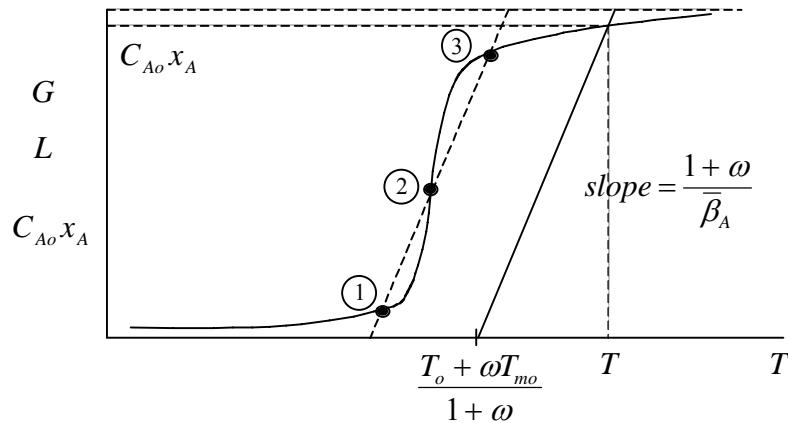For an exothermic reaction $\Delta H_r < 0$ *and* $\tilde{\beta}_A > 0$. The L-line has a positive slope.

Figure 3:   Operating point(s) for an exothermic reaction in a CSTR.

Several conclusions can be reached for exothermic reactions:

i)   L & G can intersect sometimes at more than one place and for a given set of conditions, more than one steady state may be possible.

ii)   For fixed τ and reaction, fixed G, an increase in the feed temperature moves the L line to the right increasing the operating T and x_A. An increase in coolant T_{m_o} has the same effect.

iii)   For a fixed τ and reaction, fixed G, $\tilde{\beta}_A$, an increase in heat removal, increase in ω, rotates the L-line in the counterclockwise direction and moves the intercept at the abscissa to the left if $T_o > T_{m_o}$ or to the right if $T_{m_o} > T_o$.

For exothermic reactions it is important to calculate the adiabatic temperature rise and the maximum adiabatic ΔT.

From eq (16) with $\omega \equiv 0$

$$(T - T_o)_{ad} = \tilde{\beta}_A C_{Ao} x_A \tag{18}$$

$$\Delta T_{ad.\,max} = \tilde{\beta}_A C_{Ao} \tag{19}$$

Maximum fractional temperature rise is also called the Prater number, β.

$$\beta = \frac{\Delta T_{ad.\,max}}{T_o} = \frac{\tilde{\beta}_A C_{Ao}}{T_o} \tag{20}$$

Now let us consider a number of simple illustrative examples.

Example 1.

The following information is given.

Irreversible reaction A $\rightarrow$ R

$$-R_A = e^{25} e^{-20,000/RT} C_A \left(\frac{mol}{L\,min} \right)$$

$$C_{Ao} = 1 \left(\frac{mol}{L} \right) T_o = 350°K = 77°C$$

$$\Delta H_{R_A} = -100,000 \frac{cal}{mol\,A}$$

$$\rho C_p = 500 \left(\frac{cal}{L°C} \right)$$

CSTR

a.   **Isothermal**. Find reactor space time needed for $x_A = 0.9$ at 350°K and heat to be removed.

$$\tau = \frac{C_{Ao} - C_A}{-R_A} = \frac{C_{Ao} x_A}{-R_A} = \frac{1x0.9}{e^{25} e^{-\frac{20,000}{1.987 x 300}}} = \frac{0.9}{0.0233}$$

$$\tau = 38.59 = 36\,min$$

$$\dot{q} = Q\rho\, C_p\,(T - T_o) + \dot{X}\Delta H_R$$

$$\dot{X} = F_{Ao} x_A = Q\rho C_{Ao} x_A (\Delta H_{R_A})$$

$$\dot{q}\left(\frac{cal}{min} \right) = Q\rho C_p (T - T_o) + Q C_{Ao} x_A (\Delta H_{R_A})$$

$$\frac{\dot{q}}{Q}\left(\frac{cal}{L} \right) = \rho C_p (T - T_o) + C_{Ao} x_A (\Delta H_{R_A}) = 1x0.9(-100,00)0 = -90,000 cal/L \text{ to be removed.}$$

Note that the reaction rate at 350K is only $0.0233 \left(\frac{mol}{L\,min} \right)$

b.   **Adiabatic**

Find τ for $x_A = 0.9$.

$$Q\rho\, C_p\,(T - T_o) = (\Delta H_{R_A}) Q C_{Ao} x_A$$

$$T = T_o + \frac{(-\Delta H_{R_A}) C_{Ao}}{\rho C_p} x_A$$

$$T = 350 + \frac{100,000 x1}{500} 0.9 = 530 K (257°C)$$

LECTURE 7

$$\tau = \frac{C_{Ao} - C_A}{-R_A} = \frac{C_{Ao} x_A}{-R_A} = \frac{1 \times 0.9}{e^{25} e^{-20,000/1.987 \times 530}} = \frac{0.9}{407}$$

$$\tau = 2.21 \times 10^{-3} \text{ min} = 0.133 s$$

Note that at 530K the reaction rate has increased by orders of magnitude to

$$-R_A = 407 \left(\frac{mol}{L \min} \right)$$

Nonisothermal

Find $\tau, \dot{q}/Q$ given desired $x_A = 0.9$ and desired $T = 400K$.

$$\tau = \frac{C_{Ao} x_A}{-R_A} = \frac{0.9}{e^{25} e^{-\frac{20,000}{1.987 \times 400}}} = \frac{0.9}{0.849} = 1.06 \text{ (min)}$$

$$\frac{\dot{q}}{Q} = \rho C_p (T - T_o) + C_{Ao} x_A (-\Delta H_{R_A})$$

$$= 500(400 - 350) + (-90,000)$$

$$= 25,000 - 90,000 = -65,000 cal / L$$

Note the value of the rate which is

$$-R_A = 0.849 \left(\frac{kmol}{c \min} \right)$$

Example 2

A well stirred bench scale reactor (CSTR) is used for a first order exothermic reaction $A \rightarrow R$ (practically irreversible) under the following conditions:

$$\tau = 1.0 (\text{min})$$

$$C_{Ao} = 1.0 (mol / liter) ; T_o = 350K$$

$$T_{mo} = 350K ; \omega = 1.0 = \frac{UA}{\rho_m C_{pm} Q_m + UA} \bullet \frac{\rho_m C_{pm} Q_m}{\rho C_p Q}$$

$$\dot{\beta}_A = 200 \left(\frac{K \, lit}{mol} \right) = \frac{(-\Delta H_{R_A})}{\rho \underline{C}_p}$$

$$r = e^{25} e^{-\frac{20,000}{RT}} C_A \left(\frac{mol}{lit \min} \right)$$

a) Find the operating temperature and exit conversion.
b) How many steady states are possible under these conditions?
c) What is the maximum adiabatic temperature rise?
d) How would you change some of the operating conditions (T_{mo}, T_o, ω) in order to operate at a unique steady state of high conversion.
e) What start up program should one use in order to have the reactor settle in the steady state of high conversion?

Solution

Solve simultaneously eqs (15) & (16)

$$C_{Ao}x_A = ar\tau = k_0 e^{-E_1/RT} C_{Ao}(1-x_A)\tau \tag{15}$$
$$k_0 = e^{25} \qquad E = 20,000 \; cal/mol$$

$$\frac{1+\omega}{\tilde{\beta}_A}T - \frac{T_o + \omega T_{mo}}{\tilde{\beta}_A} = ar\tau = k_0 e^{-E/RT} C_{Ao}(1-x_A)\tau \tag{16}$$

Eliminate x_A from (15).

$$x_A = \frac{k_0 e^{-E/RT}\tau}{1+k_0 e^{-E/RT}\tau}$$

Substitute into eq (16)

$$\underbrace{\frac{1+\omega}{\tilde{\beta}_A}T - \frac{T_o + \omega T_{mo}}{\tilde{\beta}_A}}_{L} = \underbrace{\frac{k_0 e^{-E/RT}\tau C_{Ao}}{1+k_0 e^{-E/RT}\tau}}_{G}$$

Substitute in the values of parameters:

$$\frac{1+1}{200}T - \frac{350+1 x 350}{200} = \frac{\exp\left\{-\dfrac{20,000}{1.9877T}\right\}}{1+\exp\left\{25-\dfrac{20,000}{1.987T}\right\}} x 1 x 1$$

$$0.01T - 3.5 = \frac{\exp\left\{25-\dfrac{20,000}{1.987T}\right\}}{1+\exp\left\{25-\dfrac{20,000}{1.987T}\right\}} \tag{*}$$

Solve * by trial and error for T. Then obtain the corresponding conversion by:

$$x_A = \frac{\exp\left\{25-\dfrac{20,000}{1.987T}\right\}}{1+\exp\left\{25-\dfrac{20,000}{1.987T}\right\}} \tag{**}$$

13

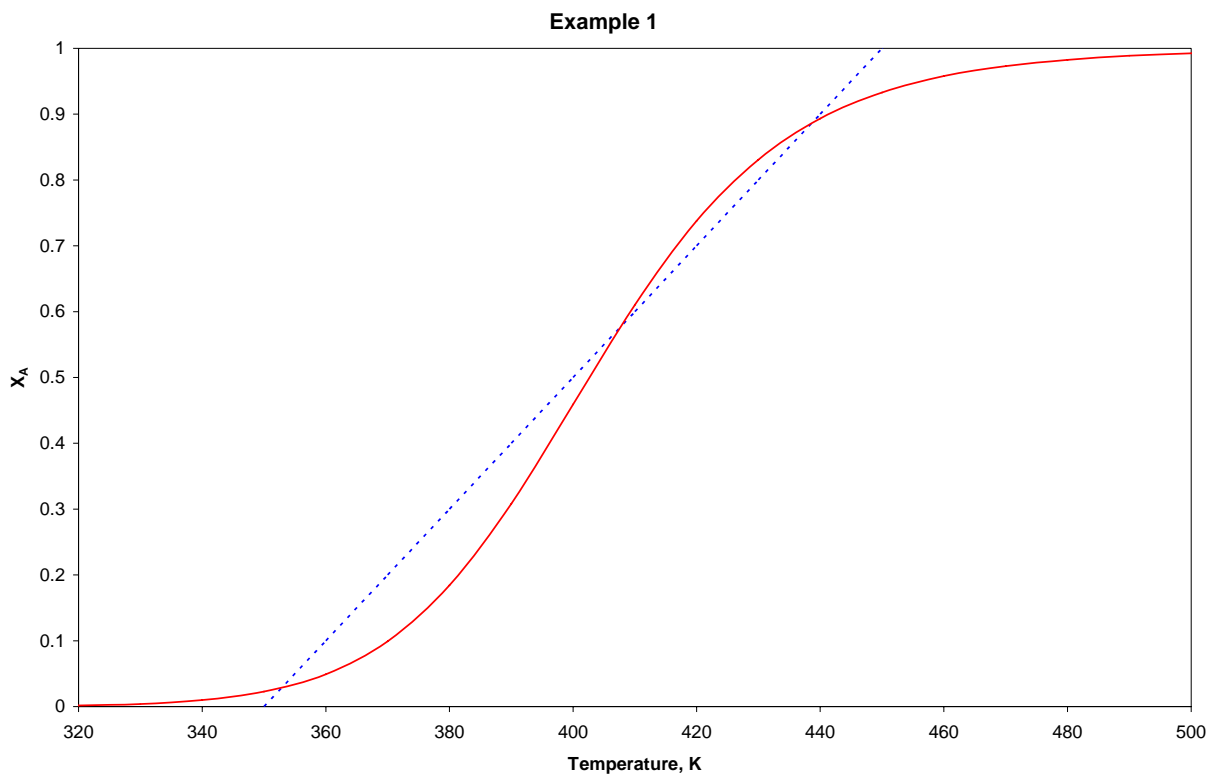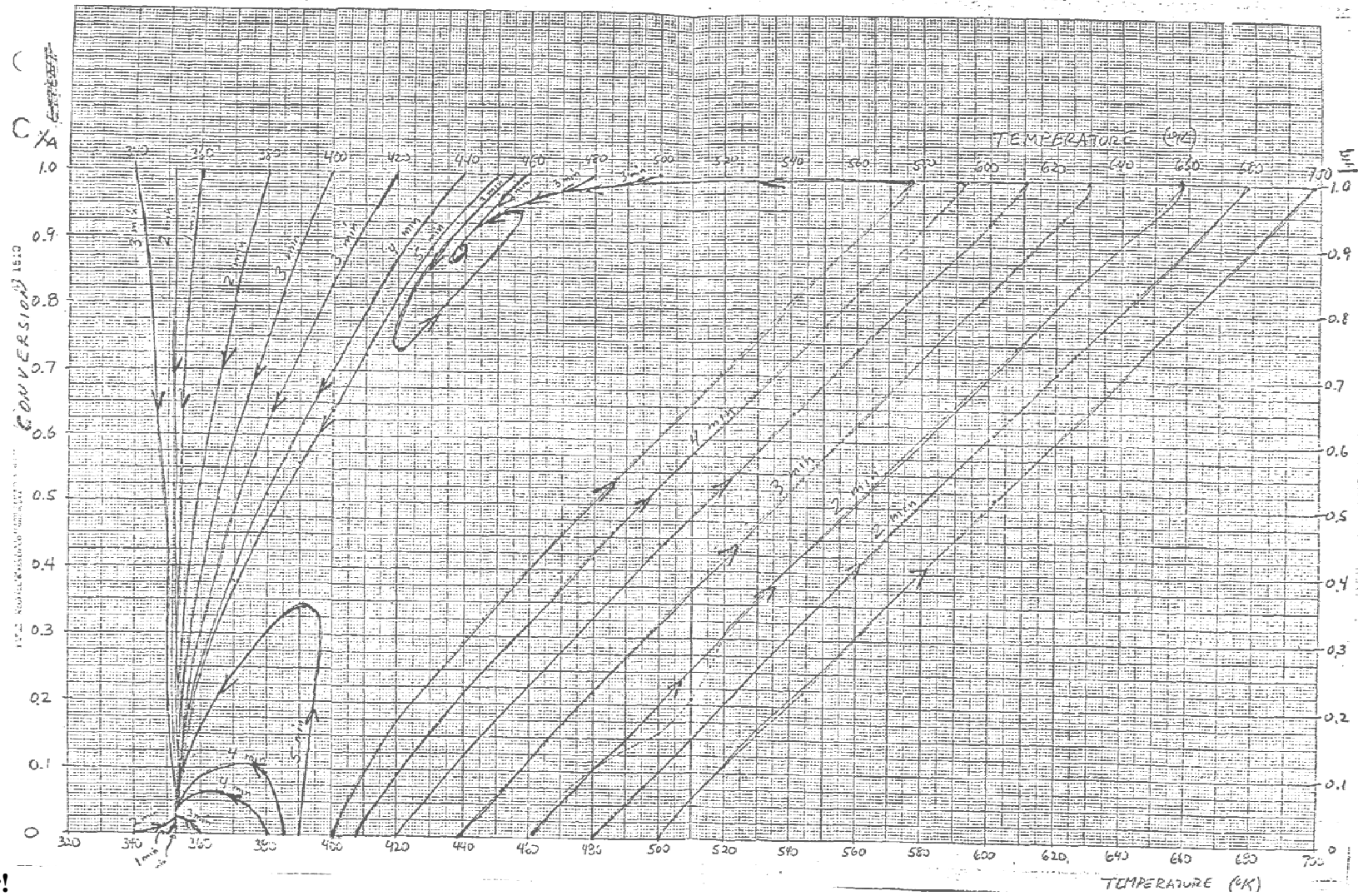We can also represent equation (*) graphically as shown below:

Example 1

Figure 4:   Operating points for the CSTR of Example 2.

Figure 5 on next page shows the dramatic temperature excursions that the reactor can experience during start-up before it settles to a steady state.

Figure 5: Transient CSTR operation for Example 2

a)   There are three intersections of the L and G line indicating 3 possible steady states.

(1) $\begin{cases} T = 353K \\ x_A = 0.03 \end{cases}$

(2) $\begin{cases} T = 408K \\ x_A = 0.576 \end{cases}$

(3) $\begin{cases} T = 439K \\ x_A = 0.886 \end{cases}$

b)   Three steady states are possible.

c)
$$\Delta T_{ad\,max} = \tilde{\beta}_A C_{Ao} = 200 x 1 = 200K$$
$$T_{ad\,max} = T_o + \Delta T_{ad\,max} = 550K!$$

d)   Increase T_o or T_{mo} to bypass the lower bump in the curve. Increase ω if possible.
e)   See attached Figure 5.

Reversible Reactions

For reversible reactions the effect of temperature on equilibrium must be considered.

For endothermic reactions, $\Delta H_r > 0$, equilibrium conversion increases with increased temperature.
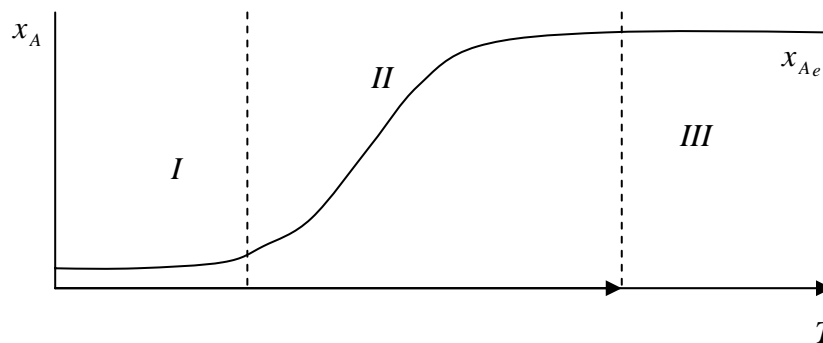

Figure 6:   Equilibrium conversion as function of temperature for endothermic reactions.

In region III the reaction can be considered practically irreversible. In region II x_{Ae} rises with increase in T.

For endothermic reactions the maximum permissible temperature is always the optimal temperature for maximizing conversion or production rate from a given CSTR.

16

The net rate of an endothermic reaction at fixed composition always increases with increased temperature.

$$r = k_{10}e^{-E_1/RT}\prod_{j=1}^{s}C_j{}^{\alpha_j} - k_{20}e^{-E_2/RT}\prod_{j=1}^{s}C_j{}^{\beta_j}$$

since $E_1 > E_2$

For exothermic reactions, $\Delta H_r < 0$, equilibrium conversion decreases with increased temperature.
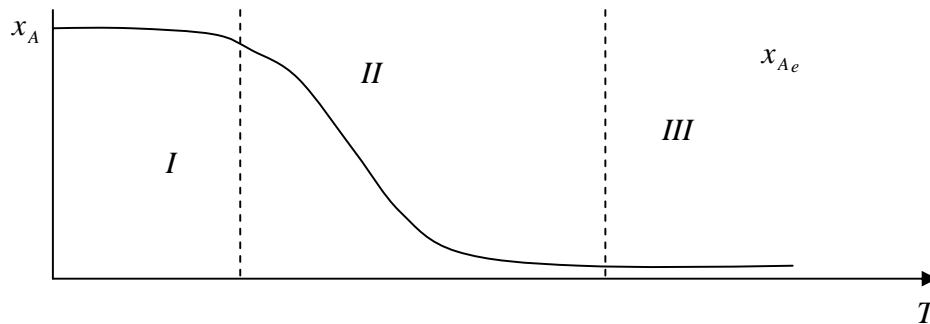
Figure 7:   Equilibrium conversion as function of temperature for exothermic reactions.

Again in region I the reaction is practically irreversible. In region II it is reversible.
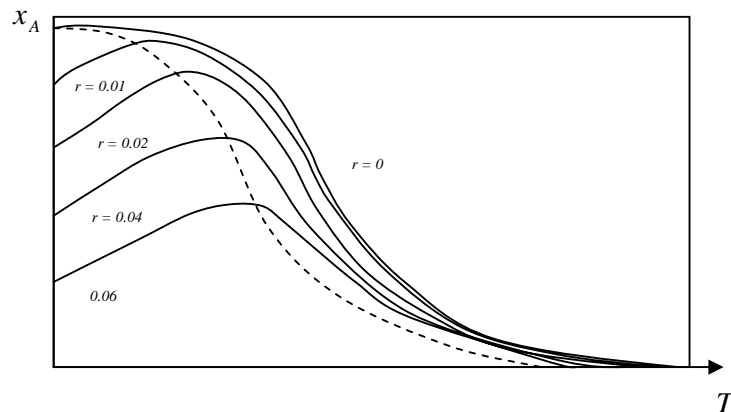
Figure 8:   Conversion temperature relation at fixed rates for exothermic reactions.

Now we notice that at fixed composition, fixed x_A, the net rate of reaction has a maximum at a certain temperature, T_m. Below that temperature the rate is lower and above it, it is lower. The reason for this is that $E_1 < E_2$.

On the above diagram we can pass a line - - - called the locus of maximum rates or a T_m line. For a given conversion the T_m line defines a temperature at which the rate is maximum and vice versa at every T the line defines an x_A a which the rate is maximum.

We should always select T_o, T_{mo}, ω in such a manner as to make sure that we operate on the T_m line.

The equation for the T_m line is obtained by

$$\frac{\partial r}{\partial T} = 0 \; from \frac{dx_A}{dT}\Big|_r = 0$$

For example if we have a reversible reaction

$$aA + bB = pP$$
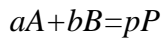
and the rate is given by

$$r = k_{10}e^{-E_1/RT}C_A^{\alpha}C_B^{\beta} - k_{20}e^{-E_2/RT}C_p^{\gamma}$$

Assuming further that we deal with liquids and that C_{Ao} and C_{Bo} are given while $C_{po} = 0$

$$K_c = C_{Ao}^{\;p-a-b}\frac{(\frac{p}{a}x_{Ae})^p}{(1-x_{Ae})^a\left(\frac{C_{Bo}}{C_{Ao}} - \frac{b}{a}x_{Ae}\right)^b} \tag{A}$$

Assuming an ideal solution

$$K_c = e^{\frac{-\Delta G_r^o}{RT}} \tag{B}$$

Using (A) and (B) we can calculate x_{Ae} as a function of temperature.

The given rate form, if it is to be viable in the vicinity of equilibrium, must satisfy the following constraint:

$$\left(\frac{C_p^{\gamma}}{C_A^{\alpha}C_B^{\beta}}\right)_{eq}^q = \frac{C_p^p}{C_A^a C_B^b}$$

The locus of maximum rates <u>i.e</u> the T_m-line can be obtained by $\dfrac{\partial r}{\partial T} = 0$ which results in

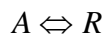$$T = T_m = \cfrac{(E_2 - E_1)/R}{\ln\left[\cfrac{k_{20}E_2}{k_{10}E_1} C_{Ao}^{\gamma-\alpha-\beta} \left(\cfrac{\left(\cfrac{p}{a}x_A\right)^\gamma}{(1-x_A)^\alpha \left(\cfrac{C_{Bo}}{C_{Ao}} - \cfrac{b}{a}x_A\right)^\beta}\right)\right]} \qquad (C)$$

For a desired conversion eq (C) gives the temperature T_m at which the rate is maximum. Substituting that conversion and temperature into the equation for the rate produces the maximum rate

Example 3 - CSTR

$A \Leftrightarrow R$

$\Delta G_{r298}^\circ = 2{,}500 cal/mol$

$\Delta H_{r298}^\circ = -20{,}000 cal/mol = const$

$\rho \underline{C}_p = 2{,}000(cal/lit) = const$

$k_1 = \underbrace{5x10^8}_{k_{10}} e - \dfrac{12{,}500}{RT} (min^{-1})$

$C_{Ao} = 2\left(\dfrac{mol}{lit}\right)$

f)   Find he optimal size CSTR necessary to achieve a production rate of $F_R = 100$ (mol/min) at $x_A = 0.9$. If the reactor is to be operated adiabatically find the necessary feed temperature.

g)   If the feed is available only a T = 298K how should one operate? Can one maintain the desired production rate and conversion?

h)   How should 2 CSTR's in series be operated to minimize the total reactor volume and keep F_R and x_A at desired levels. Feed is at 298K, T = 350K is not to be exceeded.

Solution

Find equilibrium constant at 298K

$$K_{298} = \exp\left(\frac{-\Delta G_{r298}^\circ}{RT}\right) = \exp\left(\frac{-2{,}500}{1.987x298}\right) = 68.2$$

Find equilibrium constant as a function of temperature using Van't Hoff's equation

$$\frac{d\ln K}{dT} = \frac{\Delta H_r}{RT^2}$$

$$K_T = K_{298}e^{\frac{\Delta H_r}{R}\left(\frac{1}{298}-\frac{1}{T}\right)} = 1.461x10^{-13} \exp\left(\frac{10.065}{T}\right)$$

LECTURE 7

Find equilibrium conversion variation with temperature:

$$x_{Ae} = \frac{K_T}{1+K_T} = \frac{1.461x10^{-13}\exp\left(\dfrac{10,065}{T}\right)}{1+1.461x10^{-13}\exp\left(\dfrac{10,065}{T}\right)}$$

T	298	300	310	320	330	340	350	360	370	380
x_{Ae}	0.986	0.982	0.949	0.870	0.720	0.512	0.311	0.169	0.094	0.045

Find the locus of maximum rates

$$T_m = \frac{(E_2 - E_1)/R}{\ln\left[\dfrac{k_{20}}{k_{10}}\dfrac{E_2}{E_1}\dfrac{x_A}{1-x_A}\right]} = \frac{10,065}{30.51 + \ln\left(\dfrac{x_A}{1-x_A}\right)}$$

x_A	0.94	0.95	0.9	0.85	0.8	0.6	0.4	0.2	0.1	0.01
T_m	287	301	308	312	316	326	334	346	356	388

Plot the equilibrium line, x_{Ae}, and the locus of maximum rates, T_m, in order to graphically interpret some of the later results.
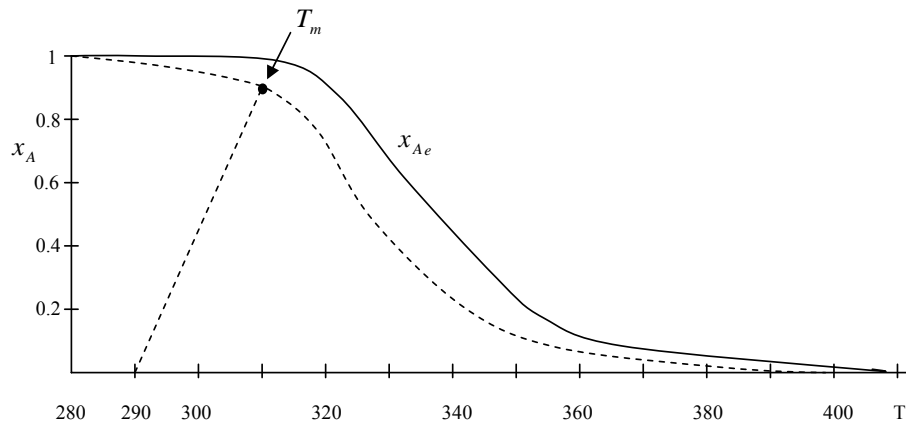
a.   At $x_A = 0.9$ $T = T_m = 308K$

The rate at the operating point is:

$$r = 5 \times 10^8\, e^{-\frac{12,500}{1.987 \times 308}} \times 2\,(1-0.9) - 3.422 \times 10^{21}\, e^{-\frac{32,500}{1.987 \times 308}} \times 2 \times 0.9$$

$$r = 0.815 \left(\frac{mol}{lit\ min}\right)$$

From the design equation (balance on R)

$$V = \frac{F_R}{R_R} = \frac{F_R}{r} = \frac{100}{0.815} = 1227 \; (lit) = 1.23 \; m^3$$

$$\boxed{V = 1.23 \; m^3}$$

For adiabatic operation

$$T_o - T + \hat{\beta}_A \left(-V_A\right) r\tau = 0 \qquad\qquad \hat{\beta} = \frac{-\Delta H_{rA}}{\rho \, C_p} = 10$$

$$T_o = T - \hat{\beta}_A \, C_{Ao} \, x_A = 308 - 10 \times 2 \times 0.9 = 290K$$

For adiabatic operation the feed temperature would have to be 290K. The same result is obtained graphically (--- adiabatic line).

    b.   If the feed is available only at $298K$ we could do one of the following:

        i)   Cool the feed from 298K to 290K and operate adiabatically
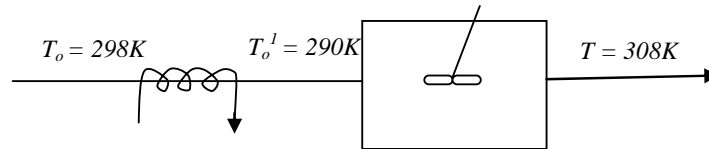
$$-\acute{q} = Q\rho \, \underline{C}_p \left(T_o - T_o^1\right) = \frac{F_R}{C_{A_o} x_A} \rho \, \underline{C}_p \left(T_o - T_o^1\right)$$

$$-\acute{q} = \frac{100}{2 \times 0.9} \times 2000 \left(298 - 290\right) = 8.889 \times 10^5 \left(\frac{cal}{min}\right)$$

        ii)   Introduce the feed at 298K and cool the reactor
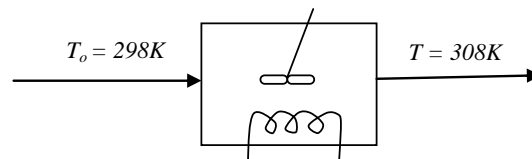
$$-\dot{\phi} = Q\rho \underline{C}_p \left(T_o - T\right) + \left(-\Delta H_{r_A}\right) C_{A_o} Q x_A$$

$$-\dot{\phi} = \frac{F_R}{C_{A_o} x_A} \rho \underline{C}_p \left(T_o - T\right) + \left(-\Delta H_r\right) F_R$$

$$-\dot{\phi} = 100\left[\frac{2000}{2 \times 0.9}(298 - 308) + 20,000\right] = \underline{8.889 \times 10^5 \frac{cal}{min}}$$

↑

The cooling rate requirement is the same, as it should be as there is no work term in the energy balance. But it is easier to remove heat from the higher reactor temperature.

iii)   Operate adiabatically with the new feed temperature while maintaining the <u>previous feed rate</u> $F_{A_o} = \left(\dfrac{100}{0.9}\right); F_{A_o} x_A = F_R$

$$Q_o = \frac{F_{A_o}}{C_{A_o}} = \frac{100}{1.8}$$

Now we must find the new operating point by a simultaneous solution of the species and energy balance.

$$C_{A_o} x_A = r \tau$$

$$T_o - T + \widetilde{\beta} \tau r = 0$$

Since we need adiabatic operation by combining the above two equations we get the relationship between conversion and temperature

$$T = T_o + \widetilde{\beta} r \tau = T_o + \widetilde{\beta} C_{A_o} x_A$$

$$T = 298 + 10 \times 2 x_A = 20\left[14.9 + x_A\right]$$

Substituting into the first equation we get:

$$2 x_A = \left|5 \times 10^8 e^{-\frac{12,500}{1.987 \times 20\left[14.9 + x_A\right]}} \times 2\left(1 - x_A\right) - 3.4 \times 10^{21} e^{-\frac{32,500}{1.987 \times 20\left(14.9 + x_A\right)}}\right| \frac{1227 \times 1.8}{100}$$

$$11.043\left\{10^9\left(1 - x_A\right) e^{-\frac{314.5}{14.9 + x_A}} - 6.8 \times 10^{21} x_A e^{-\frac{817.8}{14.9 + x_A}}\right\} - x_A = 0$$

By trial and error

$$\boxed{x_A = 0.88 \qquad\qquad T = 315.6 = 316\,K}$$

The purity (conversion) has been reduced somewhat from the required 90%.

The production rate now is F_R and rate is r.

$$r = 5 \times 10^8 \, e^{-\frac{12,500}{1.987 \times 315.6}} 2(1-0.88) - 3.4 \times 10^{21} \, e^{-\frac{32,500}{1.987 \times 315.6}} 2 \times 0.88$$

$$r = 0.0786 \left(\frac{mol}{lit \, \min} \right)$$

$$F_R = F_{A_o} \, x_A = \frac{100}{0.9} \times 0.88 = \underline{97.8 \left(\frac{mol}{\min} \right)}$$

and production rate has dropped very little.

iii)   We could operate the reactor adiabatically with the new feed temperature and maintain (via a controller) fixed exit composition at $x_A = 0.9$ which would require adjusting the feed rate.

Now

$$T = T_o + \tilde{\beta}_A \, C_{A_o} \, x_A = 298 + 20 \times 1.8 = 316K$$

$$x_A = 0.9$$

The new rate is:

$$r = 5 \times 10^8 \, e^{-\frac{12,500}{1.987 \times 316}} \times 2 (1-0.9) - 3.4 \, 10^{21} \, e^{-\frac{32,500}{1.987 \times 316}} \times 2 \times 0.9$$

$$r = 0.023 \left(\frac{mol}{lit \, \min} \right)$$

Which is much smaller than the maximum rate.

The production rate now drops to

$$F_R = r \, V = 0.023 \times 1227 = 28.2 \left(\frac{mol}{\min} \right)$$

This is too high a penalty to pay for maintaining purity i.e. keeping $x_A = 0.9$ constant!

C.   For minimum total reactor size we must find the minimum of the following expression

$$\frac{\tau_1 + \tau_2}{C_{A_o}} = \frac{x_{A_1}}{r_{m_1}} + \frac{0.9 - x_{A_1}}{r_{m_f}}$$

$$r_{m_1} = 10^9 \, e^{-\frac{12,500}{1.987 T_m}} \left(1 - x_{A_1}\right) - 6.8 \times 10^{21} \, e^{\frac{-32,500}{1.987 T_{m1}}} \, x_{A_1}$$

With $T_m = \dfrac{10,065}{30.51 + \ln\left(\dfrac{x_{A_1}}{1 - x_{A_1}}\right)}$

$$r_{m_f} = 0.0818 \, \left(mol/lit \; min\right)$$

By taking $\dfrac{d}{d \, x_{A_1}}\left(\dfrac{\tau_1 + \tau_2}{C_{A_o}}\right) = 0$ one gets by trial and error

$$x_{A_1} = 0.72 \qquad\qquad r_{m_1} = 0.5 \left(\frac{mol}{lit \; min}\right)$$
$$T_{m_1} = 320K$$

The required volumes are:

For the first reactor

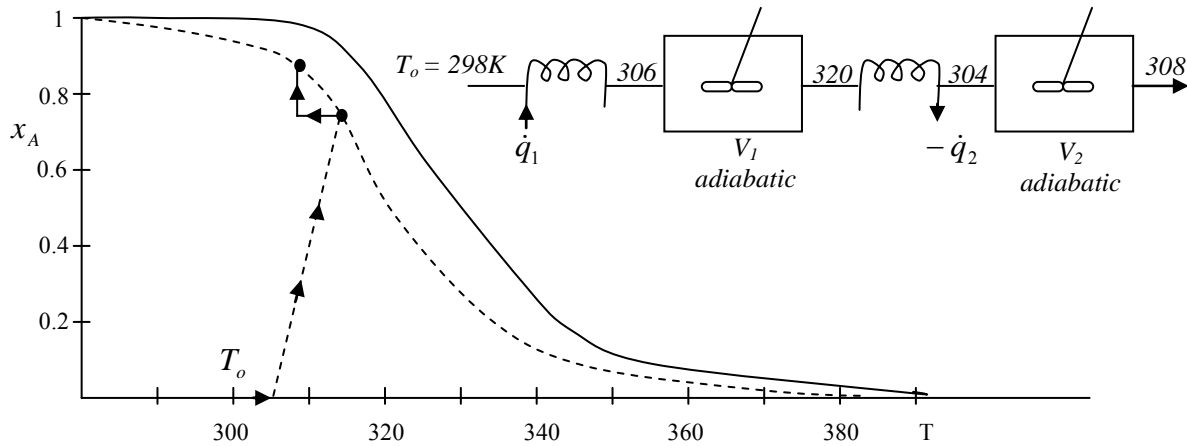$$V_1 = \frac{F_{A_o} \, x_{A_1}}{r_{m_1}} = \frac{100}{0.9} \cdot \frac{0.72}{0.5} = \underline{160 \; liters}$$

For the second reactor

$$V_2 = \frac{F_{A_o} \left(x_{A_f} - x_{A_1}\right)}{r_{m_f}} = \frac{100}{0.9} \frac{\left(0.9 - 0.72\right)}{0.0818} = \underline{244.5 \; lit}$$

Total volume $\underline{V = V_1 + V_2 = 405 \; liters}$

The graphical representation of the above system is shown below

LECTURE 7

Preheat the feed from 298K to 305.6K ≈ 306K

$$\dot{q}_1 = Q\,\rho\,\underline{C}_p\,(305.6-298) = \frac{100}{0.9\times 2}\times 2000\,(305.6-298) = 8.44\times 10^5\left(\frac{cal}{min}\right)$$

Cool the stream from 1st reactor to 304.4K ≈ 304

$$-\dot{q}_2 = Q\,\rho\,C_p\,\Delta T = \frac{700}{0.9\times 2}\times 2000\,(320-304.4) = 1.73\times 10^6\left(\frac{cal}{min}\right)$$

It should be noted that the above calculations can be made easier with a little analytical work to obtain an expression for the maximum rate as a function of conversion. This is done by substituting the T_m values

$$T_m = \frac{(E_2-E_1)/R}{\ln\left[\dfrac{k_{20}\,E_2}{k_{10}\,E_1}\dfrac{x_A}{1-x_A}\right]}$$

for temperature T in the rate expression

$$\left(-R_A\right)_m = r_m = k_{10}e^{-E_1/R\,T_m}\,C_{A_o}\left(1-x_A\right) - k_{20}\,e^{-E_2/R\,T_m}\,C_{A_o}\,x_A$$

If we recall that $e^{a\ln b} = e^{\ln b^a} = b^a$

We get:

$$r_m = \left(k_{10}\left(\frac{k_{10}\,E_1}{k_{20}\,E_2}\right)^{\frac{E_1}{E_2-E_1}} - k_{20}\left(\frac{k_{10}\,E_1}{k_{20}\,E_2}\right)^{\frac{E_2}{E_2-E_1}}\right)C_{A_o}\,\frac{\left(1-x_A\right)^{\frac{E_2}{E_2-E_1}}}{x_A^{\frac{E_1}{(E_2-E_1)}}}$$

25

In our particular example the above expression reduces to:

$$r_m = 3.22 \left(1 - x_A\right)^{1.625} x_A^{-0.625}$$

Another variation on the above problem is to have two equal size CSTRs in series. For maximum production rate then under conditions $\tau_1 = \tau_2$ we must find x_{A_1} that satisfies

$$\frac{x_{A_1}}{r_{m_1}} = \frac{x_{A_2} - x_{A_1}}{r_{m_2}}$$

This happens at $x_{A_1} = 0.75$ so $V_1 = V_2 = 205$ liters

In summary the following types of problems may be encountered:

I.   Given $V, Q, T_o, T_{m_o}, Q_m, \tilde{\beta}, \dot{q}$, find x_A and T. This is equivalent to determining the performance of an existing reactor or of one that is contemplated by design engineers. In this case species mass balance and energy balance are solved simultaneously.

II.   Given $T_o, T_{m_o}, \tilde{\beta}, F_R$ and x_A determine the required V and desired operating T.

This is the typical design problem.

III.   Production rate is specified. Exit conversion and temperature can be selected together with V in order to optimize some profit function.

This is also a typical design problem.

We have not touched here on <u>two</u> very important problems.

-       transients in a CSTR
-       control of a CSTR around an unstable steady state.

Extension to Multiple Reactions

One should keep in mind that yields and selectivities can be affected dramatically by the choice of operating temperature when activation energies of various reactions are different.

The problems consist of

a.   Finding the optimum temperature for a desired product distribution irrespective of space time requirements.

b.   Finding an optimal temperature for a given reactor (given τ) which maximizes the production of the desired product.

The equations to be solved are given R independent reactions among S species

$$\sum_{j=1}^{s} v_{ij} \, A_j = 0 \qquad\qquad\qquad i = 1, 2, \ldots\ldots R$$

$$F_{jo} - F_j + \sum v_{ij} \, r_i \, V = 0 \qquad\qquad\qquad\qquad (1)$$

$$j = 1, 2, \ldots\ldots R$$

or

$$\sum_{i=1}^{R} v_{ij} \left[\acute{X}_i - r_i \, V \right] = 0$$

$$\boxed{\acute{X}_1 - r_i \, V = 0 \quad \text{for} \quad i = 1, 2, 3 \ldots R} \qquad\qquad (1a)$$

and

$$\sum_{j=1}^{s} \left(F_{jo} \, \tilde{H}_{jo} - F_j \, \tilde{H}_j \right) + \dot{q} = 0 \;(2)$$

Equation (1) represents independent R species balances and eq (2) is the energy balance based on assumptions of

a)   no work other than flow work
b)   negligible changes in potential and kinetic energy

If we assume further c) ideal gas behavior d) ideal mixture

LECTURE 7

$$\sum_{j=1}^{s} F_{jo} \left(\Delta \underset{\sim}{H}_{fj} + \int_{T^0}^{T} \underset{\sim}{C}_{p_j} dT \right) - \sum_{j=1}^{s} F_{j} \left(\Delta \underset{\sim}{H}_{fj} + \int_{T^0}^{T} \underset{\sim}{C}_{p_j} dT \right) + \acute{q} = 0$$

$$\sum_{j=1}^{s} F_{jo} \int_{T}^{T} \underset{\sim}{C}_{pj} dT - \sum_{j=1}^{s} \sum_{i=1}^{R} v_{ij} \left(\Delta \underset{\sim}{H}_{fj} + \int_{T^o}^{T} \underset{\sim}{C}_{p_j} dT \right) r_i V + \acute{q} = 0$$

$$\sum_{j=1}^{s} F_{jo} \int_{T}^{T} \underset{\sim}{C}_{pj} dT - \sum_{i=1}^{R} v_{ij} \left(\Delta \underset{\sim}{H}_{r_{Ti}} \right) r_i V + \acute{q} = 0 \qquad (2a)$$

Where $\Delta \underset{\sim}{H}_{r_{Ti}}$ is the heat of reaction of reaction i at temperature T.

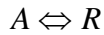If we further assume e) constant heats of reaction and f) constant mean specific heats we get

---

$$\rho \underline{C}_p \, Q \left(T_o - T \right) + \sum_{i=1}^{R} \left(-\Delta H_{r_i} \right) r_i V + \acute{q} = 0 \qquad (2b)$$

PROBLEMS

A.   Consider the following simple reaction

$$A \Leftrightarrow R$$

The reaction rate is given by:

$$\pi = k_1 \, C_A - k_2 \, C_R \quad (mol/lit \ s)$$

$$k_1 = \exp\left(7 - \frac{83,000}{RT}\right) \times 10^3 \ (s^{-1})$$

$$k_2 = \exp\left(18 - \frac{167,400}{RT}\right) \times 10^3 \ (s^{-1})$$

Note: the activation energies are given in (J/mol) use the value of the gas constant accordingly.

The heat of reaction is:

$$\Delta H_r = -80,000 \ (J/mol)$$

Specific heat of the reaction mixture is:

$$\underset{\sim}{C}_p = 40 \ (J/mol \ K)$$

Assume that these are constant.

1.   The above reaction occurs in the liquid phase. The pressure is high enough so that the liquid will not volatize in the permissible temperature operating range which is: 300 to 900K.

The feed conditions are:

$$Q_o = 100 \ (lit/s); \ C_{Ao} = 1 \ (mol/lit); T_o = 300K$$

You have a $V = 100$ liters CSTR reactor. How would you operate this CSTR in order to maximize the production rate of R?.

a)   What is $F_R(mol/s)$ -maximum production rate?
b)   What are $x_A \ \& \ T$ -operating conditions?
c)   What is the heat duty for the system?
d)   Sketch your system and location and heat duty of all heat exchangers, if any.

NONISOTHERMAL OPERATION OF

IDEAL REACTORS

Plug Flow Reactor

(CHE 471)

M.P. Dudukovic

Chemical Reaction Engineering Laboratory

(CREL),

Washington University, St. Louis, MO

NONISOTHERMAL OPERATION OF IDEAL REACTORS
Plug Flow Reactor
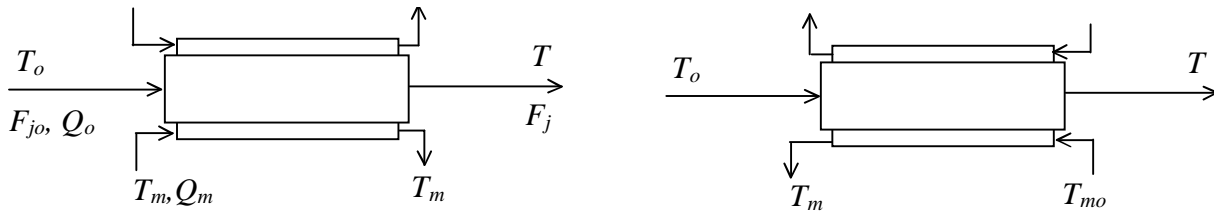
Assumptions:

1. Homogeneous System
2. Single Reaction
3. Steady State

Two types of problems:

1. Given desired production rate, conversion and kinetics and other parameters, determine the required reactor size, heat duty and temperature profile.
2. Given reactor size, kinetics, etc., determine the composition of the exit stream.

Let us consider a single reaction

$$\sum_{j=1}^{s} \upsilon_j A_j = 0 \tag{1}$$

with the rate given by

$$r = k_{10} e^{-E_1/RT} \prod_{j=1}^{s} C_j^{\alpha_j} - k_{20} e^{-E_2/RT} \prod_{j=1}^{s} C_j^{\beta_j} \tag{2}$$

with

$$C_j = C_{Ao} \frac{M_{j/A} - \dfrac{\upsilon_j}{\upsilon_A} x_A}{1 + \varepsilon_A x_A} \frac{T_o P}{T P_o} \tag{3}$$

The mass balance in the reactor for species j can be written as:

$$\frac{dF_j}{dV} = \upsilon_j r \tag{4}$$

$$v = 0 \quad F_j = F_{jo} \tag{4a}$$

or

$$F_{Ao} \frac{dx_A}{dV} = (-v_A) r = -R_A \tag{4'}$$

$$V = 0 \quad x_A = 0 \tag{4'a}$$

The energy balance based on (a) negligible changes in potential and kinetic energy and (b) no work other than flow work is

$$-\frac{d}{dV}\left(\sum_{j=1}^{s} F_j \tilde{H}_j \right) + \acute{q}_v = 0 \tag{5}$$

$$V = 0 \quad F_j \mathring{H}_1 = F_{jo} \mathring{H}_{jo} \tag{5a}$$

Based on further assumptions of (c) ideal mixtures and (d) ideal gases one gets:

$$-\sum_{j=1}^{s} F_j \underset{\sim}{C}_{P_j} \frac{dT}{dV} - \sum_{j=1}^{s} H_{\underset{\sim}{j}} \frac{dF_j}{dV} + \acute{q}_v = 0 \tag{6a}$$

Using the idea of (e) mean specific heats which are constant and (f) constant heat of reaction, one gets

$$-(Q\rho)\underline{C}_p \frac{dT}{dV} + (-\Delta H_r) r + \acute{q}_v = 0 \tag{6}$$

$Q\rho = \overset{Y}{m}_{tot}$ is the mass flow rate which is constant

$\acute{q}_v \left(\dfrac{J}{m^3 s} \right)$ is the rate of heat addition per unit reactor volume

The simplest constitutive relationship for the rate of heat exchange is:

$$\acute{q}_v = U a_v (T_m - T) \tag{7}$$

$a_v \left(\dfrac{m^2}{m^3} \right)$ - area for heat transfer per unit reactor volume

The equations to be solved simultaneously are:

$$F_{ao} \frac{dx_A}{dV} + \upsilon_A r = 0 \tag{A}$$

$$Q\rho \underline{C}_{P_m} \frac{dT}{dV} - (-\Delta H_r)_r + \overbrace{U_{av}(T - T_m)}^{-\dot{\phi}_v} = 0 \tag{B}$$

$$\mp Q_m \rho_m \underline{C}_{P_m} \frac{dT_m}{dV} - \overbrace{U_{av}(T_m - T)}^{-\dot{\phi}_v} = 0 \tag{C}$$

$V = 0$; $x_A = 0$; $T = T_{o,}$, ($T_m = T_{mo}$ for cocurrent flow

$V = V$; ($T_m = T_{mo}$ for countercurrent flow) $\tag{D}$

and

$$G\frac{du}{dz} + \frac{dp}{dz} + F = 0 \tag{E}$$

$G = \rho u$ - mass velocity

$P = $ pressure

$z = \dfrac{V}{A}$ - axial distance

$u = \dfrac{Q}{A}$ - velocity

A – cross sectional reactor area

F – frictional losses

Equation (E) is the momentum balance. However this equation is usually solved separately and a mean pressure is selected for evaluation of gas concentrations in eq (3).

For gases the use of mass fractions, w_j, and extent per unit mass, ξ'' is recommended. (See lecture 1).

The equations can then be written as:

$$G\frac{d\xi''}{dz} = r \tag{8}$$

$$G\frac{dT}{dz} = \beta'' r + q_v'' \tag{9}$$

$$z = 0 \quad \xi'' = 0, \quad T = T_o \tag{10}$$

3

$$\beta'' = \frac{-\Delta H_r}{\underline{C}_p} \quad ; \quad q''_v = \frac{q_v}{\underline{C}_p} \tag{11}$$

where the rate is expressed by:

$$r = k_{10}e^{-E_1/RT} \prod_{j=1}^{s} C_{jo}^{\alpha_j}\left(1+\upsilon_j\frac{\overset{\lll}{m}_{tot}}{F_{jo}}\xi^{\copyright\copyright}\right)^{\alpha_j}\left[\frac{T_oP}{TP_o}\frac{1}{1+\sum_{j=1}^{s}\upsilon_j M_{av_o}\xi''}\right]^{\sum_{j=1}^{s}\upsilon_j}$$

$$-k_{20}e^{-E_2/RT} \prod_{j=1}^{s} C_{jo}^{\beta_j}\left(1+\upsilon_j\frac{\acute{m}_{bot}}{F_{jo}}\xi''\right)^{\beta_j}\left[\frac{T_oP}{TP_o}\frac{1}{1+\left(\sum y\right)M_{av_o}\xi'''}\right]^{\sum\upsilon_j} \tag{12}$$

M_{av_o} - average molecular weight at feed conditions

$\overset{\circ}{m}_{tot} = GA$ − mass flow rate

$$\frac{\overset{\lll}{m}_{tot}}{F_{jo}} = \frac{M_j}{w_{jo}}$$

w_{jo} − mass faction of j in the feed.

For liquids one can write

$$\frac{d\xi}{d\tau} = r \tag{13}$$

$$\frac{dT}{d\tau} = \tilde{\beta}r + \tilde{q}_v \tag{14}$$

$$\tau = 0 \quad ; \quad \xi = 0 \quad ; \quad T = T_o \tag{15}$$

$$\tilde{\beta} = \frac{-\Delta H_r}{\rho\underline{C}_p} \quad ; \quad \tilde{q}_v = \frac{q_v}{\rho\underline{C}_p} = \frac{Q''_v}{\rho} \tag{16}$$

where the rate is given by

$$r = k_{10}e^{-E_1/RT} \prod_{j=1}^{s}\left(C_{jo}+\upsilon_j\xi\right)^{\alpha_j} - k_{20}e^{-E_2/RT} \prod_{j=1}^{s}\left(C_{jo}+\upsilon_j\xi\right)^{\beta_j} \tag{17}$$

$$\tau = \frac{z}{u} = \frac{V}{Q} \text{ - residence time along the reactor.}$$

From eqs (8) and (9) or (13) & (14) we can always get the following relationship between temperature and extent

$$T = T_o + \beta'' \xi'' + \frac{1}{G}\int_o^z q_v'' dz \tag{18a}$$

or

$$T = T_o + \tilde{\beta}\xi + \sum_o^\tau \tilde{q}_v d\tau \tag{18b}$$

For <u>adiabatic operation</u> ($q_v'' = 0, \tilde{q}_v = 0$) this yields the equation of the adiabatic line, <u>i.e</u> extent and temperature satisfy the relationship below at any and every point of the reactor

$$T = T_o + \beta'' \xi'' \tag{19a}$$

$$T = T_o + \tilde{\beta}\xi \tag{19b}$$

The maximum fractional adiabatic temperature rise is given by the Prater number just like in the case of a CSTR.

$$\frac{\Delta T_{ad\,max}}{T_o} = \beta = \frac{(-\Delta H_r)C_{Ao}}{(-\upsilon_A)T_o\rho \underline{C}_p} \tag{20}$$

Basic types of problems

1. <u>The temperature in the reactor is prescribed</u>

    a.   T(z) = T_o – isothermal reactor.   Integrate (8) or (13) and find extent along the reactor. From eq. (9) or (14) find the heat addition/removal requirement along the reactor and the overall heat duty for the reactor.

    b.   T(z) specified. Integrate (8) or (13) find ξ(z). Use ξ(z) and T(z) in eq (9)or (14) to get q_v (z)

2. <u>The heat addition (removal) rate is prescribed</u>

    a)   Adiabatic operation. $T = T_o + \beta'' \xi''$ or $T = T_o + \beta\xi$. Substitute into eq (8) or (13) and integrate

b)   Heat duty is prescribed. $q_v^{''}(z) \, or \, \overline{q}_v(z)$ prescribed.   Simultaneously integrate (8) or (9) or substitute

$$T = T_o + \beta^{''} \xi^{''} + \frac{1}{G} \int_o^z q_v^{''} dz \quad \text{into (8) and integrate.}$$

3. <u>Rate of heat addition (removal) controlled by another equation</u>

$$\acute{q}_v = Ua_v (T - T_m)$$

a) T_m = const.   Integrate eqs (8) and (9) or eqs (13) and (14) simultaneously.
     This is the case when reactor tubes are immersed in boiling medium or condensing medium.

b) T_m determined with T and $\xi^{''}$ by equations (A) to (E).

$$G_m \frac{dT_m}{dz} = \mp \kappa_m^{'} (T_m - T)$$

$$\kappa_m = \frac{Ua_{v_m}}{C_{p_m}} \qquad G_m = \frac{Q_m \rho_m}{A_m}$$

<u>Note:</u> With cocurrent cooling a PFR can be kept isothermal with countercurrent cooling it cannot in the case of n-th order reactions. Prove that for an exercise.
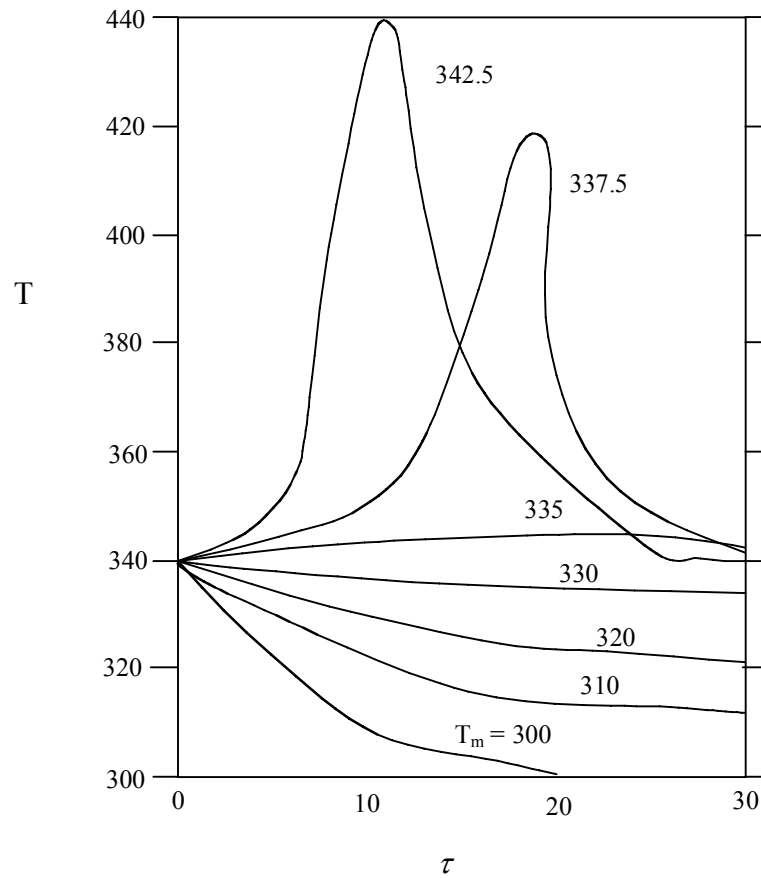
There is always a unique steady state in a PFR. Main problem with PFR's is:

hot spot formation
parametric sensitivity and temperature runaway.

Classical example of temperature runaway presented by Bilous & Amundson (AIChE J., 2, 117 (1956).

PFR cooled from the wall t constant $T_m = T_{wall.}$

A "hot spot" is formed due to a very small change in wall temperature. The system shows extreme parameter sensitivity.

Reaction runaway is the phenomenon when a small change in feed concentration, temperature, flow rate or in coolant temperature triggers a dramatic change in he temperature profile and leads to runaway reactions and explosions. Exact criteria for runaways are difficult to develop.

Approximate criteria are given on the enclosed graph..

Example 1

A reversible first order reaction (considered earlier in a CSTR) is now to be per formed in a PFR.

$$A \underset{\leftarrow}{\overset{\rightarrow}{}} R \qquad \text{(liquid phase)}$$
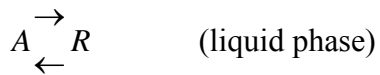
$$k_1 = 5x10^8 e^{-12,500/RT} \, (\text{min}^{-1})$$

$$k_2 = 3.4x10^{21} e^{-32,500/RT} \, (\text{min}^{-1})$$

$$\Delta H_r = -20,000 \, cal/mol \quad \Delta G_{298}^o = -2,500 \, cal/mol$$

$$\rho \underline{C}_p - 2,000 \, (cal/lit^\circ C)$$

$$C_{Ao} = 2 \, (mol/lit)$$

7

If the feed rate is Q = 100 (lit/min) and the PFR size is V = 1,500 (lit):

a)   find final conversion in an isothermal reactor operated at 0, 10, 20, 100°C

b)   determine conversion in an adiabatic reactor if the feed is at i) 0°C, ii) 20°C,

c)   if the maximum permissible temperature is 80°C determine the optimal temperature profile along the reactor necessary to maximize exit conversion.

d)   If the desired conversion is 85% find the minimum reactor volume and the desired heat removal rate along the reactor. Permissible temperature range is 0° to 100°C.

Solution

a)   For an isothermal reactor only the mass balance has to be solved

$$\tau = \frac{V}{Q_o} = C_{Ao} \int_o^{x_A} \frac{dx_A}{-r_A}$$

$$-r_A = k_1 C_A - k_2 C_R = C_{Ao}\left[k_1(1 - x_A) - k_2 x_A\right]$$

$$-r_A = k_1 C_{Ao}\left[1 - x_A - \frac{x_A(1 - x_{Ae})}{x_{Ae}}\right] \quad sin \quad ce \quad k_2 = \frac{k_1}{K} = \frac{k_1(1 - x_{Ae})}{x_{Ae}}$$

$$(-r_A) = \frac{k_1 C_{Ao}}{x_{Ae}}(x_{Ae} - x_A) \qquad x_{Ae} = \frac{K}{1 + K} = \frac{k_1}{k_1 + k_2}$$

$$(-r_A) = (k_1 + k_2)C_{Ao}(x_{Ae} - x_A)$$

$$\tau = \frac{1}{k_1 + k_2}\int_o^{x_A} \frac{dx_A}{x_{Ae} - x_A} = \frac{1}{k_1 + k_2} \ell n\left(\frac{x_{Ae}}{x_{Ae} - x_A}\right)$$

Solve for conversion

$$x_A - \left[1 - \exp(-k_1(1 + \frac{1}{K})\tau)\right]$$

$$= x_{Ae}\left[1 - \exp\left(\frac{-k_1}{x_{Ae}}\tau\right)\right] \qquad \tau = \frac{1500}{100} = 15 \text{ min}$$

We get the following results:

T	K	k_1	x_{ae}	x_a
273	1494	0.0498	0.999	0.526
283	407	0.112	0.998	0.813
293	121	0.239	0.992	0.965
303	40	0.486	0.975	0.974
313	13.5	0.943	0.931	0.931
323	5.0	0.755	0.833	0.833
333	2.0	3.149	0.662	0.662
343	0.81	5.46	0.448	0.448
353	0.35	9.17	0.262	0.262
363	0.16	15.0	0.139	0.139
373	0.08	23.8	0.071	0.071

Same as equilibrium conversion

The reactor space time is so large that above 50°C practically equilibrium conversion is obtained.

a)   The adiabatic operating line is

$$T = T_o + \tilde{\beta}_A C_{Ao} x_A$$

$$\tilde{\beta}_A = \frac{-\Delta H_{r_A}}{\rho \underline{C}_p} = \frac{20,000}{2,000} = 10 \left(\frac{lit \,^\circ C}{mol} \right)$$

$$C_{Ao} = 2 \left(\frac{mol}{lit} \right)$$

$$T = T_o + 20 \, x_A$$

Substitute this relationship into the mass balance and integrate:

$$C_{Ao} \frac{dx_A}{d\tau} = (k_1 + k_2) C_{Ao} (x_{Ae} - x_A) = k_1 C_{Ao} - (k_1 + k_2) C_{Ao} x_A$$

$$\tau = 0 \quad x_A = 0$$

$$k_1 = k_{10} e^{E_1 / R T_{ad}} = k_{10} e^{-E_1 / R(T_o + 20 x_A)}$$

$$k_2 = k_{20} e^{-E_2 / R(T_o + 20 x_A)}$$

$$x_{Ae} = \frac{K}{1 + K} = \frac{k_1}{k_1 + k_2}$$

Thus integrate numerically

$$\frac{dx_A}{d\tau} = k_{10} e^{-E_1 / R T(T_o + 20 x_A)} - \left(k_{10} e^{-E_1 / R \left(T_{o+20 x A} \right)} + k_{20} e^{-E_2 / R(T_o + 20 x_A)} \right) x_A$$

$$\tau = 0 \qquad x_A = 0$$

$$\frac{dx_A}{d\tau} = 5x10^8 e^{-\frac{12,500}{1.987(T_o+20x_A)}} - \left[5x10^8 e^{-\frac{12,500}{1.987(T_o+20x_A)}} + 3.4x10^{21} e^{-\frac{32,500}{1.987(T_o+20x_A)}}\right]x_A$$

$$\tau = 0 \quad ; \quad x_A = 0$$

Desired result is obtained at $\tau = 15$.

Alternatively we could solve by trial and error the following integral:

$$\tau = 15 = \int_o^{x_A} \frac{dx}{5x10^8 e^{-\frac{12,500}{1.987(T_o+20x)}} - \left[5x10^8 e^{-\frac{12,500}{1.987(T_o+20x)}} + 3.4x10^{21} e^{-\frac{32,500}{1.987(T_o+20x)}}\right]x}$$

We find:

  i) $T_o = 0°C = 273\ K \quad x_A = 0.78$
       $\Delta T_{adiabatic} = 15.7K = 16K \quad T = 289\ K$
  ii) $T_o = 20°C = 293\ K \quad x_A = 0.94 = x_{Ae}$
       $\Delta T_{adiabatic} = 18.8 = 19K \quad T = 292K$

c)   In order to maximize conversion at given space time we should follow the line of maximum rates.

$$T_m = \frac{(E_2 - E_1 / R)}{\ln\frac{k_{20}E_2}{k_{10}E_1} + \ln\frac{x_A}{1-x_A}} = \frac{10,065}{30.51 + \ln\left(\frac{x_A}{1-x_A}\right)}$$

Since maximum permissible temperature is 80°C (353 K) we have to preheat the feed to 33 K, cool the reactor and keep it isothermal a 353 K until the locus of maximum rate is reached and then run along the locus of maximum rates.

The intersection of the isothermal line T = 353 K and the T_m line determines up to which point the reactor has to be run isothermally.

$$T = 353 = T_m = \frac{10,065}{30.51 + \ln\left(\frac{x_A}{1-x_A}\right)}$$

$$x_A = \frac{\exp\left(\frac{10,065 - 353x30.51}{353}\right)}{1 + \exp\left(\frac{10,065 - 353x30.1}{353}\right)} = 0.119$$

$$\tau = \frac{1}{k_1 + k_2} \int_{o}^{0.119} \frac{dx}{(x_{Ae} - x_A)} = \frac{1}{(k_1 + k_2)} \ell n\left(\frac{x_{Ae}}{x_{Ae} - x_A}\right)$$

At 80˚C (353 K) from the table given earlier

$$\tau = \frac{1}{9.17(1 + \frac{1}{0.35})} \ell n\left(\frac{0.262}{0.262 - 0.119}\right) = 0.017 (\text{min})$$

The isothermal operation should occur in the very entry section of he reactor. After that the T_m line should be followed.

$$\frac{dx_A}{d\tau} = 5x10^8 e^{-\frac{12,500}{1.987 T_m}} (1 - x_A) - 3.42x10^{21} e^{-\frac{32,500}{1.987 T_m}} x_A$$

$$T_m = \frac{10,065}{30.51 + \ell n\left(\frac{x_A}{1 - x_A}\right)}$$

$$\tau = 0.017 \qquad x_A = 0.119$$

Desired result at $\tau = 15$

$$x_{A=0.988} \qquad T_{exit} = 288K$$

Really one should preheat only to adiabatic line. Adiabatic line should end at T = 353 K, $x_A = 0.119$. Hence, the fluid must be preheated up to $T_o = T - \tilde{\beta}_A C_{Ao} x_A = 353 - 20x0.119 = 350K$

The graphical representation of parts (a-c) has the following form:
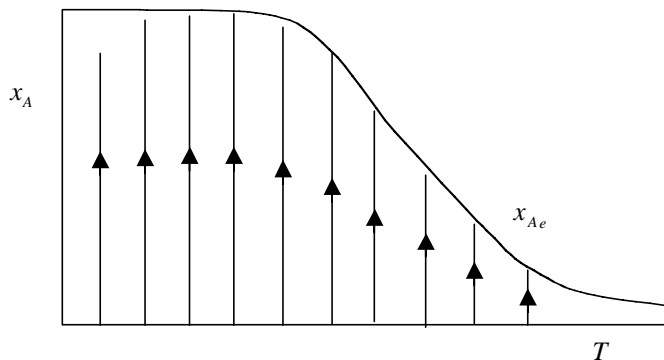
a.   Isothermal. Solid lines are operating lines for $\tau = 15$ min
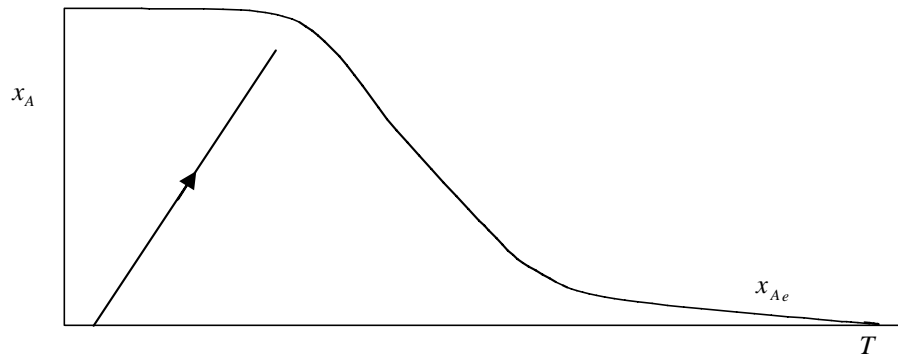
b.   Adiabatic. Adiabatic line with $\tau = 15$
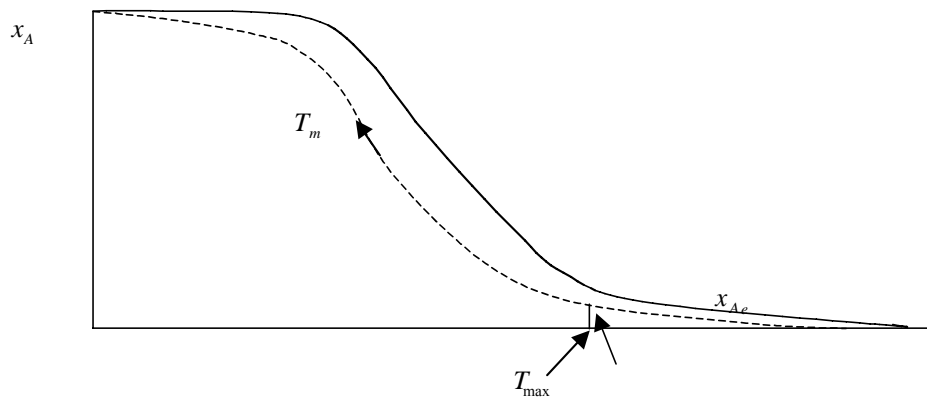
c.   Operating along the locus of maximum rates

d)   Permissible temperature range is 0°C to 100°C. We want minimum reactor size for $x_A = 0.85$.
        Preheat to 100°C, run along the locus of maximum rates

$$\tau = \int\limits_{o}^{x_A = 0.85} \frac{dx}{5x10^8 e^{-\frac{12,500}{1.987 T_m}} \left[5x10^8 e^{-\frac{12,500}{1.987 T_m}} + 3.4x10^{21} e^{-\frac{32,500}{1.987 T_m}} \right] x}$$

with $T_m = \dfrac{10,065}{30.51 + \ell n\left(\dfrac{x_A}{1 - x_A}\right)}$

$\tau = 1.8\, min$ Thus with Q = 100 lit/min we need only V = 160 *liters*

The desired temperature profile along the reactor is presented in the enclosed graph. The heat removal
per unit volume is

$$-\frac{\acute{\phi}}{Q} = \rho \underline{C}_p (T_o - T) + (-\Delta H_r) C_{Ao} x_A$$
$$= 2,000(100 - T) + (20,000 x 2) x_A$$

This curve is also presented in the figure. The total heat density is:

$$-\left(\frac{\acute{q}}{Q}\right)_{tot} = 2,000(100 - 70) + 40,000 x 0.85$$
$$= 1.56 x 10^5 (cal/lit)$$

With Q = 100 lit/min $-\acute{q}_{tot} = 1.56 x 10^7 (cal/min)$

For comparison, if cooling failed and reactor ran adiabatically with $T_o = 100°C$ one would get

$$x_{A_{ad}} = 0.068, T_{exit} = 126°C$$

The adiabatic temperature profile is shown also on the enclosed figure.

Extension to Multiple Reactions

$$\sum_{j=1}^{s} \upsilon_{ij} A_j = 0 \qquad i = 1,2,...R \tag{1}$$

$$-\frac{dF_j}{dV} + \sum_{i=1}^{R} \upsilon_{ij} r_i = 0 \qquad j = 1,2,...R \tag{2}$$

or

$$-\sum_{i=1}^{R} \upsilon_{ij} \frac{d\breve{X}_i}{dV} + \sum_{i=1}^{R} \upsilon_{ij} r_i = 0$$

$$-\frac{d\acute{X}_i}{dV} + r_i = 0 \tag{2a}$$

$$-\frac{d(F_j \tilde{H}_j)}{dV} + \acute{q}_v = 0 \tag{3}$$

$$V = 0 \quad ; \quad F_j = F_{jo}(\breve{X}_i = \breve{X}_i^o) \quad ; \quad \tilde{H}_j = \tilde{H}_{jo}$$

With the usual assumptions made about the energy balance (see the lecture on CSTR) one gets:

$$-\sum_{j=1}^{s} F_{jo} \underset{\sim}{C}_{p_j} \frac{dT}{dV} + \sum_{i=1}^{R} \left(-\Delta H_{r_{Ti}}\right)_i + \overset{\text{ó}}{q}_v = 0 \tag{4}$$

The equations to be solved for a set of multiple reactions are:

$$-\frac{d\overset{\text{Ў}}{X}_i}{dV} + r_i = 0 \qquad i = 1,2...R \tag{A}$$

$$-\rho \underline{C}_p Q \frac{dT}{dV} + \sum_{i=1}^{R} \left(-\Delta H_{r_i}\right)_i + \overset{\text{ó}}{q}_v = 0 \tag{B}$$
$$V = 0 \quad ; \quad \overset{\text{Ў}}{X}_i = \overset{\text{Ў}}{X}_{io} \quad T = T_o$$
$$\rho Q = const$$

$$r_i = k_{i10}e^{-E_{1i}/RT} \prod_{j=1}^{s} C_j^{\alpha_{ij}} - k_{i20}e^{-E_{2i}RT} \prod_{j=1}^{s} C_j^{\beta_{ij}} \tag{C}$$

with

$$C_j = C_{jo} \frac{\rho T_o}{\rho_o T} \left(\frac{1 + \dfrac{\sum\limits_{i=1}^{R} \upsilon_{ij} \overset{\text{ó}}{X}_i}{F_{jo}}}{1 + \dfrac{\sum\limits_{i=1}^{R}\sum\limits_{j=1}^{s} \upsilon_{ij} \overset{\text{ó}}{X}_i}{F_{bot\,o}}} \right) \tag{D}$$

The constitutive relationship for $\overset{\text{Ў}}{q}_v$ is:

$$\overset{\text{Ў}}{q}_v = U_{a_v}\left(T_m - T\right)$$

a) T_m= const

b) T_m is governed by another D.E.

$$\mp \rho_m Q_m \underline{C}_{P_m} \frac{dT_m}{dV} - \overset{\text{ó}}{q}_v = 0 \tag{E}$$

V=0　　$T_m = T_{mo}$ (cocurrent flow)

V = V　　　　$T_m = T_{mo}$ (countercurrent flow)

Problems

Consider the reaction introduced in he last lecture $A \underset{\leftarrow}{\overset{\rightarrow}{}} R$

$R = k_1 C_A - k_2 C_R$ (mol/lit s)

$$k_1 = \exp\left(7 - \frac{83,700}{RT}\right) x 10^3 \ (s^{-1})$$

$$k_2 \exp\left(18 - \frac{167,400}{RT}\right) \times 10^3 \ (s^{-1})$$

$$\Delta H_r = -80,000 \ (J/mol)$$
$$\underset{\sim}{C}_p = 40(J/mol \ K)$$

Activation energies given in joules.

1. The above reaction occurs in liquid phase! Permissible temperature range of operation is 300 <T < 900 K.

    Feed conditions:

    $Q_o = 100$ (lit/s) ; $T_o = 300$ K   ; $C_{Ao} = 1$(mol/lit)

    You have a V = 100 liters PFR. How would you operate this reactor if the only objective is to maximize the production rate of R.

    a) What is maximum F_R.

    b) What are final x_A and ΔT.

    c) What is the profile of heat addition or removal for every 10% of reactor volume.

    d) What is the overall heat duty for the reactor and any heat exchangers preceding it.

    e) Sketch your system.

2. The above reaction occurs in gas phase.

    The gas feed ate is

    $Q_o = 100(lit/s) \ at \ T_o = 300K, P_o = 24.6 \ atm$

    The feed is 50%A, 50% inerts. Permissible temperature range is 250< T < 900 K. Pressure is constant in the reactor. Gases start to condense below 250 K. Desired conversion is 85%.

15

    a)   What reactor volume is needed if you operate along the locus of maximum rates?

    b)   What is the distribution of heat duty along the reactor?

    c)   What is the production rate of R?

3.   For the above problem what would F_R and x_A be if you had a reactor (PFR) of $V = 100$ liters available?

4.   Suppose that the reactor can only be operated adiabatically and the desired conversion is 85%. Minimize the required reactor size.

    a)   What reactor type do you recommend?

    b)   What feed temperature would you use?

    c)   What is the heat duty?

WALL COOLED TUBULAR REACTORS: AVOIDANCE OF HOT SPOTS

(CHE 471)

M.P. Dudukovic

Chemical Reaction Engineering Laboratory (CREL),

Washington University, St. Louis, MO

WALL COOLED TUBULAR REACTORS: AVOIDANCE OF HOT SPOTS

The pioneering work of Bilous and Amundsen (AIChE J. 2, 117, 1956) showed that a plug flow reactor (PFR) cooled from the wall can exhibit extreme parametric sensitivity to small changes in the wall temperature or heat transfer parameters. Their observation is sketched in Figure 1 below:

Wall Temperature T_w

1	–	300 $^\circ C$
2	–	320 $^\circ C$
3	–	330 $^\circ C$
4	–	335 $^\circ C$
5	–	337.5 $^\circ C$
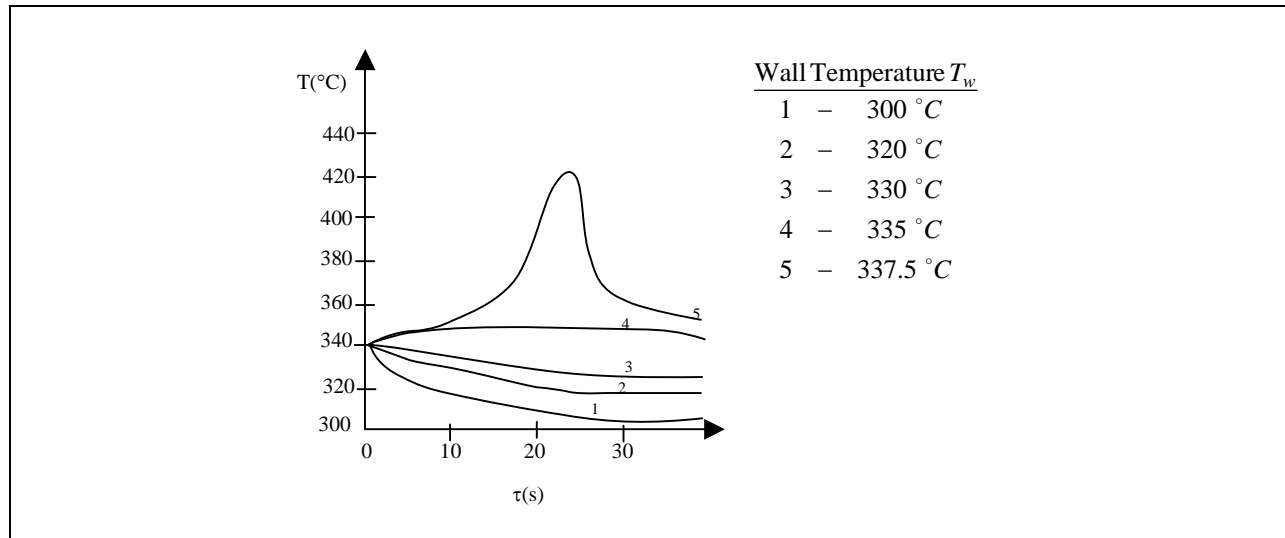
FIGURE 1:   Temperature Profiles in a Wall Cooled Tubular Reactor as a Function of Wall Temperature

Clearly a small variation in the wall temperature of 2.5 °C (from 335˚C to 337.5 °C) caused an 80˚C local rise in reactor temperature! This 'hot spot' generation can lead to reactor runaway for many reasons. Undesirable reactions of high activation energy can take off at this elevated temperature, vapor formation can cause increased pressure, rate of reaction may reach extreme values, etc. Therefore, it is imperative to operate the wall cooled tubular reactor in such a manner that it does not exhibit such extreme parametric sensitivity and, hence, is not prone to runaway.

To identify the parameter space for safe operation one starts with the mass and energy balance for the reactor. Assuming for simplicity, constant volumetric flow rate, Q = const., and a single simple irreversible reaction, A $\rightarrow$ products, the governing equations are:

Mass balance on species A:

$$\frac{dx_A}{d\tau} = \frac{\left(-R_A\right)}{C_{Ao}} \tag{1}$$

Energy balance (assuming constant average physical properties and constant heat of reaction):

$$\rho \, C_p \frac{dT}{d\tau} = \left(-\Delta H_{r_A}\right)\left(-R_A\right) - Ua_v\left(T - T_w\right)$$

(2)

The initial conditions are:

$$\tau = 0 \quad x_A = 0, \quad T = T_o$$

(2a)

In the above equations:

$\tau = \dfrac{V}{Q}(\text{min})$ is the space time measured from the reactor entrance as reactor internal volume V is also measured from the entrance.

$C_{Ao}\left(\dfrac{mol}{m^3}\right)$ =   molar feed concentration of A

$\rho\left(kg/m^3\right)$ =   fluid density

$C_p\left(J/kg\,^\circ K\right)$ =   mean specific heat of the reaction fluid

$\Delta H_{r_A}\left(\dfrac{J}{mol\;A}\right)$ =   heat of reaction per mole of A

$-R_A\left(\dfrac{mol\;A}{m^3\;min}\right)$ =   rate of reaction of A

T(°K)   =   temperature in kelvin

x$_A$ =   conversion of A

$U\left(\dfrac{J}{m^2K\;min}\right)$ =   overall heat transfer coefficient

$a_v\left(m^2/m^3\right) = \dfrac{4}{d_t}$ =   area for heat transfer per unit internal reactor volume

T$_w$ (°K)   =   coolant (wall) temperature

T$_o$ (°K)   =   inlet feed temperature

d$_t$ (m)   =   tube (reactor) diameter

To simplify the algebra, but without loss of generality of the result to be derived, we will take T$_o$= T$_w$ thus assuming the inlet and wall temperature to be the same.

We can now divide eq (2) by eq (1) and rearrange the result to get:

$$\frac{dT}{dx_A} = \frac{-\Delta H_{r_A}\,C_{Ao}}{\rho\,C_p} - \frac{4U\left(T - T_o\right)}{d_t\rho C_p\left(-R_A\right)/C_{Ao}}$$

(3)

2

Let us define the characteristic reaction time based on the value of the reaction rate at the feed conditions of concentration and temperature:

$$\tau_R = \frac{C_{Ao}}{(-R_A)_o} = \frac{C_{Ao}}{k_o e^{-E/RT_o} C_{Ao}{}^n} \tag{4}$$

Here we have assumed for simplicity an n-th order irreversible reaction and $(-R_A)_o$ means that we evaluate the rate at feed conditions of concentrations and temperature.
We also have a characteristic heat transfer time:

$$\tau_h = \frac{d_t \rho C_p}{4U} \tag{5}$$

Based on these, two dimensionless groups arise naturally:

$$\kappa = N = \frac{\tau_R}{\tau_h} = \frac{4U\, C_{Ao}}{(-R_A)_o d_t \rho C_p} \tag{6}$$

and

$$\beta = \frac{(-\Delta H_{r_A}) C_{Ao}}{\rho\, C_p T_o} \tag{7}$$

Equation (3) now becomes (recall we assumed $T_o = T_w$)

$$\frac{dT}{dx_A} = \beta T_o - \kappa \frac{T - T_o}{(-R_A)/(-R_A)_o} \tag{8}$$

This last expression contains the dimensionless rate of reaction, $(-R_A)/(-R_A)_o$, which for an n-th order irreversible reaction can be written as:

$$\frac{(-R_A)}{(-R_A)_o} = \frac{k_o e^{-E/RT} C_A^n}{k_o e^{-E/RT_o} C_{Ao}{}^n} = e^{\frac{E}{RT_o}\left(1 - \frac{T_o}{T}\right)} (1 - x_A)^n \tag{9}$$

Dimensionless activation energy is:

$$\gamma = \frac{E}{RT_o} \tag{10}$$

and dimensionless temperature is conveniently defined by:

$$\theta = \gamma \frac{T - T_o}{T_o} \tag{11}$$

Upon substitution of eqs (9), (10), (11) into equation (8) we get:

$$\frac{d\theta}{dx_A} = \beta\gamma - \frac{\kappa\theta}{e^{\theta/(1+\theta/\gamma)}(1-x_A)^n} \tag{12}$$

The product $\beta\gamma$ in the literature is often denoted by δ or S:

$$S = \delta = \beta\gamma \tag{13}$$

We can rewrite eq (12) as:

$$\frac{d\theta}{dx_A} = \delta e^{-\theta/(1+\theta/\gamma)}(1-x_A)^{-n}\left[e^{\theta/(1+\theta/\gamma)}(1-x_A)^n - \frac{\kappa}{\delta}\theta\right] \tag{14}$$

Since the term on the right hand side of eq (14) that multiplies the term in the brackets is always positive the sign of the derivative of the dimensionless temperature with respect to conversion, i.e sgn $\frac{d\theta}{dx_A}$, depends on the terms in the brackets in eq (14). By taking the coolant temperature T_c to be equal to the feed temperature T_o, we have assured that $\frac{d\theta}{dx_A} > 0$ and temperature rises with conversion. This is obvious by observing and plotting the terms in the brackets in eq (14). Physically this tells us that if we try to cool an exothermic reaction with the coolant at feed temperature, unless the characteristic heat transfer time is infinitesimal in comparison to characteristic reaction time, i.e $\kappa \to \infty$, or stated differently the heat removal rate is infinitely faster than the heat generation rate by reaction at the feed (wall) temperature, then the reactor temperature must rise with conversion. We can allow for this but we want to know what values of parameters δ, κ, γ will keep that temperature rise within safe limits.

We can think of the first exponential term in the brackets of eq (14) as the heat generation term by reaction and the second as the heat removal rate. Indeed heat generation term has an Arrhenius dependence on temperature, heat removal rate is linear in temperature. Now the heat generation term is difficult to plot as a function of dimensionless temperature θ because of the presence of the $(1-x_A)^n$ conversion dependent term. We would need to integrate eq (14), save values of x_A vs θ and then we could plot the terms in brackets of eq (14) against θ. However, since we are interested in preventing excessive maximum temperatures in the reactor, we can take a conservative approach by assuming the worst possible scenario. In the n-th order reaction $(n > 0)$ the rate of heat generation is being slowed down as conversion increases with θ as the $(1-x_A)^n$ term becomes smaller and smaller at increased conversion. The worst possible scenario is then if the heat generation rate (and hence the rate of temperature rise) is not affected by increased conversion. This is the case of zeroth order reaction.

For a conservative approach assume $n = 0$ and now consider the term in the brackets of eq (14)

$$F(\theta) = e^{\theta/(1+\theta/\gamma)} - \frac{\kappa}{\delta}\theta = y_1(\theta) - y_2(\theta) \tag{15}$$

Clearly, as $\theta = 0$, $y_1(0) = 1$; and as $\theta \to \infty$, $y_1 \to e^{\gamma}$ and y_1 is bounded. At the same time, as $\theta = 0$, $y_2(0) = 0$; and as $\theta \to \infty$, y_2 is unbounded. Thus, $y_1(\theta)$ is a sigmoidal (S-shape) curve and $y_2(\theta)$ is a straight line through the origin as shown in Figure 2.

Depending on the value of the ratio of the two dimensionless groups κ/δ the three scenarios depicted in Figure 2 may occur.
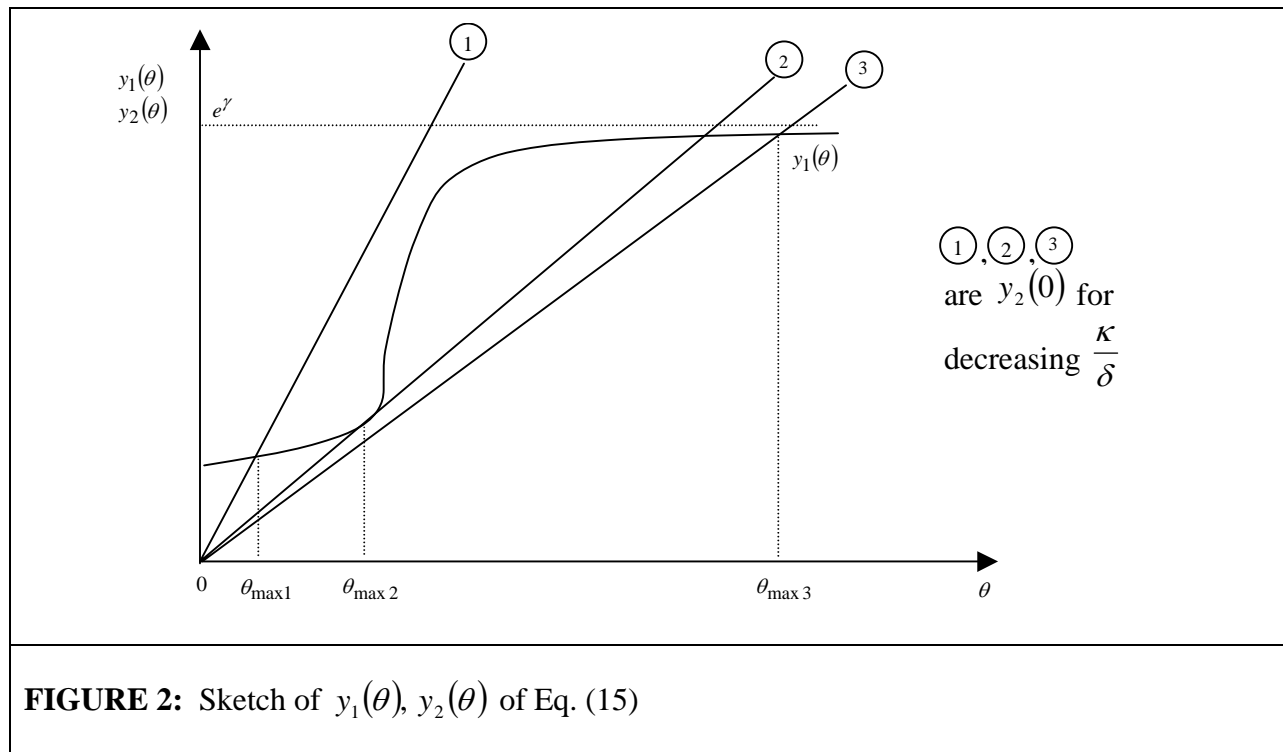
FIGURE 2: Sketch of $y_1(\theta), y_2(\theta)$ of Eq. (15)

The three straight lines in Figure 2 represent $y_2(\theta)$ at three different values of the parameter κ/δ. Please, recall that at $\kappa/\delta \to \infty$ our $y_2(\theta)$ would be a vertical line guaranteeing $\theta = 0$, i.e $T = T_o = T_w$. For the three scenarios depicted above

$$\left(\frac{\kappa}{\delta}\right)_1 > \left(\frac{\kappa}{\delta}\right)_2 > \left(\frac{\kappa}{\delta}\right)_3 \tag{16}$$

and the rate of cooling decreases as we go from case 1 to case 3. Also remember that the value of θ at which $y_1(\theta) = y_2(\theta)$ signifies $F(\theta) = 0$ i.e. $\dfrac{d\theta}{dx_A} = 0$ and yields the maximum temperature that is observed in the reactor at such conditions. So, in case of rapid heat removal rate (Case 1) the maximum temperature θ_{max1} is relatively small and of no concern. At the

certain lower value of heat transfer rate than in case 1, $y_2(\theta)$ not only intersects but is a tangent of $y_1(\theta)$ (Case 2). In this case the maximum temperature $\theta_{max\,2}$ is still tolerable but any further, even very small, decrease in κ/δ would lead to an excessive maximum temperature as depicted in Case 3 where clearly $\theta_{max\,3}$ is a hot spot to be avoided.

This tells us that in order to prevent a hot spot we must have:

$$y_1(\theta) = y_2(\theta) \qquad\qquad \text{which yields } \theta_{max} \qquad\qquad (17a)$$

and

$$\left. \frac{dy_1}{d\theta} \right|_{\theta_{max}} \leq \left. \frac{dy_2}{d\theta} \right|_{\theta_{max}} \qquad\qquad \text{for avoiding the hot spot} \qquad\qquad (17b)$$

This means that at the maximum temperature, θ_{max}, the slope of the heat generation line, $y_1(\theta)$, must be less than the slope of the heat removal line, $y_2(\theta)$. The condition at which the slopes are equal corresponds to using the equality sign in eq (17b) and is illustrated by line 2 in Figure 2. This defines the maximum allowable maximum temperature $\theta_{max\,2}$. Beyond this point excessive hot spots may arise.

We now apply eq (17a) and (17b) to eq (15) to get

$$e^{\theta/(1+\theta/\gamma)} = \frac{\kappa}{\delta}\theta \qquad\qquad (18a)$$

and

$$\frac{1}{\left(1+\dfrac{\theta}{\delta}\right)^2} e^{\theta/(1+\theta/\gamma)} \leq \frac{\kappa}{\delta} \qquad\qquad (18b)$$

By eliminating $e^{\theta/(1+\theta/\gamma)}$ in equation (18b) in terms of $\dfrac{\kappa}{\delta}\theta$, as per eq (18a), and by using the equality sign in eq (18b), we can develop an equation for the maximum permissible temperature. Do that for an exercise by solving the resulting quadratic equation for θ_{max}. Substitution of the result for θ_{max} in the inequality of eq (18b) determines the parameter space that guarantees the absence of hot spots. The result is not pretty looking.

To get a clear and easy formula to remember an approximate analytical solution is developed via a conservative approach in which one replaces $e^{\theta/(1+\theta/\gamma)}$ by a rising exponential e^{θ}. This is equivalent to replacing $k=k_o e^{-E/RT}$, i.e the Arrhenius temperature dependence with $k^{'} = k_o^{'} e^{\alpha T}$ and demanding that at T = T$_o$, k = k$^{'}$ and $\dfrac{dk}{dT} = \dfrac{dk'}{dT}$ at $T = T_o$ i.e at that point of $T = T_o$ both

functions are equal and their derivatives are equal. Indeed e^θ and $e^{\theta/(1+\theta/\gamma)}$ have the same value and the same value of the first derivative at $\theta = 0$. In Figure 3 we sketch the approximation of $y_1 = e^{\theta/(1+\theta/\gamma)}$ with e^θ
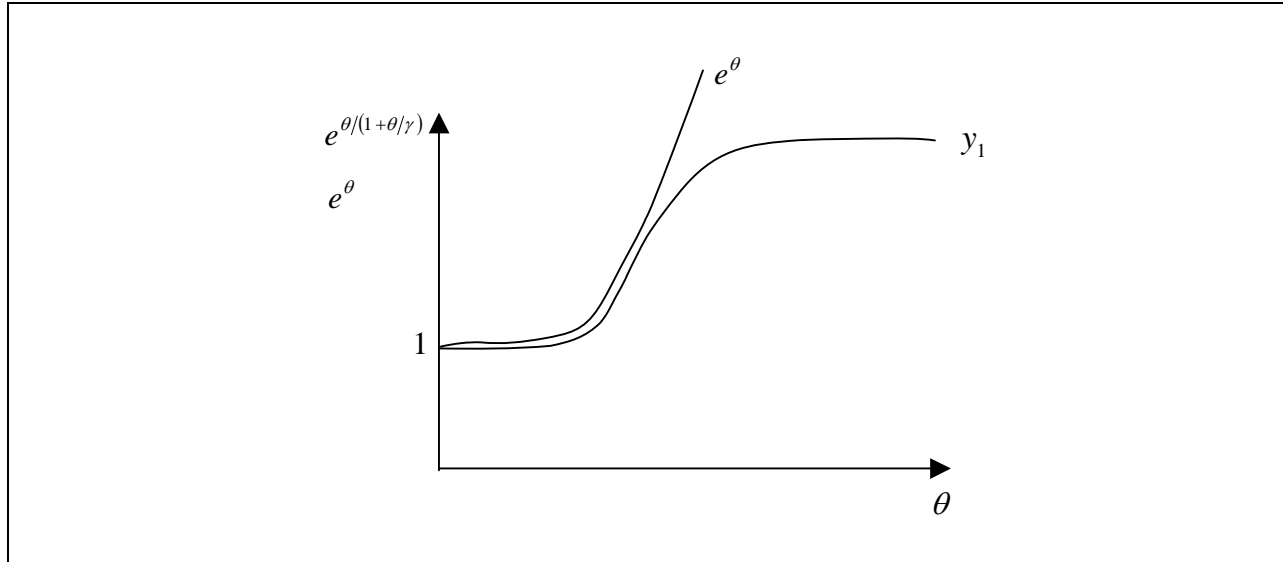
Figure 3: Approximation of the Arrhenius dependence of the rate constant with an exponential function.

Since we are interested in limiting the θ_{max} the two curves are pretty close for small θ. Clearly, if we replaced $y_1(\theta)$ with e^θ in Figure 2 we would lose the intersection with $y_2(\theta)$ for Case 3 but this is not of concern since we are not interested in $\theta > \theta_{max\,2}$, and for Case 2 the intersection of $y_2(\theta)$ with e^θ is close to that of $y_2(\theta)$ with $y_1(\theta)$ in Figure 2. The advantage of this approximation is that the criteria of equations (17a) and (17b) applied to

$y_1(\theta) = e^\theta$ and $y_2(\theta) = \dfrac{\kappa}{\delta}\theta$ yield

$$e^\theta = \frac{\kappa}{\delta}\theta \tag{19a}$$

and

$$e^\theta \le \frac{\kappa}{\delta} \tag{19b}$$

From which it follows:

$$\theta_{max} = 1 \tag{20}$$

7

Substitution of this into the inequality described by eq (19b) yields the parameter space that guarantees absence of hot spots

$$e \leq \frac{\kappa}{\delta} \tag{21}$$

Replacing the above dimensionless quantifies in terms of actual physical variables we get from eq (20) the maximum permissible temperature that can be tolerated in absence of hot spots

$$T_{max} \leq \left(\frac{1}{\gamma} + 1\right) T_o \tag{22}$$

From eq (21) we get the conditions that the system parameters must satisfy to guarantee absence of hot spots.

$$\frac{4 \, U \, R \, T_o^2}{\left(k_o e^{-E/RT_o} C_{Ao}^n\right)\left(-\Delta H_{r_A}\right) E \, d_t} \geq e \tag{23}$$

where R is the ideal gas constant in proper units.

This equation is usually written in terms of tube diameter that will guarantee absence of hot spots by providing sufficient heat transfer area per unit volume

$$d_t \leq \frac{4 U \, R \, T_o^2 e^{-1}}{E\left(-\Delta H_{r_A}\right) k_o e^{-E/RT_o} C_{Ao}^n} \tag{24}$$

Clearly, other permutations of eq (23) are possible. Given kinetic and reaction parameters, feed temperature and tube diameter one can calculate the maximum permissible feed concentration that guarantees safe operation, etc.

Approximate analysis, using the approximate exponential dependence of the rate constant, but accounting for the effect of reactant depletion, is possible for an n-th order reaction and yields the following result which is a little less conservative than equation (23).

$$\frac{\kappa}{\delta} \geq \frac{e}{1 + 2.703 n^{2/3} \delta^{-2/3}} \tag{25}$$

This result is due to Chandler Barkelew, Chem. Engr. Progress Symp. Ser. No. 25, Vol. 55, p. 37 (1959) and is one of the most useful expressions for nonisothermal tubular or batch reactors.

The graph showing the parameter space that is safe, based on Barkelew's and similar criteria, is appended as Figure 3.

$U_{av} \; C_{Ao} \; x_{Ae}$

Figure 3:   Runaway diagram

SAFE OPERATION OF TUBULAR (PFR) ADIABATIC REACTORS

(CHE 471)

M.P. Dudukovic

Chemical Reaction Engineering Laboratory

(CREL),

Washington University, St. Louis, MO

SAFE OPERATION OF TUBULAR (PFR) ADIABATIC REACTORS

In an exothermic reaction the temperature will continue to rise as one moves along a plug flow reactor until all of the limiting reactant is exhausted. Schematically the adiabatic temperature rise as a function of space time, measured from the reactor entrance, takes the form shown in Figure 1.

FIGURE 1: Temperature as a function of space time in an adiabatic PFR with exothermic reaction.
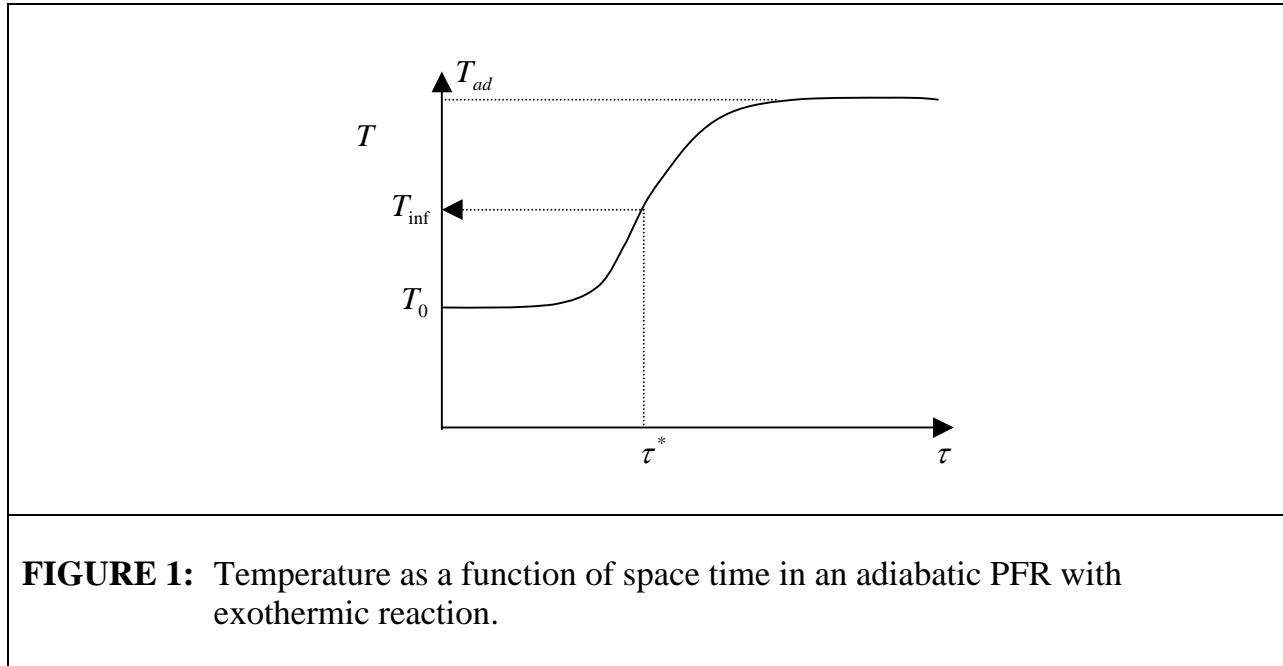
The final adiabatic temperature T_{ad} :

$$T_{ad} = T_o \left[1 + \frac{\left(-\Delta H_{r_A} \right) C_{Ao}}{\rho \, C_p \, T_o} \right] = T_o \left[1 + \beta \right] \tag{1}$$

is often excessive for highly exothermic systems (β large) and needs to be avoided. In such situations the old rule of thumb suggests that we should operate in such a way that the inflection point, <u>i.e.</u> the point of maximum temperature rise $\left(\dfrac{dT}{d\tau} \right)_{max}$, is never reached. This implies that we operate with $\tau < \tau^*$ where τ^* is the value of space time at which the inflection point $\left(\dfrac{d^2 T}{d\tau^2} = 0 \right)$ occurs.

Let us now develop a convenient and simple formula for use by practicing engineers which would guarantee safe operation. Consider an n-th order irreversible reaction:

$$- R_A = k_o e^{-E/RT} \; C_{Ao}{}^n \left(1 - x_A\right)^n \tag{2}$$

At adiabatic conditions temperature and conversion are related by the adiabatic line equation

$$T = T_o \left(1 + \beta\, x_A\right) \tag{3}$$

If we define, as in the case of wall cooled reactors, the dimensionless temperature by

$$\theta = \gamma \, \frac{T - T_o}{T_o} \tag{4}$$

then conversion in Eq. (3) can be expressed in terms of dimensionless temperature as:

$$x_A = \frac{\theta}{\delta} \tag{5}$$

where

$$\delta = \beta\, \gamma \tag{6}$$

with

$$\gamma = E/RT_o \tag{7}$$

The rate of reaction evaluated at adiabatic conditions in terms of dimensionless temperature is obtained by using the adiabatic line eq (5) to replace conversion. The result is:

$$\left(- R_A\right)_{ad} = \left(- R_A\right)_o \; e^{\gamma\theta/(\theta + \gamma)} \left(1 - \frac{\theta}{\delta}\right)^n \tag{8}$$

where the rate evaluated at the feed condition is:

$$\left(- R_A\right)_o = k_o e^{E/RT_o} \; C_{Ao}{}^n \tag{9}$$

The energy balance for adiabatic PFR operation is:

$$\rho\, C_p \, \frac{dT}{d\tau} = \left(- \Delta H_{r_A}\right)\left(- R_A\right)_{ad} \tag{10}$$

Written in terms of dimensionless temperature it becomes:

$$\frac{d\theta}{d\tau} = \frac{\delta}{\tau_R} e^{\gamma\theta/(\theta+\gamma)} \left(1 - \frac{\theta}{\delta}\right)^n \tag{11}$$

where the characteristic reaction time is:

$$\tau_R = \frac{C_{Ao}}{(-R_A)_o} \tag{12}$$

The initial condition is

$$\tau = 0 \qquad \theta = 0 \tag{13}$$

We can rewrite Eq. (11) in the most compact way by defining the Damkohler number as the ratio of characteristic process time and reaction time, i.e.

$$Da = \frac{\tau}{\tau_R} = \frac{(-R_A)_o \, \tau}{C_{Ao}} \tag{14}$$

Equation (11) and initial condition (13) become:

$$\frac{d\theta}{d(Da\delta)} = e^{\gamma\theta/(\theta+\gamma)} \left(1 - \frac{\theta}{\delta}\right)^n \tag{15}$$

At $Da\delta = 0 \qquad \theta = 0$ \hfill (16)

Now we want to have the reactor "short" enough (limit the conversion achievable) so that we can keep the inflection point $\frac{d^2\theta}{d\tau^2} = 0$ out of the reactor i.e. we do not let it occur in the reactor.

The critical temperature at inflection point, θ_{inf}, is obtained by setting

$$\frac{d^2\theta}{d(Da\delta)^2} = 0 \tag{17}$$

which results in an equation for $\theta = \theta_{inf}$ yielding:

$$\theta_{inf} = \frac{\gamma}{2n} \left[\sqrt{\gamma^2 + 4n(\gamma + \delta)} - 2n - \gamma\right]; n \neq 0 \tag{18a}$$

$$\theta_{inf} = \delta, \quad n = 0 \tag{18b}$$

The result for the zeroth order reaction, eq (18b), can be obtained by applying the L'Hospital rule to eq (18a). A better approach is to notice that for $n = 0$ equation (15) indicates that $d\theta/d(Da\delta) > 0$ always, so that there is no inflection point as the rate of temperature rise keeps rising until all reactant is depleted. Then at $x_A = 1$, from eq (5) it follows that $\theta_{max} = \delta$ and therefore $T_{max} = T_{ad}$.

We can integrate the differential equation (15) by separating the variables to obtain the critical value of $Da\delta^*$ and, hence, of τ^*

$$Da\delta^* = \int_0^{Da\delta^*} d(Da\delta) = \int_0^{\theta_{inf}} \frac{e^{-\gamma\theta/(\theta+\gamma)}}{\left(1 - \dfrac{\theta}{\delta}\right)^n} d\theta \tag{19}$$

Clearly for given values of parameters $\gamma, \beta, \delta = \beta\gamma$, and reaction order n, we can evaluate θ_{inf} from eq (18a) and then calculate the value of $Da\delta^*$ by numerically evaluating the integral in eq (19).

Using then the definitions of Da and δ we get the criterion for safe operation $Da\delta < Da\delta^*$ which can be expressed as:

$$\frac{k_o \, e^{-E/RT_o} \, C_{Ao}{}^n \left(-\Delta H_{r_A}\right) E \, \tau^*}{R \, \rho \, C_p \, T_o{}^2} \leq Da\delta^* \tag{20}$$

To get a convenient, easy to remember value of $Da\delta^*$, the following approximations are often made. First, the Arrhenius dependence of the rate constant on temperature is replaced by an exponential dependence, in effect

$$e^{\gamma\theta/(\theta+\gamma)} \approx e^{\theta} \tag{21}$$

Substituting this approximation in eq (15) yields via eq (17) to a new approximate value of the temperature at inflection point

$$\left(\theta_{inf}\right)_{app} = \delta - n \tag{22}$$

Substituting eq (21) and eq (22) into eq (19) yields

$$\left(Da\delta^*\right)_{app} = \int_0^{\delta-n} \frac{e^{-\theta}}{\left(1 - \dfrac{\theta}{\delta}\right)^n} d\theta = \delta^n \, e^{-\delta} \int_n^{\delta} \frac{e^u}{u^n} du \tag{23}$$

The final approximation (which is conservative in nature as it assumes the worst possible case of zeroth order reaction) ignores the slowdown of the temperature rise due to the consumption of the reactant, which is the same as taking $n = 0$ in eq (23).

This yields

$$
\begin{aligned}
\left(Da\delta^*\right)_{app,0} &= e^{-\delta} \int_0^{\delta} e^u \, du = e^{-\delta} \left(e^u\right)_0^{\delta} \\
&= e^{-\delta}\left[e^{\delta} - 1\right] = 1 - e^{-\delta} = 1 \qquad \left(\text{for large enough } \delta\right)
\end{aligned}
\tag{24}
$$

For highly exothermic reactions $\delta \geq 10$ and clearly $\left(Da\delta^*\right)_{app,o} = 1$.

Substituting this into eq (20) gives the conservative criterion for safe operation.

It is constructive to note that this same equation (20a) with time t replacing τ

$$
\frac{k_o \, e^{-E/RT_o} \, C_{A_o}^{\ n} \left(-\Delta H_{r_A}\right) E \, t^*}{R \, \rho \, C_p \, T_o^{\ 2}} < 1
\tag{20a}
$$

is used to determine the so called "time of no return" or time to explosion in batch systems. This time to inflection point t^* may be very long for low T_o but becomes quite short if the system of high activation energy is exposed to higher T_o. Hence, chemicals that may be safe to store at 25°C may be explosion prone if exposed to 40 – 50°C!

SAFE OPERATION OF ADIABATIC CSTR

The mass balance for an irreversible n-th order reaction is:

$$
C_{Ao} \, x_A = \left(-R_A\right)\tau
\tag{25}
$$

The adiabatic equation relates conversion and temperature

$$
x_A = \frac{T - T_o}{\left(-\Delta H_{r_A}\right)C_{Ao}/\rho \, C_p}
\tag{26}
$$

Upon substitution of dimensionless temperature we get from eq (25)

$$
\frac{1}{Da_n \, \delta} \theta = e^{\gamma\theta/(\theta + \gamma)}\left(1 - \frac{\theta}{\delta}\right)^n
\tag{27}
$$

let

$$
G\left(\theta\right) = e^{\gamma\theta/(\theta + \gamma)}\left(1 - \frac{\theta}{\delta}\right)^n
\tag{28a}
$$

$$L(\theta) = \frac{1}{Da_n \delta} \theta \tag{28b}$$

We know from before that G is a sigmoidal curve in θ and represents heat generated by reaction. L is the heat removal rate (i.e., heat removed by sensible heat of the fluid that flows through the CSTR).

We know that up to three intersections are possible between G and L lines. To avoid the intersection leading to excessively high temperatures we must assure that intersections at low temperatures are available. The last permissible operating condition is the one when line L is also tangent to curve G as schematically shown in Figure 2.

FIGURE 2: Schematic of the G, L vs. θ
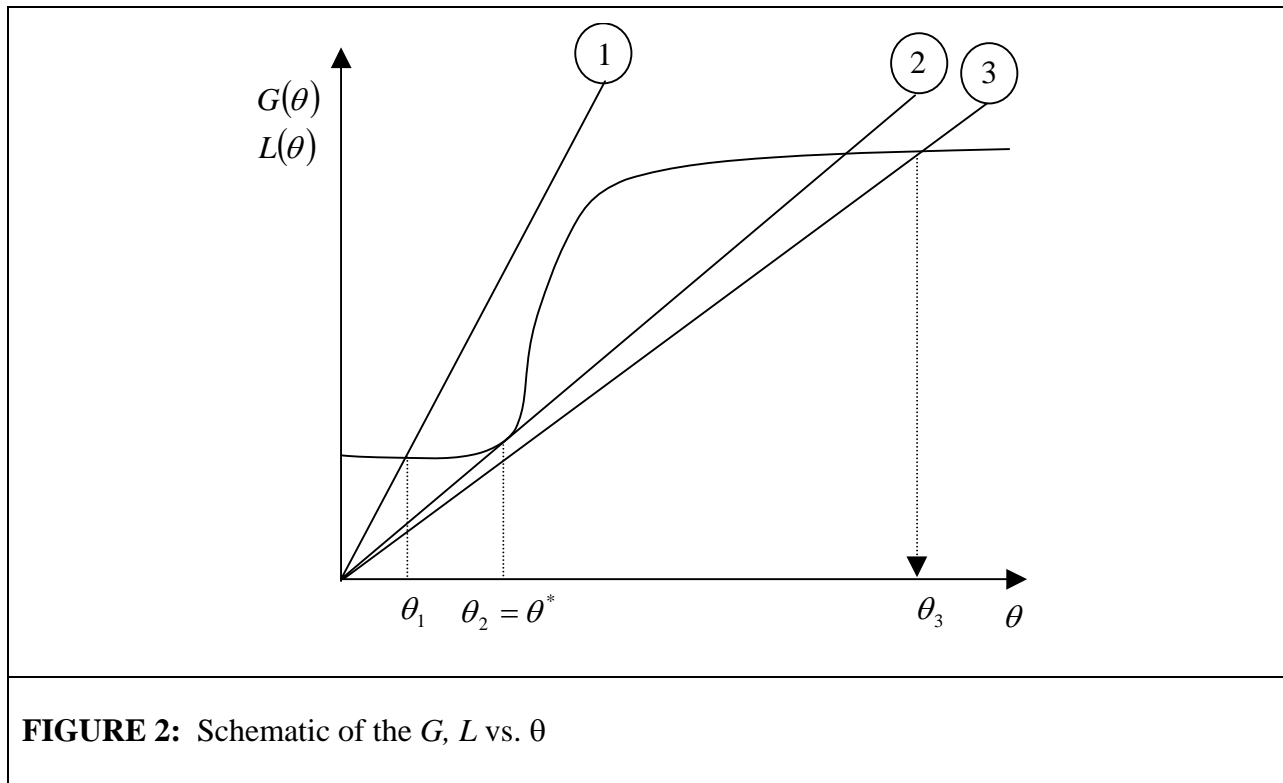
Clearly as $Da\delta$ increases the slope of the L line decreases so that

$$(Da\delta)_1 < (Da\delta)_2 < (Da\delta)_3 \tag{29}$$

While operating adiabatic temperatures at θ_1 and θ_2 are acceptable, θ_3 represents too large a temperature jump. Hence, we must assure that the L line always intersects the G line at its lower temperature branch. The critical point is reached when L is also tangent to the G line.

For safe adiabatic operation we therefore require

$$L = G \tag{30}$$

$$\frac{dL}{d\theta} \geq \frac{dG}{d\theta} \tag{31}$$

Applying the above to eqs (28a) and (28b), and using the equality sign in eq (31), we get the equation for the maximum permissible temperature $\theta_{\max\ perm} = \theta^*$. The critical value of the space time τ^* can be obtained from the critical value of $Da\delta^*$, which in turn results from substituting the expression for θ^* into eq (30).

To get a simple, easy to remember expression, usually we again replace $e^{\gamma\theta/(\theta + \gamma)}$ with e^{θ}. This yields

$$\theta^* = \frac{1}{2}\left[\delta - n + 1 - \sqrt{(\delta - n + 1)^2 - 4\,\delta}\right] \tag{32}$$

The negative sign in front of the square root needs to be taken as we are interested in the lower of the two temperatures at which the L line could be tangent to the curve G. Then equation (30) yields:

$$\left(Da\delta\right)^*_{app} = \theta^*\left(1 - \frac{\theta^*}{\delta}\right)^{-n} e^{-\theta^*} \tag{33}$$

A conservative estimate, with $n = 0$, yields $\theta^* = 1$ and

$$Da\delta^* \leq e^{-1} \tag{34}$$

For safe operation then

$$\frac{k_0\ e^{-E/RT_o}\ C_{Ao}{}^n\left(-\Delta H_{r_A}\right)E\tau}{R\ \rho\ C_p\ T_o{}^2} \leq e^{-1} \tag{35}$$

ARC Experiments

Sample Calculation for Run #326

Bomb weight = 82.0 grams
Sample weight = 2.5 grams
Bomb material (stainless steel) - heat capacity = 0.11 cal/g °C
Sample heat capacity $C_p = C_v = 0.5$ cal/g °C

I.   Calculate "thermal inertia" factor ϕ

$$\phi = \frac{M_{Bomb} C_{P_{steel}}}{M_{sample} C_{P_{sample}}} = \frac{82.0 \; x \; 0.11}{2.5 \; x \; 0.5} = 7.22$$

II.   Calculation of basic parameters

From the enclosed Figure of log $\frac{dT}{dt}$ vs $\frac{1}{T}$ and data

1.   Starting temperature $T_o = 122.7$ °C = 395.9 K
2.   Final temperature $T_f = 180.3$ °C = 453.5 K
3.   Adiabatic temperature rise $T_f - T_o = \Delta T_{ad} = 170$ °C = 57.6 °K
4.   Temperature at maximum rate $T_m = 170$ °C = 443.2 K
5.   Temperature rise from point of maximum rate to final adiabatic
     T_f: $\Delta T_m = T_f - T_m = 10.3$ °C = 10.3 °K

6.   Activation energy by taking a slope of the tangent to the log $\frac{dT}{dt}$ vs $\frac{1}{T}$

     curve at $T = T_o$

$$E = -R(slope) = -1987 \left(\frac{\ln 6 - \ln 00.1}{\frac{1}{443.2} - \frac{1}{377.2}} \right) = 32,200 \; \frac{cal}{mol}$$

Note: A better way to get activation energy would be to find both E and n from $\ln k^*$ vs $\frac{1}{T}$ plot

$$k^* = k_o C_{Ao}^{n-1} e^{-E/RT} = \frac{m}{\Delta T_{ad} \left(\dfrac{T_f - T}{\Delta T_{ad}} \right)^n}$$

7.   Reaction order $n = \dfrac{E \overbrace{\Delta T_m}^{T_f - T_n}}{RT_m^2} = \dfrac{32,200 \; x \; 10.3}{1.987 \; x \; 443.2^2} = 0.85$

8.   Conversion at maximum rate

$$\frac{C_A}{C_{Ao}} = \frac{T_f - T_m}{\Delta T_{ad}} = \frac{10.3}{57.6} = 0.18 = 1 - x_A$$

$$x_{A_m} = 0.82$$

III.   Critical time to explosion (0-th order)

$$t_{o_m}^* = \frac{RT_o^2}{Em_o} = \frac{1987 \; x \; 395.9^2}{32,200 \; x \; 0.076 \, (\textit{from graph})} = \underline{\underline{127.3 \min}}$$

Note: $T_o = 122.7 \,°C = 395.9 \, K$ is the first temperature at which an accurate reading of $\dfrac{dT}{dt}$

could be obtained and deviated from the $\left(\dfrac{dT}{dt}\right)_{ramp}$ to which the ARC is exposed.

Conversion at that starting T is essentially zero

$$x_A \big| T_o = 1 - \frac{T_f - T_o}{\Delta T_{ad}} = 1 - 1 = 0$$

This means that the tangent to the rate curve at $T = T_o$ can be used to represent the rate at values $T < T_o$ since $x_A = 0$ at those T.

Time to explosion can now be evaluated at any T.

$$t_{o_m}^* = \frac{RT^2}{E(m_T)_o}$$

Comparison is shown in the enclosed Table.

Note: The calculated time to explosion only becomes inaccurate where $T \to T_m$.

By plotting $\ell n \, t_{o_m}^*$ vs $\dfrac{1}{T}$ from the slope one finds

       $E = -31,200$ cal/mol in close agreement to previously estimated values.

III. Correction for "thermal inertia" effects

$$m_{system} = m_{exp}(1 + \phi) = 8.22\ m_{exp}$$

$$t^*_{o_{system}} = t^*_{o_{exp}}/(1 + \phi) = \frac{t^*_{o_{exp}}}{8.22}$$

$$\Delta T_{ad_{system}} = \Delta T_{ad_{exp}}(1 + \phi) = 8.22\ x\ 57.6 = 473.5°C(K)$$

$$T_{m_{system}} = \frac{E}{2nR}[\sqrt{1 + \frac{4nR(T_o + \Delta T_{ad_{system}})}{E}} - 1]$$

$$T_{m_{system}} = \frac{32,200}{2\ x\ 0.85\ x\ 1.987}[\sqrt{1 + \frac{4\ x\ 0.85\ x\ 1.987(395.9 + 473.5)}{37,200}} - 1]$$

$$T_{m_{system}} = 838\ K = 564.8\ °C$$

Now at $T_o = 122.7\ °C$

$$t^*_{o_{system}} = \frac{t^*_{o_{exp}}}{8.22} = \frac{127.3}{8.22} = \underline{15.5\ min}$$

TABLE A-1

SAMPLE CALCULATION BASIS

ARC 526 DI-T-BUTYL PEROXIDE

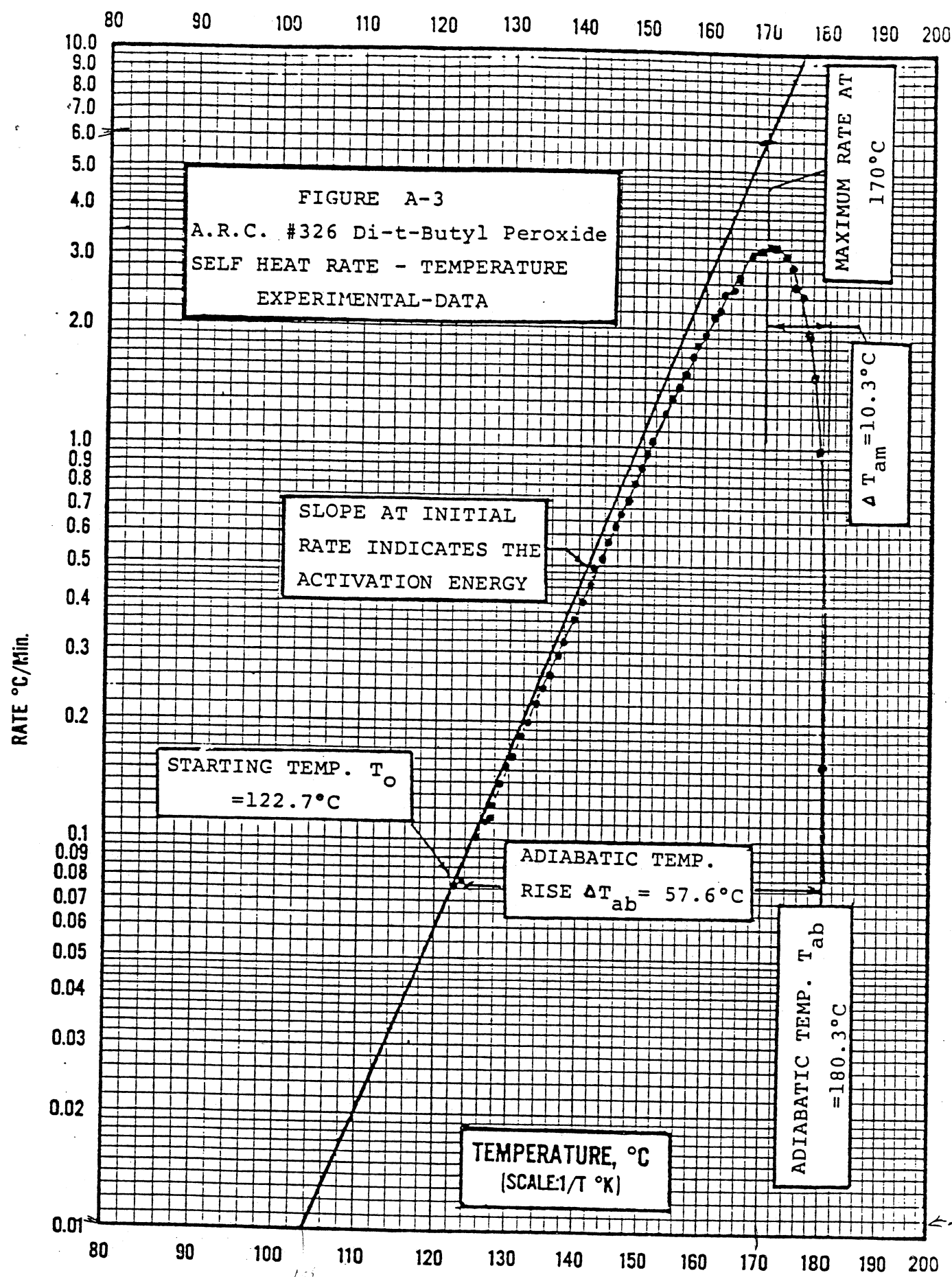DATA ANALYSIS AS OF 08/12/76

NUMBER OF DATA POINTS IN FILE = 53

REACTION NUMBER 1

TEMPERATURE	HEAT RATE
122.7000	0.077100
123.5000	0.079300
125.8000	0.102100
126.8000	0.112300
127.8000	0.122200
128.8000	0.138900
129.8000	0.154300
130.8000	0.160300
131.8000	0.182200
132.8000	0.199200
133.8000	0.220400
134.8000	0.242600
135.9000	0.263500
136.9000	0.295800
137.9000	0.318100
139.5000	0.365700
140.6000	0.402300
141.6000	0.441800
142.6000	0.492100
143.6000	0.529000
144.6000	0.584100
145.6000	0.637100
146.7000	0.672500
147.7000	0.747200
148.7000	0.809700
149.7000	0.900000
150.8000	0.967600
151.8000	1.059999
153.6000	1.209999
154.7000	1.339999
155.7000	1.410000
156.8000	1.530000
157.8000	1.700000
158.9000	1.830000
159.9000	1.959999
160.9000	2.160000
162.0000	2.200000
163.1000	2.440000
164.1000	2.520000
165.2000	2.730000
167.6000	2.879999
168.7000	3.030000
169.8000	3.129999
170.8000	3.200000
171.9000	3.129999
173.0000	3.040000
174.1000	2.879999
175.1000	2.589999
176.2000	2.419999
177.3000	1.990000
178.3000	1.549999
179.3000	0.990000
180.3000	0.157200

NUMBER OF DATA POINTS IN REACTION 1 = 53

NUMBER OF DATA POINTS DISCARDED = 0

FIGURE A-3
A.R.C. #326 Di-t-Butyl Peroxide
SELF HEAT RATE - TEMPERATURE
EXPERIMENTAL-DATA

MAXIMUM RATE AT 170°C

$\Delta T_{am} = 10.3°C$

SLOPE AT INITIAL
RATE INDICATES THE
ACTIVATION ENERGY

STARTING TEMP. T_o
= 122.7°C

ADIABATIC TEMP.
RISE ΔT_{ab} = 57.6°C

ADIABATIC TEMP. T_{ab}
= 180.3°C

RATE °C/Min.

TEMPERATURE, °C
(SCALE: 1/T °K)

Temperature (°C) →

Experimental and Predicted Time to Explosion   ARC No. 326

Temperature °C	0-order self Heat Rate	Calculated 0-order Time to Explosion	Experimental Actual ARC Time to Explosion
104.0	.01°C/min.	878 min.	(Not measured)
112.0	.0244	375 min.	381 min.
116.1	.0380	246 min.	261 min.
120.1	.0580	164 min.	181 min.
125.8	.1045	94 min.	100 min.
130.8	.1728	58 min.	63 min.
134.8	.2561	40 min.	44 min.
139.5	.4025	26 min.	29 min.
145.6	.7130	15 min.	17 min.
150.8	1.146	10 min.	11 min.
160.9	2.789	4 min.	3.5 min.