UGent Francqui Chair 2013 / 6-7th Lectures

Response and dynamics of chemical reactors and instrumentation

Nikos Papayannakos, Professor
National Technical University of Athens
School of Chemical Engineering
Unit of Hydrocarbons and Biofuels Processing

10 April 2013

Contents

Dynamics is related to changes with time

Dynamic equations describe the evolution of systems with time

Although the fashion in the field of dynamics is the study of complicated systems, the study of simple systems, which in many cases compose the bigger systems, provides useful knowledge to the chemical engineers' background

The basis for building the dynamic equations in Chemical Engineering systems Is the Mass and Energy balances

The dynamic equations and their solutions must be well understood "physical meaning"
Not be considered simply as a way to 'produce' numbers describing the evolution of the system

First Order Dynamic systems

$$\tau \frac{dy}{dt} + y = f(t) \text{ or } A,$$ Initial Conditions

First order ordinary differential equations are often exactly solvable by separation of variables

For I. C. : $t = 0, \ y = y_0$

$$\boxed{y(t) - A = (y_0 - A) \times (e^{-t/\tau})}$$

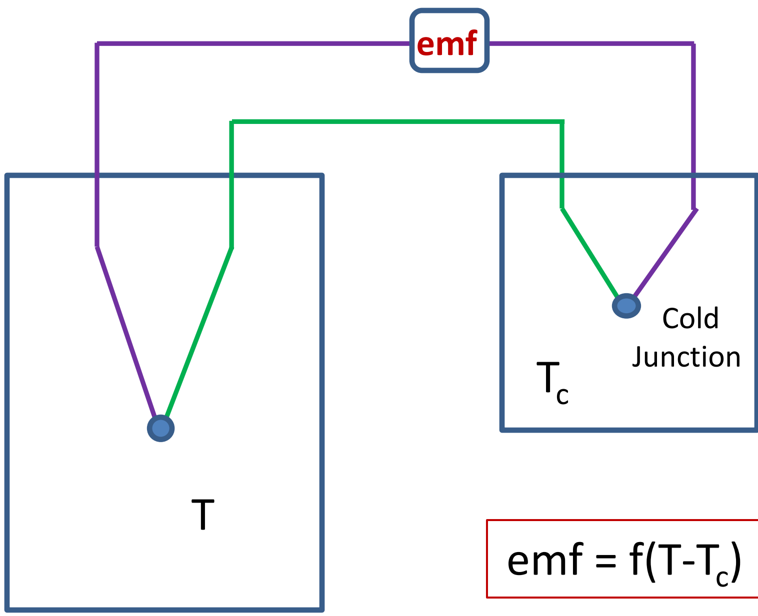
$$\boxed{y(t) - y_0 = (A - y_0) \times (1 - e^{-t/\tau})}$$

$$\boxed{y(t) = A + (y_0 - A) \times (1 - e^{-t/\tau})}$$

Thermocouple

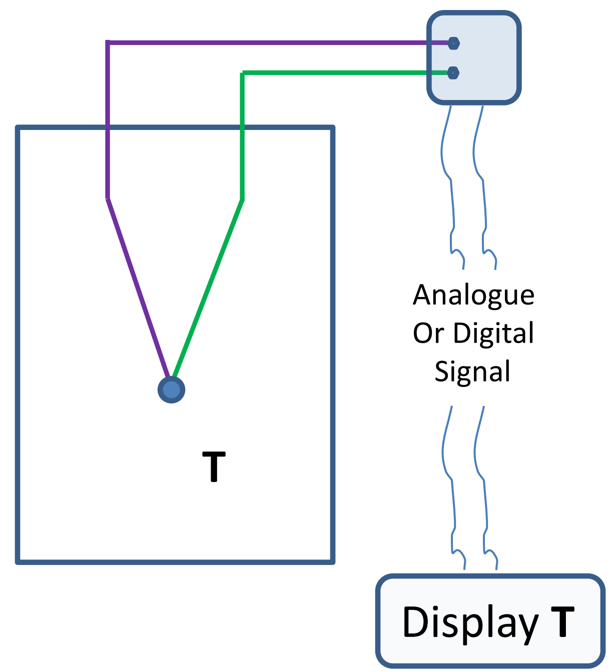
Small and easy to use device for temperature measurements in process equipments

Principle of Operation



$emf = f(T-T_c)$

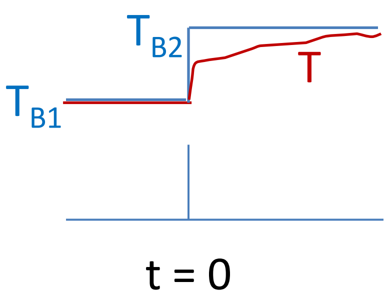
Contemporary techniques

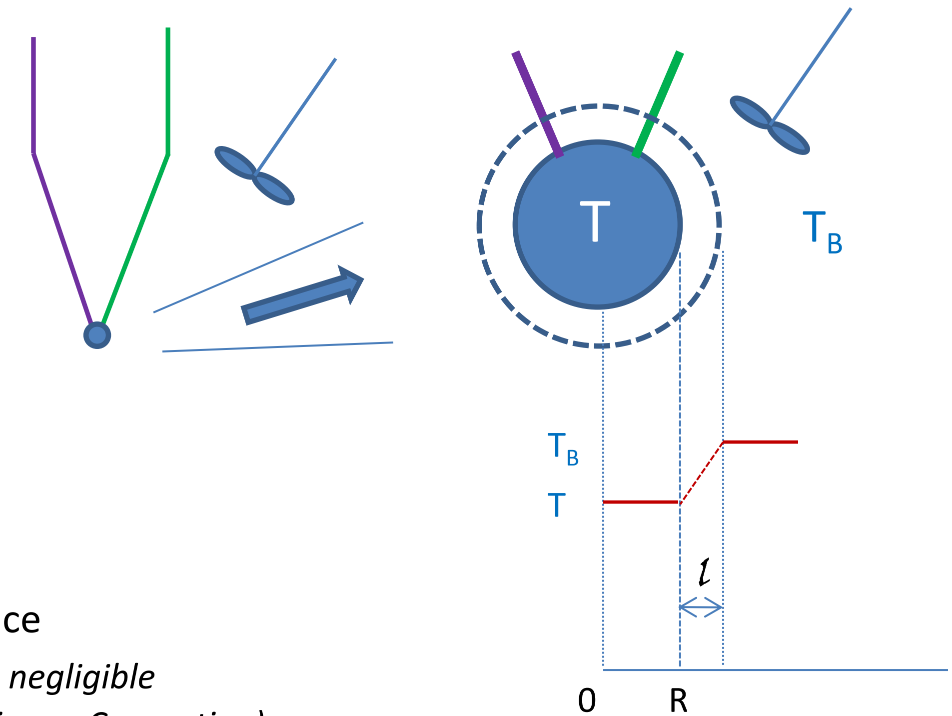


- Electronic compensation for the Joints Cold Point T_c
- Fast signal transmission from measuring junction to display

Simulation of the Dynamic operation of a Thermocouple

What will be the response to a step Stimulus?





Assumption to set up the Enegry balance

- *The energy conveyed through the cables negligible*
- *Isothermal thermocouple bulb (Conduction>> Convection)*

Energy balance

Heat flow into bulb = Accumulation

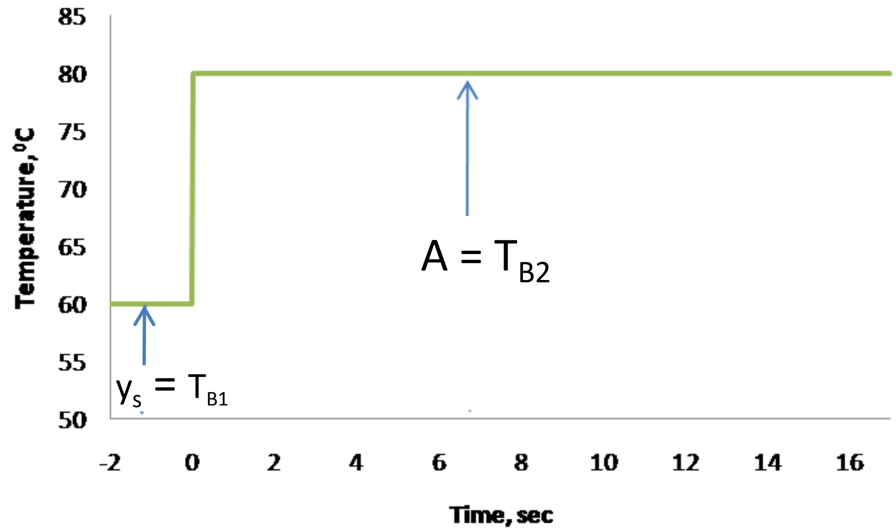
$$A_{sph} \times h_f \times (T_B - T) \times dt = m_{th} \times c_{pth} \times dT$$

Final Equation

$$\frac{m_{th} x c_{pth}}{A_{sph} x h_f} \frac{dT}{dt} + T = T_B$$

τ = time constant

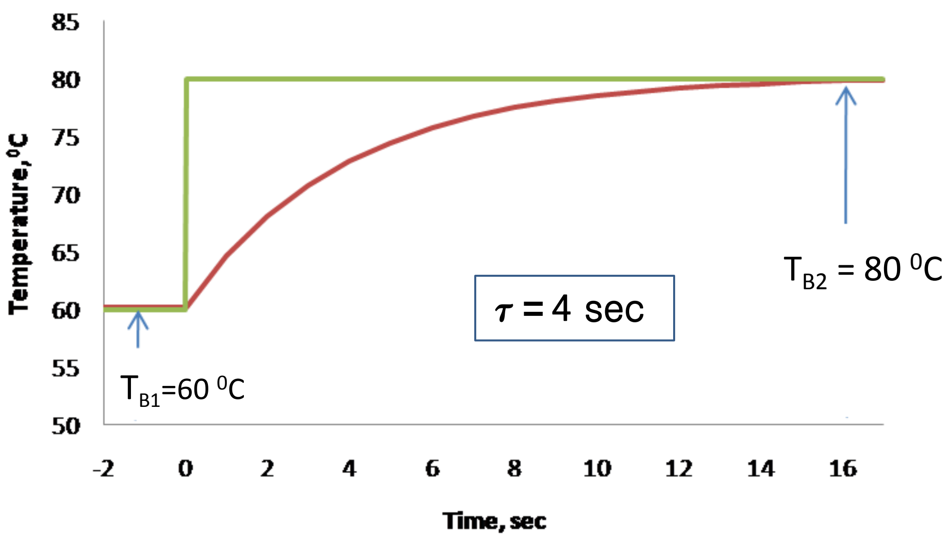
Typical Response



Step Stimulus

$t < 0,\ T = T_{B1} = 60\ ^0C$

$t \geq 0,\ T_{B2} = 80\ ^0C$

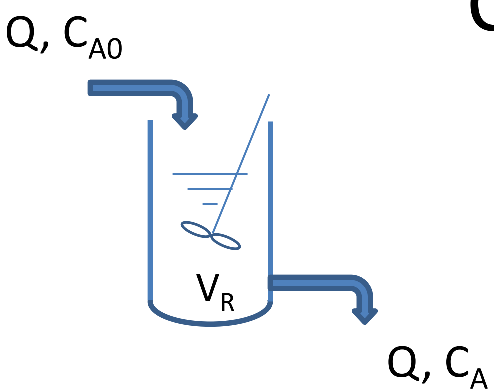


$$y(t) = 80 - 20*(1 - e^{-t/4})$$

y(t) : T, ^0C

t : sec

Continuous Stirred Mixer



Mass Balance

Mass In-flow - Mass Out-flow = Accumulation

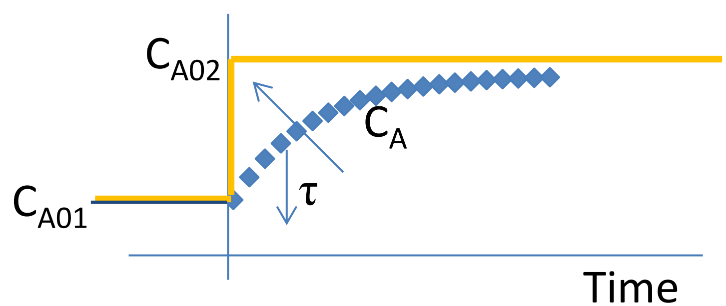
$$Q \times C_{A0} - Q \times C_A = V_R \frac{dC_A}{dt}$$

Final Form : $$\frac{V_R}{Q}\frac{dC_A}{dt} + C_A = C_{A0}$$

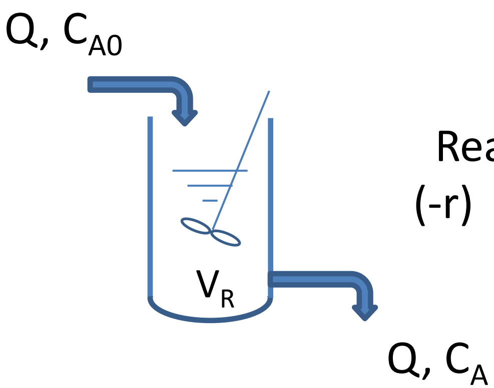
τ = time constant = space time = τ^*

For a Step Stimulus from C_{A01} (t < 0) to C_{A02} (t ≥ 0) the analytical solution :

$$\boxed{C_A = C_{A02} + (C_{A01} - C_{A02})(e^{-t/\tau})}$$



CSTReactor



Reaction A → P

$(-r) = [\, k\, f(C_A)\,] = k\, C_A$

Mass Balance

Mass In-flow - Mass Out-flow - Mass Reacting = Accumulation

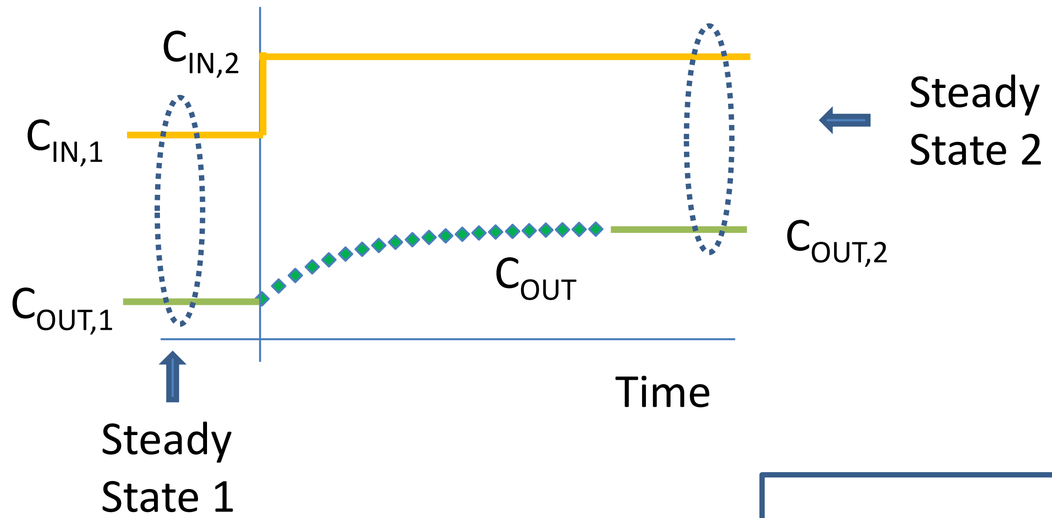
$$Q \times C_{A0} - Q \times C_A - (-r) \times V_R = V_R \frac{dC_A}{dt}$$

Final Form :

$$\frac{V_R}{Q + kV_R}\frac{dC_A}{dt} + C_A = \frac{Q}{Q + kV_R} C_{A0} = \frac{1}{1 + k\tau^*} C_{A0}$$

τ = time constant = $\dfrac{\tau^*}{1 + k\tau^*} < \tau^*$

Steady State Gain



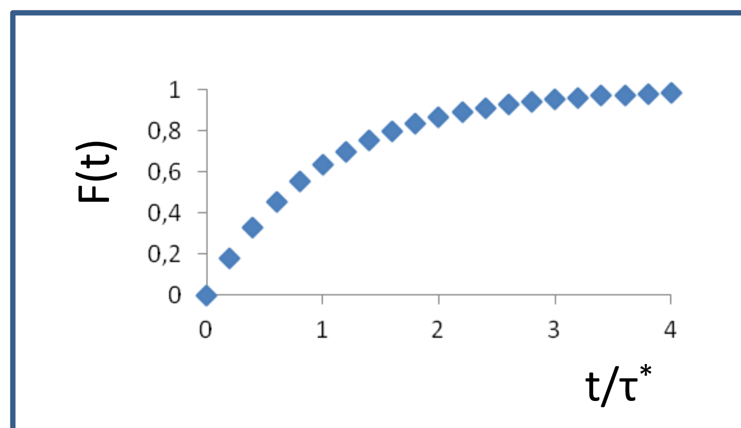
At Steady State :

$$\frac{C_{OUT,1}}{C_{IN,1}} = \frac{C_{OUT,2}}{C_{IN,2}} = \frac{C_{OUT}}{C_{IN,}} = \frac{1}{1 + k\tau^*}$$

What is the reason of existence of Transition Period in Perfect Mixing?

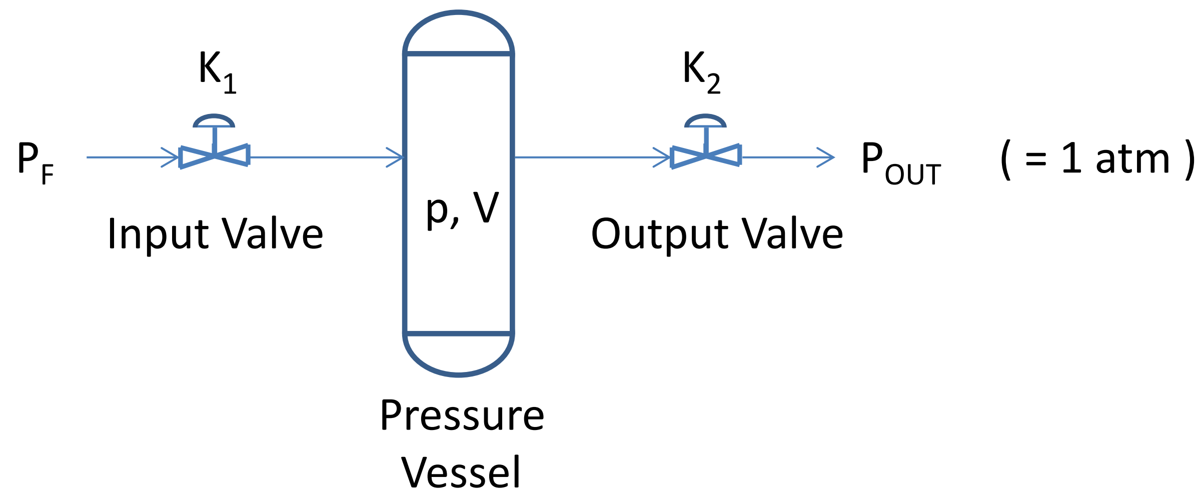
The different Residence Times

Cumulative Distribution Function F(t)



Non-linear Systems

Pressure vessel with relief valve



Mass Balance

Mass In-flow - Mass Out-flow = Accumulation

$$K_1 \times (P_F - P)^{1/2} - K_2 \times (P - P_{OUT})^{1/2} = \frac{dm_{Gas}}{dt} = \frac{V \times MW_{Gas}}{RT} \frac{dP}{dt}$$

$C \neq \tau$

Non-linear Terms

At Steady State : $k_1(p_{F0} - p_0)^{1/2} - k_2(p_0 - 1)^{1/2} = 0$

Taylor Series approximation

$$k_1(p_F - p)^{1/2} = k_1(p_{F0} - p_0)^{1/2} + \frac{\partial}{\partial p_F}\left[k_1(p_F - p)^{1/2}\right]_0 (p_F - p_{F0}) + \frac{\partial}{\partial p}\left[k_1(p_F - p)^{1/2}\right]_0 (p - p_0)$$

$$= k_1(p_{F0} - p_0)^{1/2} + \frac{k_1}{2}(p_{F0} - p_0)^{-1/2}(p_F - p_{F0}) - \frac{k_1}{2}(p_{F0} - p_0)^{-1/2}(p - p_0)$$

$$k_2(p - 1)^{1/2} = k_2(p_0 - 1)^{1/2} + \frac{\partial}{\partial p}\left[k_2(p - 1)^{1/2}\right]_0 (p - p_0)$$

$$= k_2(p_0 - 1)^{1/2} + \frac{k_2}{2}(p_0 - 1)^{-1/2}(p - p_0)$$

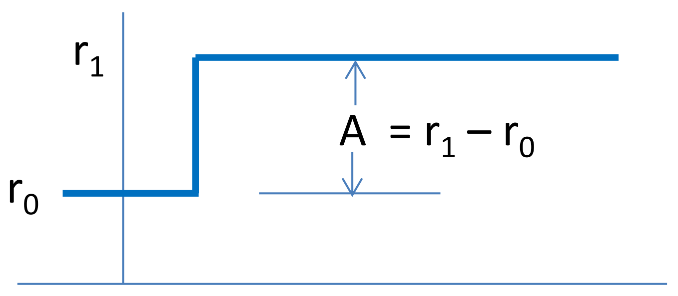
Final Form :

$$\underbrace{\frac{C}{\alpha + \beta}}_{\tau} \frac{dP}{dt} + P = \frac{\alpha}{\alpha + \beta}(P_F - P_{F0}) + P_0$$

$$\alpha = \frac{k_1}{2}(p_{F0} - p_0)^{-1/2}, \quad \beta = \frac{k_2}{2}(p_0 - 1)^{-1/2}$$

Responses to Standard Stimuli

1. Step Input - Stimulus



Dynamic Equation

$$\tau \frac{dy}{dt} + y = A$$

I. C. : $t = 0, \; y = 0$

Solution of the Equation

$$y = y_S + y_t$$

y_S = Steady State or Particular Solution

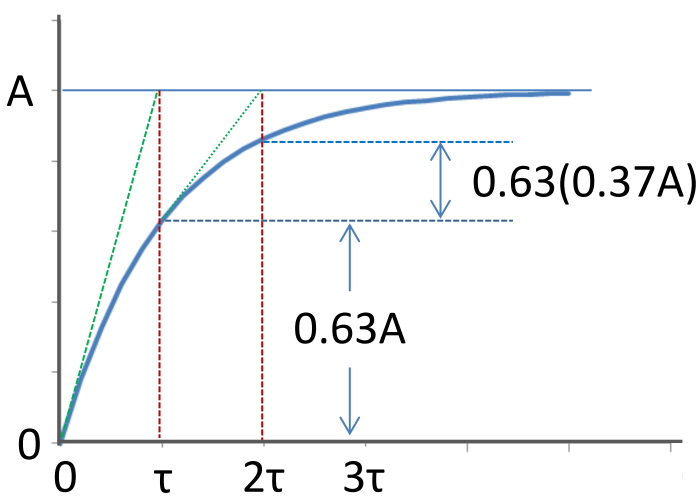
y_t = Transient or Complimentary Solution

- Method of separation of variables
- Laplace method
- **Method of Undetermined Coefficients**

$$\tau \frac{d(y_S + y_t)}{dt} + y_S + y_t = A \quad \Rightarrow \quad \begin{cases} \tau \dfrac{dy_t}{dt} + y_t = 0 \quad \longrightarrow \quad y_t = B\, e^{st} \\ y_S = A \end{cases}$$

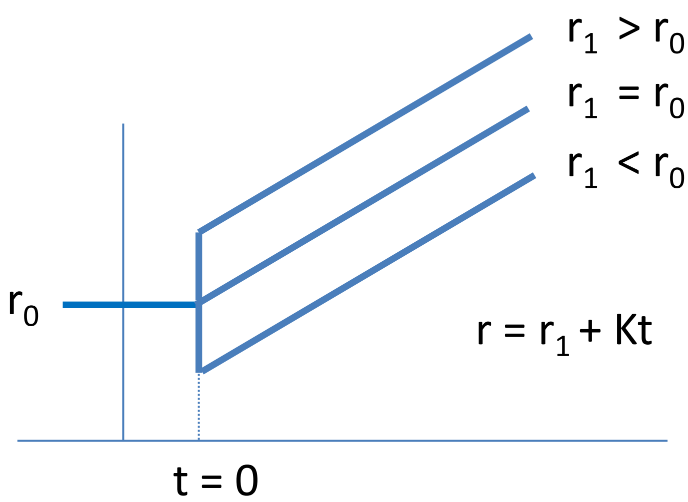
$$\underline{y = y_S + y_t = B\, e^{-t/\tau} + A}$$

$$\boxed{y = A\,(1 - e^{-t/\tau})} \quad \text{or} \quad \boxed{\frac{y - y_0}{y_1 - y_0} = 1 - e^{-t/\tau}}$$



- The system has no memory
- For any time period of τ, 63 % of the remaining distance to the new steady state is covered
- After $t=3\tau$, 95% of the distance to new steady state (A) is covered

2. Ramp/liner forcing



Dynamic Equation

$$\tau \frac{dy}{dt} + y = Kt + r_1$$

I. C. : $t = 0, \quad y = y_0 = r_0$

Solution :

$$y = y_S + y_t$$

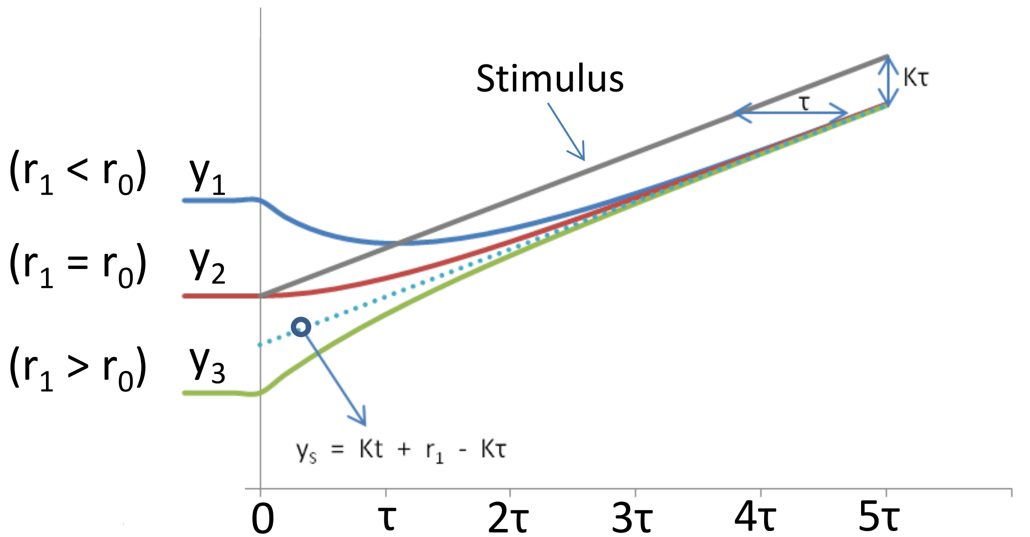
$$\tau \frac{d(y_S + y_t)}{dt} + y_S + y_t = Kt + r_1$$

$$\tau \frac{dy_t}{dt} + y_t = 0 \quad \Rightarrow \quad y_t = B e^{st}$$

$$y_S = \alpha t + \beta$$

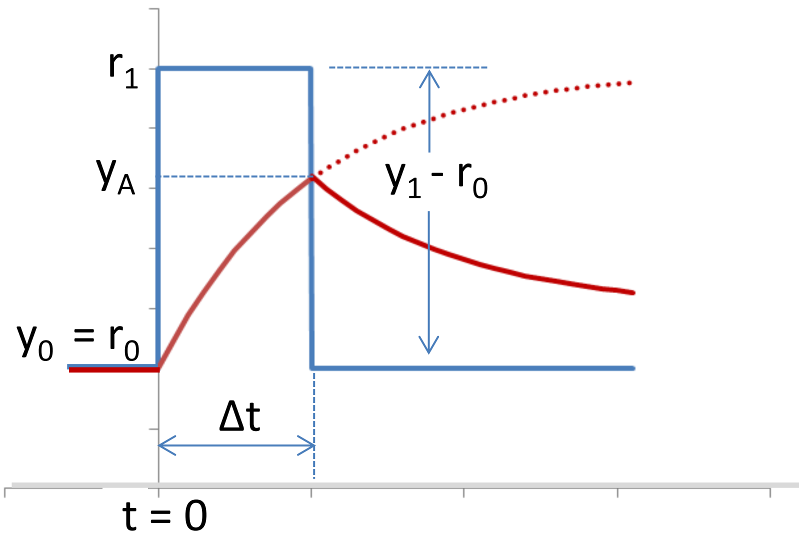
$$\boxed{y = (Kt + r_1 - K\tau) + [(r_0 - r_1) + K\tau]e^{-t/\tau}}$$

General Response to a Ramp/liner forcing



- Dynamic Error Velocity Error at Steady State : **Kτ**
- The Time lag at Steady State : **τ**

3. Impulse Forcing and Response



Response for $0 \leq t \leq \Delta t$

$$\frac{y - y_0}{y_1 - y_0} = 1 - e^{-t/\tau}$$

or

$$y_A - y_0 = (y_1 - y_0)(1 - e^{-\Delta t/\tau})$$

$$(1 - e^{-\Delta t/\tau})_{\Delta t \to 0} = \Delta t/\tau$$

$$y_A = y_0 + (y_1 - y_0)\Delta t/\tau$$

Response for $t > \Delta t$

$$\frac{y - y_A}{y_0 - y_A} = 1 - e^{-t/\tau}$$

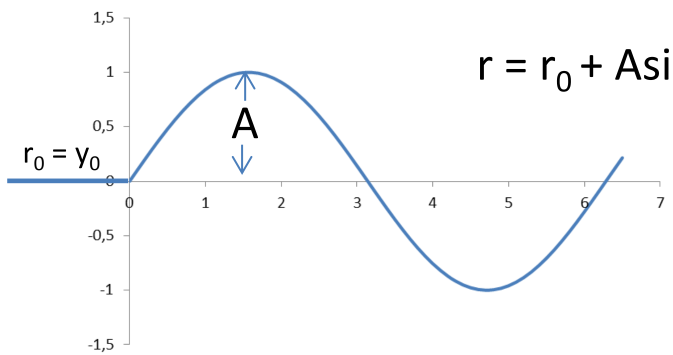
$$\boxed{y = y_0 + (y_1 - y_0)(\Delta t/\tau)e^{-t/\tau} = y_0 + \frac{I}{\tau} e^{-t/\tau}}$$

$$\boxed{\text{Where } I = (y_1 - y_0)\Delta t}$$

- The response depends on the ‘total’ Input and not on the real form of the Impulse

4. Sine Input

One of the most important stimuli that represents all the periodic Inputs and its study gives useful deductions for system behavior



$$r = r_0 + A\sin(\omega t)$$

For $y_0 = r_0 = 0$ and No signal amplification

$$\boxed{\tau \frac{dy}{dt} + y = A\sin(\omega t)}$$

$$y = y_S + y_t$$

$$y_S = \mathbf{C}\sin(\omega t + \mathbf{\Psi})$$

$$y_t = \mathbf{B}e^{-t/\tau}$$

$$C\omega\tau \cos(\omega t + \Psi) + C \sin(\omega t + \Psi) = A \sin(\omega t)$$

$$\boxed{\mathbf{\Psi} = \textbf{\textit{arc tan}}\ (\mathbf{-\omega\tau}) < 0 \ : \text{ Phase delay}}$$

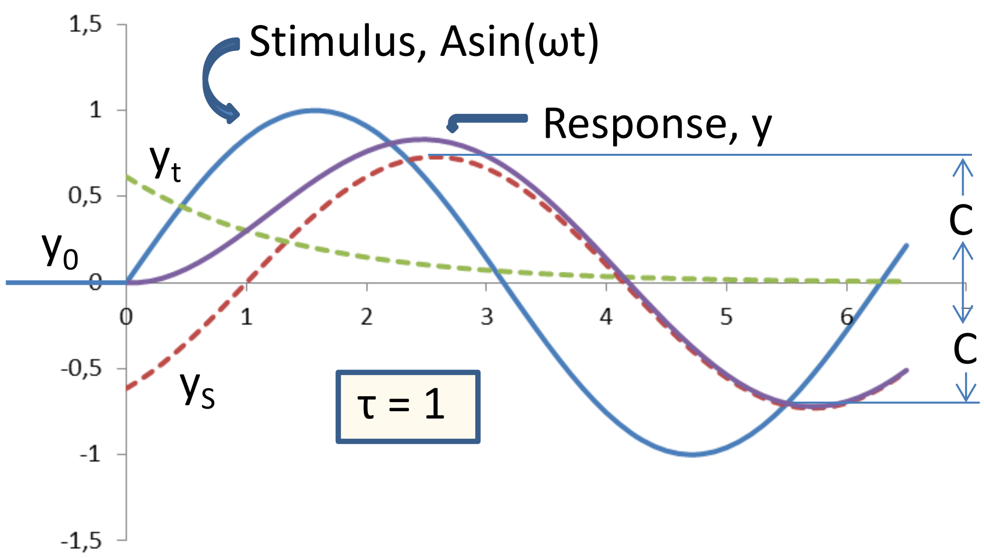
$$\boxed{\mathbf{C} = \frac{\mathbf{A}}{\sqrt{1+\omega^2\tau^2}}}$$

$$\boxed{\mathbf{B = C}\ \textbf{\textit{sin}}\ (\textbf{\textit{arc tan}}\ (\mathbf{\omega\tau}))}$$

$$y = \frac{A}{\sqrt{1+\omega^2\tau^2}}\left(\sin(\arctan(\omega\tau))\, e^{-t/\tau} + \sin(\omega t + \arctan(-\omega\tau)) \right)$$

For $y_0 \neq 0$:

$$y = y_0 + \underbrace{\frac{A}{\sqrt{1+\omega^2\tau^2}}}_{C}\left(\sin(\arctan(\omega\tau))\, e^{-t/\tau} + \sin(\omega t + \arctan(-\omega\tau)) \right)$$



- The **higher** the stimulus **frequency**

and

The **higher** the **System's inertia**

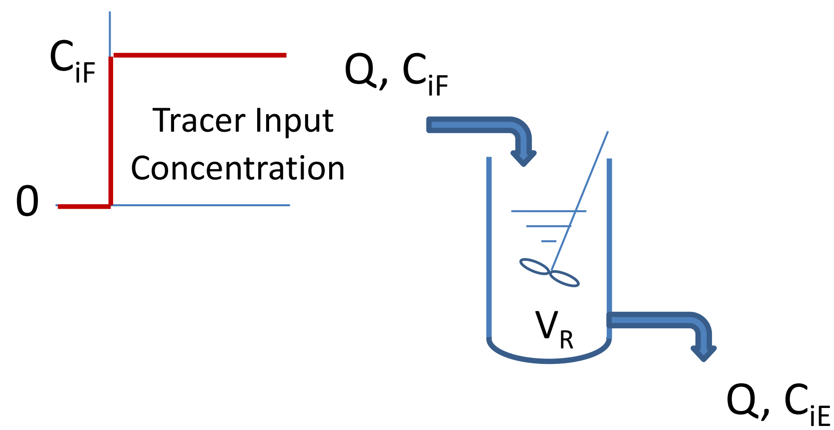
The **smaller** the **response amplitude**

Application of Stimulus/Response techniques to study Ideal – Non-Ideal flow

<u>CSTR</u>

– Assumption : Total mixing

- Step Tracer Input 0 → C_{iF}



Mass balance :

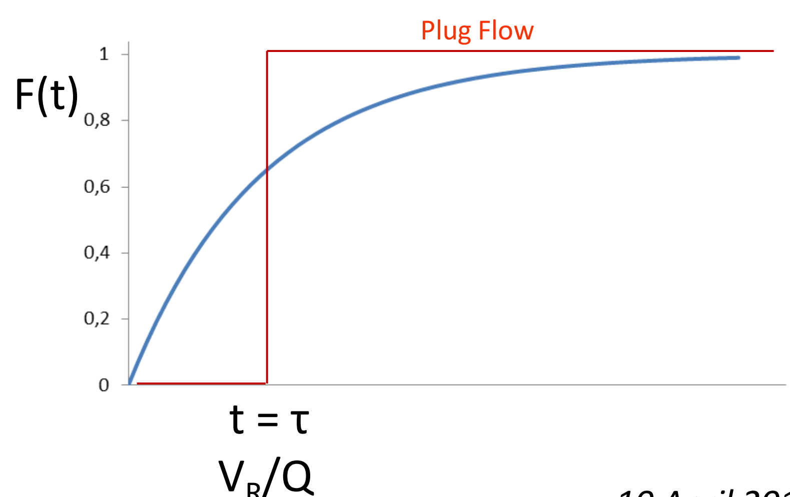
$$Q\,C_{iF} - Q\,C_{iE} = V_R \frac{dC_{iE}}{dt}$$

I. C. : t=0, $C_{iE} = 0$

From solution :

$$\frac{C_{iE}}{C_{iF}} = 1 - e^{-t/\tau} = F(t)$$

Cumulative residence time distribution = % flow with Residence Time < t

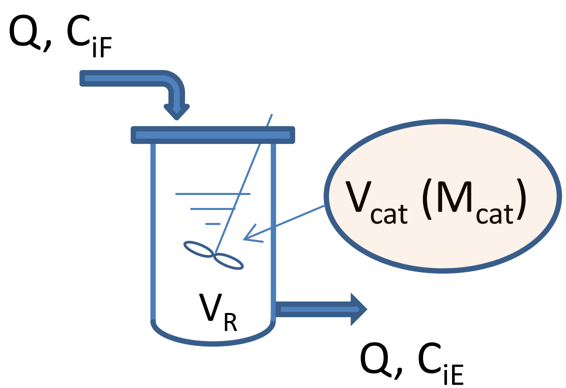


Dynamics of non-homogenuous CSTReactors

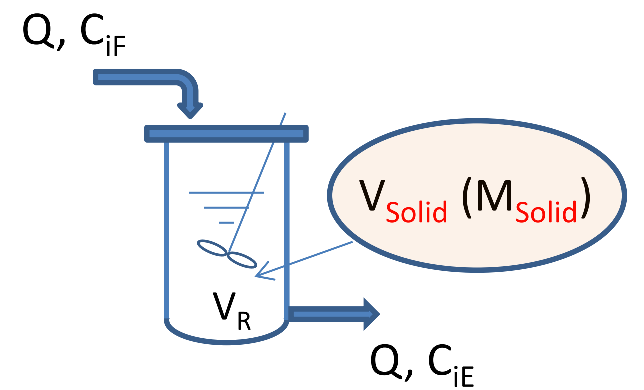
Berty Stationary Basket Catalyst Reactor

Carberry Spinning Basket Catalyst Reactor

Free flowing Catalyst Reactor



Non-catalytic solid decomposition



τ : time constant

Measure of System's Inertia

$$\frac{V_R}{Q + \mathbf{k^* V_{Cat}}}$$

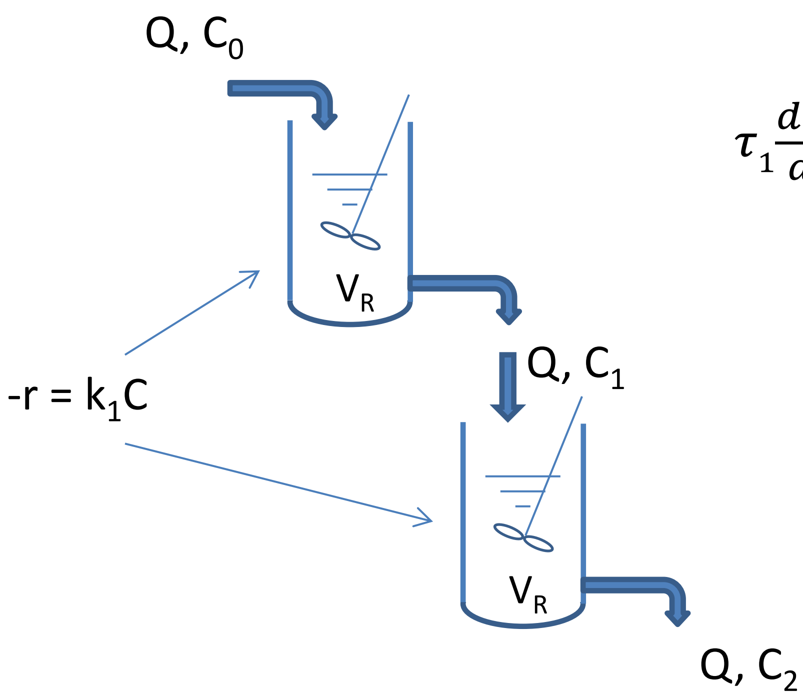
K* = first or linearized-first order catalytic reaction rate constant

$$\frac{V_R}{Q + \mathbf{k^{**}\, V_{Solid}}}$$

K** = first or linearized-first order decomposition rate constant

Second Order Dynamic systems

System with two ***non-interacting*** 1st Order stages in series



$$\tau_1 \frac{dC_1}{dt} + C_1 = \frac{Q}{Q+k_1 VR_1} y_0 = K_1 y_0 \qquad \text{(A)}$$

$$\tau_1 = V_{R1}/(Q + k_1 V_{R1})$$

$$\tau_2 \frac{dC_2}{dt} + C_2 = \frac{Q}{Q+k_2 VR_2} y_1 = K_2 y_1 \qquad \text{(B)}$$

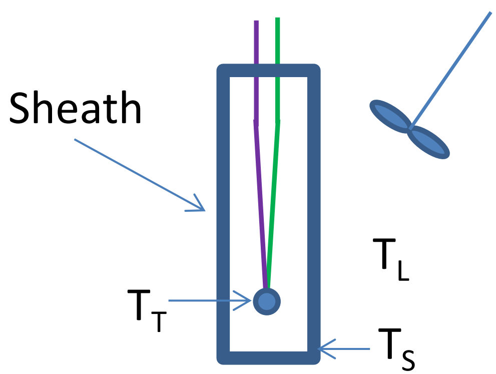
$$\tau_2 = V_{R2}/(Q + k_1 V_{R2})$$

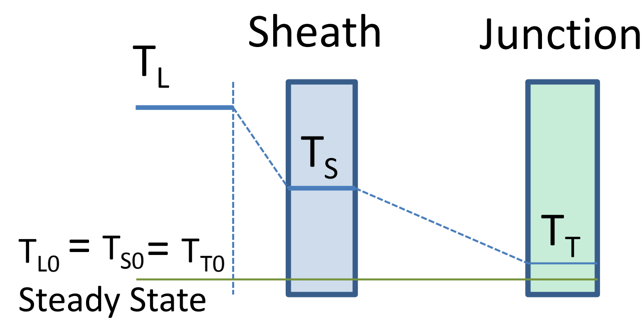
Laplace Transform : (A) → $\dfrac{Ly_2}{Ly_1} = \dfrac{K_2}{1 + \tau_2 s}$

(B) → $\dfrac{Ly_1}{Ly_0} = \dfrac{K_1}{1 + \tau_1 s}$

$$\boxed{\frac{Ly_2}{Ly_0} = \frac{K_1}{1 + \tau_1 s}\ \frac{K_2}{1 + \tau_2 s}}$$

System with two ***interacting*** 1st Order stages in series





Assumptions :

1. Negligible heat loss through cables and sheath top
2. Isothermal sheath walls
3. Isothermal bulb of the measuring junction

Resistances to Heat Flow :

1. From the fluid to the thermowell

$$\overset{o}{q}_L = h_L (T_L - T_S)$$

2. From the sheath to the thermometer junction

$$\overset{o}{q}_V = h_V (T_S - T_T)$$

Thermal Accumulations :

1. In the sheath

$$\overset{o}{q}_S = m_S c_S \frac{dT_S}{dt}$$

2. In the thermometer head

$$\overset{o}{q}_T = m_T c_T \frac{dT_T}{dt}$$

Energy Balances :

1. **Sheath** : $\mathring{q}_L = \mathring{q}_S + \mathring{q}_V$

2. **Thermometer Bulb** : $\mathring{q}_V = \mathring{q}_T$

Final Equation :

$$\tau_S \tau_T \frac{d^2 T_T}{dt^2} + (\tau_S + \tau_T + \tau_{ST})\frac{dT_T}{dt} + TT = TL$$

$$\tau_S = \frac{m_S c_S}{h_L} \qquad \tau_T = \frac{m_T c_T}{h_V} \qquad \tau_{ST} = \frac{m_T c_T}{h_L}$$

With Initial Conditions : at t = 0 : $T_T = 0$, $\frac{dT_T}{dt} = 0$
and Laplace transform

$$G(s) = \frac{LT_T}{LT_L} = \frac{1}{1 + (\tau_S + \tau_T + \tau_{ST})s + \tau_S \tau_T s^2}$$

$$\frac{LT_T}{LT_L} = \frac{1}{(1 + \tau_1 s)\,(1 + \tau_2 s)}$$

Where :

$$\tau_1\,\tau_2 \;=\; \tau_S\,\tau_T$$

$$\tau_1 + \tau_2 \;=\; \tau_S + \tau_T + \tau_{ST}$$

τ_1 and τ_2 are the *'apparent'* time constants of the system

- Both systems composed of two first order systems in series either interacting or non-interacting are described by the same Laplace equation
- For the non-interacting system the two time constants are those corresponding to each first order system
- For the interacting system the time constants are combinations of the characteristic parameters of the system

Response of systems represented by two 1^{st} Order systems is series

$$\boxed{\frac{Ly}{Ly_0} = \frac{K_1K_2}{(1+\tau_1 s)(1+\tau_2 s)}}$$

$$Ly = MK_1K_2 \frac{1/\tau_1}{(s+1/\tau_1)} \frac{1/\tau_2}{(s+1/\tau_2)} \frac{1}{s}$$

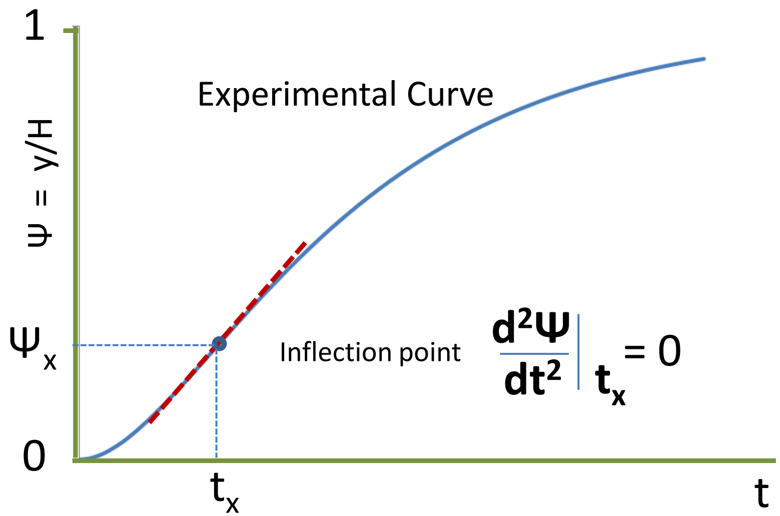
1^{st} Case $\boxed{\tau_1 \neq \tau_2}$

$$Ly = MK_1K_2 \left[\frac{A}{(s+1/\tau_1)} + \frac{B}{(s+1/\tau_2)} + \frac{C}{s} \right]$$

$$\boxed{y = H \left[1 + \frac{\tau_1}{\tau_2 - \tau_1} e^{-t/\tau 1} - \frac{\tau_2}{\tau_2 - \tau_1} e^{-t/\tau 2} \right]}$$

$$\boxed{H = MK_1K_2}$$

Properties of a 2nd Order response curve



$$\left.\frac{d^2\Psi}{dt^2}\right|_{t_x} = 0$$

$$t_x = \frac{\tau_1\,\tau_2 \ln(\tau_1/\tau_2)}{\tau_2 - \tau_1}$$

$$\Psi_x = 1 + (\tau_1 + \tau_2)\left.\frac{d\Psi}{dt}\right|_{t_x}$$

Calculate τ_1, τ_2

2nd Case $\boxed{\tau_1 = \tau_2 = \tau}$

$$Ly = MK_1K_2\,\frac{1/\tau}{(s + 1/\tau)}\,\frac{1/\tau}{(s + 1/\tau)}\,\frac{1}{s}$$

$$\mathbf{y = H\,(\,1 - (1+t/\tau)e^{-t/\tau}\,)}$$

$\Psi_x = 0.265$

$t_x = \tau$

General Second Order Dynamic System

The General Form of 2^{nd} Order Systems is :

$$A\frac{d^2y}{dt^2} + B\frac{dy}{dt} + y = f(t)$$

And for a step stimulus it can be transformed to :

$$\frac{1}{c^2}\frac{d^2y}{dt^2} + 2znc\frac{dy}{dt} + c^2y = c^2H \qquad c = \frac{1}{\sqrt{A}} \qquad z_n = \frac{B}{2\sqrt{A}}$$

With Laplace transform :

$$Ly = \frac{Hc^2}{s(s^2 + 2z_n cs + c^2)} \qquad \text{With roots :} \quad s_{1,2} = -z_n c \pm c\sqrt{z_n{}^2 - 1}$$

1. $z_n > 1$: $s_{1,2}$ real numbers corresponding to two 1^{st} order systems in series
2. $z_n = 1$: Two equal roots. As previously described

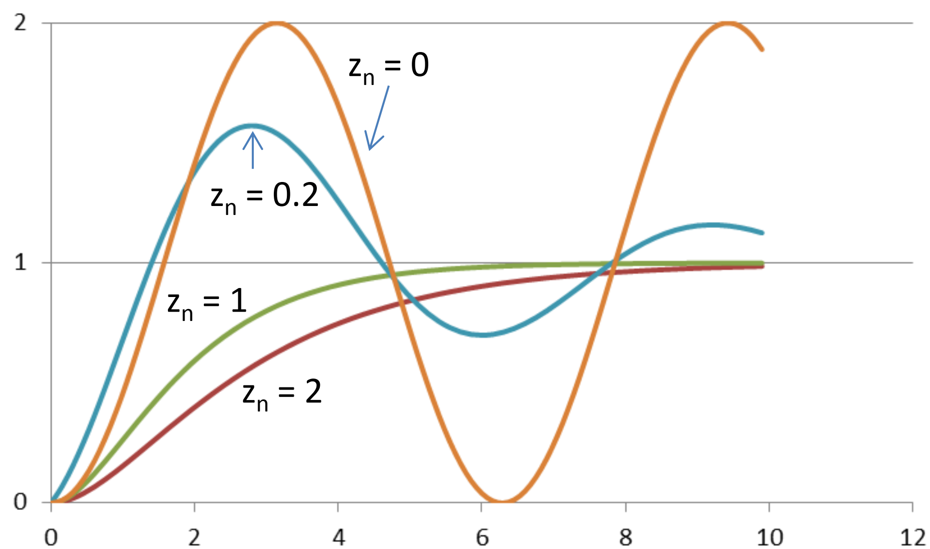
3. $z_n < 1$: In this case the response to a step stimulus will be

$$y = H\left[1 + \frac{1}{\sqrt{1-zn^2}}\, e^{-znct} sin(ct\sqrt{1-zn^2} - \phi)\right]$$

$$\phi = sin^{-1}\sqrt{1-zn^2}$$

3.1 Special case : $z_n = 0$

$$y = H(1 - \cos(z_n t))$$



$z_n > 1$ Over-damped behavior

$z_n = 1$ Critically damped behavior

$0 < z_n < 1$ Under-damped behavior

$z_n = 0$ Undamped behavior
Sustained Oscilation

Transfer Delay in Plug Flow Reactors

By definition of the ideal situation of Plug Flow all the molecules/masses will have the same Residence Time inside the reactor

The elementary masses entering the reactor can be considered as batch reactors operating for a time period equal to Residence Time.

Residence Time

Empty Tubes – Homogeneous reactions $\bar{t} = \tau = \frac{V_R}{Q}$

Tubes filed with solids (catalyst – inerts)

One fluid phase $\bar{t} = \tau = \frac{\varepsilon V_R}{Q}$

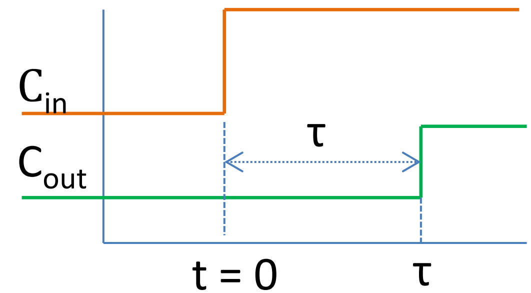
Two fluid phases $\bar{t} = \tau = \frac{h(\varepsilon) V_R}{Q}$

Possible changes during Operation : C_{in}, Q, T/P

C_{IN} Change

Response at the exit **delays** for t = τ

$$\boxed{C_{out}(t) = K\, C_{in}(t-\tau)}$$



K : Attenuation/Amplification Constant

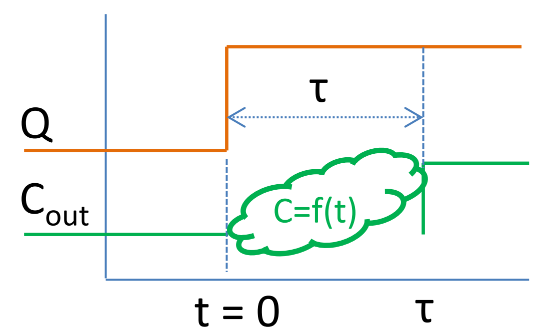
For 1st Order Reaction : $K = 1\text{-}\exp(-k_1\tau)$

Q Change

Residence time will vary according to the Q change

Response at the exit has **no-delay**

f(t) is a function of reaction kinetics and residence time change

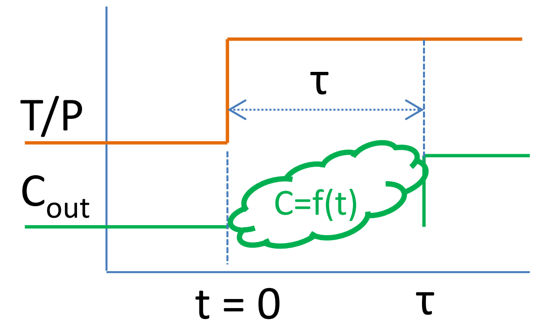


T/P Change

Residence time is constant

Response at the exit has **no-delay**

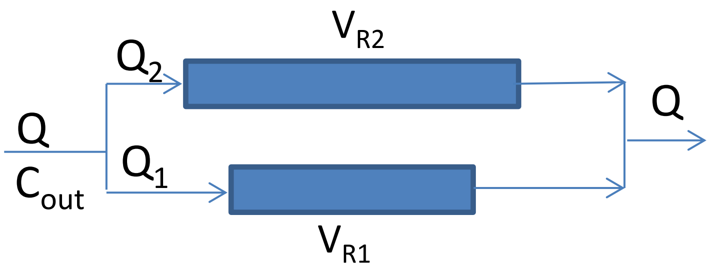
f(t) is a function of reaction kinetics and residence time change

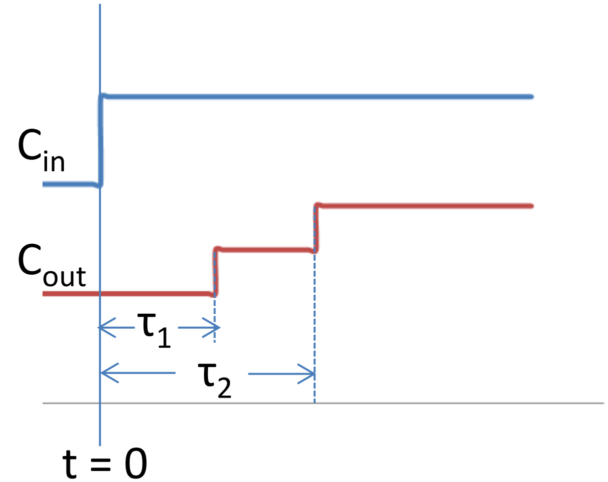


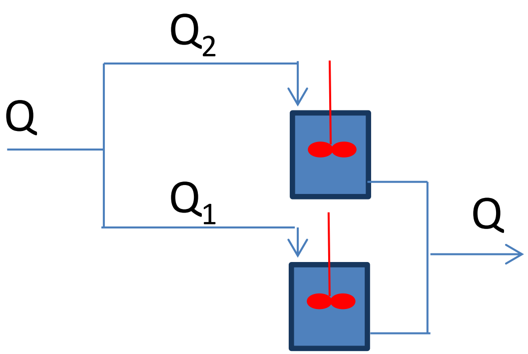
For a step change of T/P

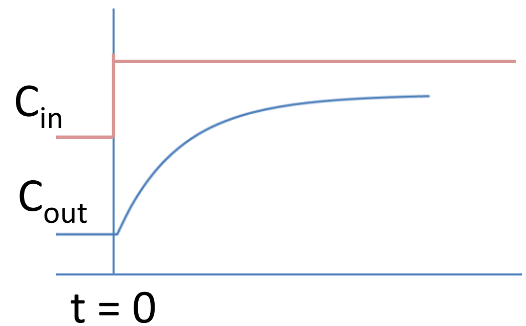
During the transition period (0<t<τ) the exit concentration will be a combination of the initial period before the stimulus and the second period after the stimulus.

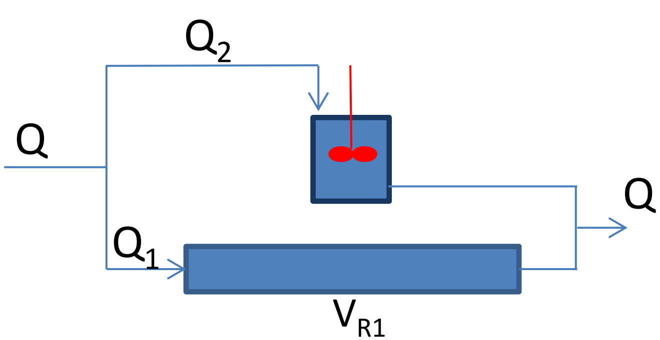
Systems with CSTR and PFR

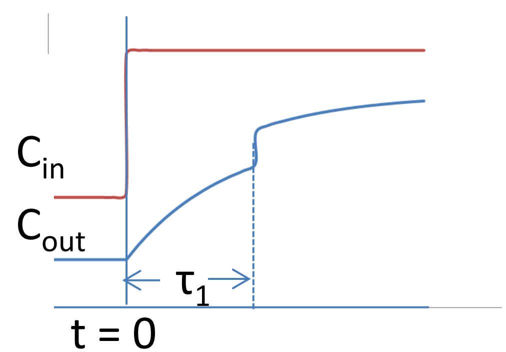












CONCLUSIONS

First Order Systems

1. The way of imposing an Impulse Stimulus does not affect the Response
2. A continuously Changing stimulus results in response Delay and Offset
3. For a Periodic Stimulus an Attenuation of the amplitude is observed with input frequency. The response frequency is the same as the stimulus frequency

Second Order Systems

4. For Non-Interacting two first order systems in series the system's time constants are those of the two 1^{st} Order systems
5. A sigmoid response curve can be simulated by a second order system with time constants calculated from the time and the response of the inflection point

Plug flow reactors

6. The response of a plug flow reactor depends on the Stimulus.
   Changes in input concentration result in response delays equal to R.T. (τ)
   Changes in feed flow rate or operating conditions result in response without delay