Lecture 13

Chemical Reaction Engineering (CRE) is the field that studies the rates and mechanisms of chemical reactions and the design of the reactors in which they take place.

Lecture 13 – Tuesday

- Complex Reactions:

$$A + 2B \rightarrow C$$

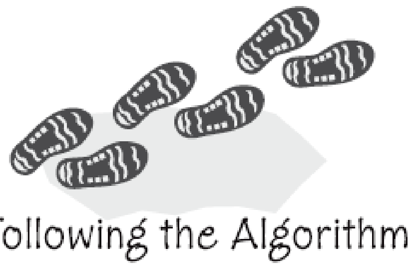
$$A + 3C \rightarrow D$$

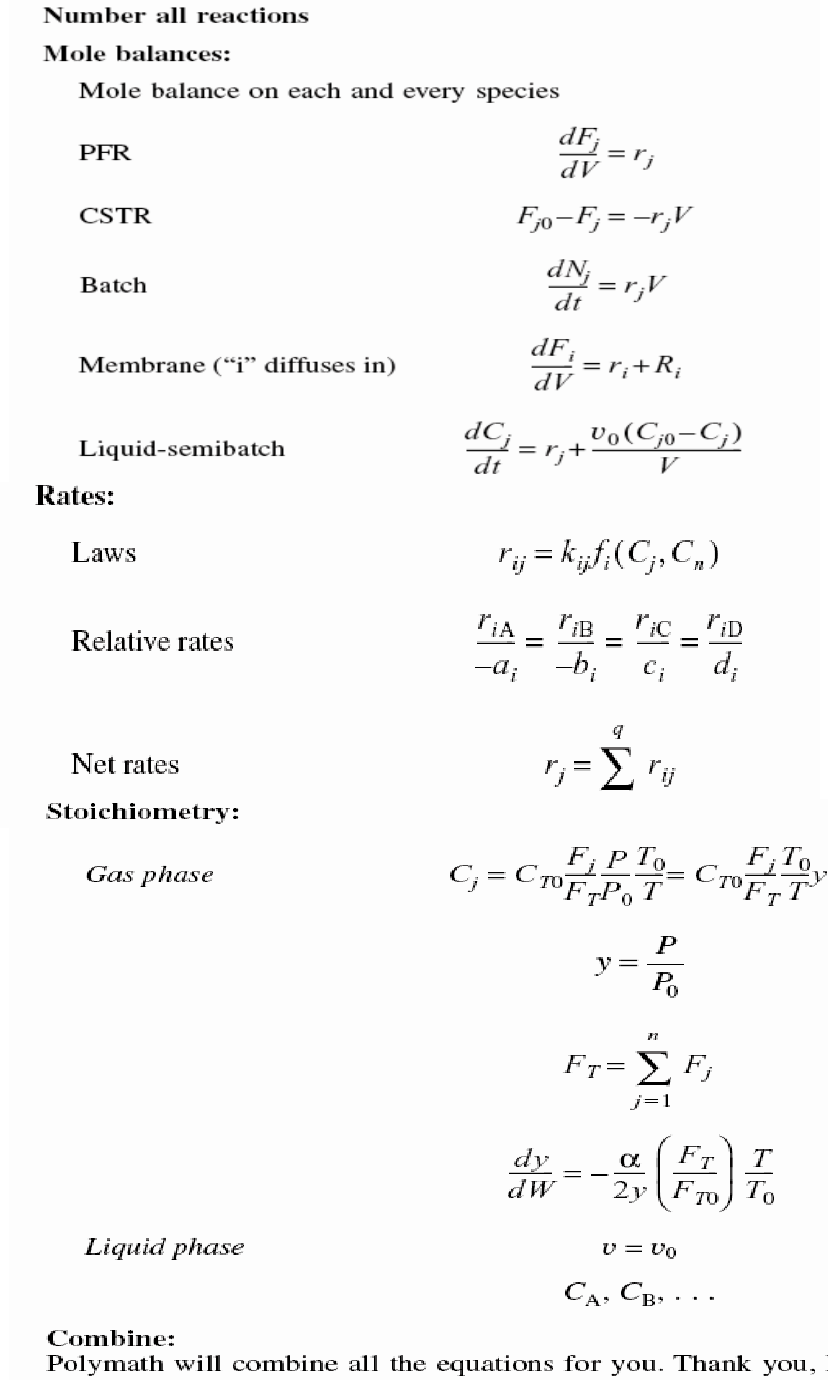
  - Example A: Liquid Phase PFR
  - Example B: Liquid Phase CSTR
  - Example C: Gas Phase PFR
  - Example D: Gas Phase Membrane Reactors

    Sweep Gas Concentration Essentially Zero

    Sweep Gas Concentration Increases with Distance
  - Example E: **Semibatch Reactor**

Gas Phase
Multiple Reactions





Number all reactions

Mole balances:

Mole balance on each and every species

PFR $$\frac{dF_j}{dV} = r_j$$

CSTR $$F_{j0} - F_j = -r_j V$$

Batch $$\frac{dN_j}{dt} = r_j V$$

Membrane ("i" diffuses in) $$\frac{dF_i}{dV} = r_i + R_i$$

Liquid-semibatch $$\frac{dC_j}{dt} = r_j + \frac{v_0(C_{j0} - C_j)}{V}$$

Rates:

Laws $$r_{ij} = k_{ij} f_i(C_j, C_n)$$

Relative rates $$\frac{r_{iA}}{-a_i} = \frac{r_{iB}}{-b_i} = \frac{r_{iC}}{c_i} = \frac{r_{iD}}{d_i}$$

Net rates $$r_j = \sum^{q} r_{ij}$$

Stoichiometry:

Gas phase $$C_j = C_{T0}\frac{F_j}{F_T}\frac{P}{P_0}\frac{T_0}{T} = C_{T0}\frac{F_j}{F_T}\frac{T_0}{T}y$$

$$y = \frac{P}{P_0}$$

$$F_T = \sum_{j=1}^{n} F_j$$

$$\frac{dy}{dW} = -\frac{\alpha}{2y}\left(\frac{F_T}{F_{T0}}\right)\frac{T}{T_0}$$

Liquid phase $$v = v_0$$

$$C_A, C_B, \ldots$$

Combine:

Polymath will combine all the equations for you. Thank you,

New things for multiple reactions are:

1. Number Every Reaction

2. Mole Balance on every species

3. Rate Laws

(a) Net **Rates** of Reaction for every species

$$r_A = \sum_{i=1}^{N} r_{iA}$$

(b) **Rate** Laws for every reaction

$$r_{1A} = -k_{1A} C_A C_B^2$$

$$r_{2C} = -k_{2C} C_A^2 C_C^3$$

(c) Relative **Rates** of Reaction for every reaction

For a given reaction i: (i) $\mathbf{a_i}A + \mathbf{b_i}B \rightarrow \mathbf{c_i}C + \mathbf{d_i}D$:

$$\frac{r_{iA}}{-a_i} = \frac{r_{iB}}{-b_i} = \frac{r_{iC}}{c_i} = \frac{r_{iD}}{d_i}$$

Reactor **Mole Balance** Summary

Reactor Type	Gas Phase	Liquid Phase
Batch	$\frac{dN_A}{dt} = r_A V$	$\frac{dC_A}{dt} = r_A$
Semibatch	$\frac{dN_A}{dt} = r_A V$	$\frac{dC_A}{dt} = r_A - \frac{\upsilon_0 C_A}{V}$
	$\frac{dN_B}{dt} = r_B V + F_{B0}$	$\frac{dC_B}{dt} = r_B + \frac{\upsilon_0 \left[C_{B0} - C_B \right]}{V}$

Reactor **Mole Balance** Summary

Reactor Type	Gas Phase	Liquid Phase
CSTR	$V = \frac{F_{A0} - F_A}{-r_A}$	$V = \upsilon_0 \frac{\left(C_{A0} - C_A\right)}{-r_A}$
PFR	$\frac{dF_A}{dV} = r_A$	$\upsilon_0 \frac{dC_A}{dV} = r_A$
PBR	$\frac{dF_A}{dW} = r'_A$	$\upsilon_0 \frac{dC_A}{dW} = r'_A$

Note: The reaction **rates** in the above **mole balances** are net rates.

Batch

$$C_B = \frac{N_B}{V}$$

$$V = V_0 \frac{N_T}{N_{T0}} \frac{P_0}{P} \frac{T_0}{T}$$

$$C_B = \frac{N_B}{N_T} \frac{N_{T0}}{V_0} \frac{P}{P_0} \frac{T_0}{T}$$

$$C_B = C_{T0} \frac{N_B}{N_T} \frac{P}{P_0} \frac{T_0}{T}$$

Flow

$$C_B = \frac{F_B}{\upsilon}$$

$$\upsilon = \upsilon_0 \frac{F_T}{F_{T0}} \frac{P_0}{P} \frac{T_0}{T}$$

$$C_B = \frac{F_B}{F_T} \frac{F_{T0}}{\upsilon_0} \frac{P}{P_0} \frac{T_0}{T}$$

$$C_B = C_{T0} \frac{F_B}{F_T} \frac{P}{P_0} \frac{T_0}{T}$$

Stoichiometry

Concentration of Gas:

$$C_A = C_{T0}\left(\frac{F_A}{F_T}\right)y\left(\frac{T_0}{T}\right) \qquad F_T = F_A + F_B + F_C + F_D$$

Note: We could use the gas phase mole balances for **liquids** and then just express the concentration as:

Flow: $C_A = \dfrac{F_A}{\upsilon_0}$

Batch: $C_A = \dfrac{N_A}{V_0}$

Example A: Liquid Phase PFR

The complex liquid phase reactions follow elementary rate laws:

$$(1)\ \ A + 2B \rightarrow C \qquad -r_{1A} = k_{1A} C_A C_B^2$$

NOTE: The specific reaction rate k_{1A} is defined with respect to species A.

$$(2)\ \ 3C + 2A \rightarrow D \qquad -r_{2C} = k_{2C} C_C^3 C_A^2$$

NOTE: The specific reaction rate k_{2C} is defined with respect to species C.

Example A: Liquid Phase PFR

Complex Reactions

$$(1)\quad A + 2B \rightarrow C$$

$$(2)\quad A + 3C \rightarrow D$$

1) Mole Balance on each and every species

$$(1)\quad \frac{dF_A}{dV} = r_A \qquad (2)\quad \frac{dF_B}{dV} = r_B$$

$$(3)\quad \frac{dF_C}{dV} = r_C \qquad (4)\quad \frac{dF_D}{dV} = r_D$$

Example A: Liquid Phase PFR

2) Rate Laws:

Net Rates

$$(5)\ r_A = r_{1A} + r_{2A} \qquad (7)\ r_B = r_{1B} + r_{2B}$$

$$(6)\ r_C = r_{1C} + r_{2C} \qquad (8)\ r_D = 0 + r_{2D}$$

Rate Laws

$$(9)\ r_{1A} = -k_{1A} C_A C_B^2$$

$$(10)\ r_{2C} = -k_{2C} C_A^2 C_C^3$$

Relative Rates

Reaction 1

$$\frac{r_{1A}}{-1} = \frac{r_{1B}}{-2} = \frac{r_{1C}}{1}$$

$$(11)\ r_{1B} = 2r_{1A}$$

$$(12)\ r_{1C} = -r_{1A}$$

Example A: Liquid Phase PFR

Relative Rates
Reaction 2

$$\frac{r_{2A}}{-2} = \frac{r_{2C}}{-3} = \frac{r_{2D}}{1}$$

$$(13)\ r_{2A} = \frac{2}{3} r_{2C}$$

$$(14)\ r_{2D} = -\frac{r_{2C}}{3}$$

$$r_A = -k_{1A} C_A C_B^2 - \frac{2}{3} k_{2C} C_A^2 C_C^3$$

$$r_B = -2k_{1A} C_A C_B^2$$

$$r_C = k_{1A} C_A C_B - k_{2C} C_A^2 C_C^3$$

$$r_D = \frac{k_{2C}}{3} C_A^2 C_C^3$$

Example A: Liquid Phase PFR

3) Stoichiometry

Liquid

$$(15)\ C_A = F_A / \upsilon_0$$

$$(16)\ C_B = F_B / \upsilon_0$$

$$(17)\ C_C = F_C / \upsilon_0$$

$$(18)\ C_D = F_D / \upsilon_0$$

$$(19)\ \tilde{S}_{C/D} = if\ (V > 0.00001)\ \text{then}\left(\frac{F_C}{F_D}\right)\text{else}\ 0$$

Example A: Liquid Phase PFR

Others

$F_T = \text{Liquid} - \text{Not Needed}$

$(19)\ \alpha = \text{Liquid} - \text{Not Needed}$

$(20)\ C_{T0} = \text{Liquid} - \text{Not Needed}$

4) Parameters

$(21)\ k_{1A} = 10$

$(22)\ k_{2C} = 20$

$(23)\ \alpha = \text{Liquid}$

$(24)\ C_{T0} = \text{Liquid}$

$(25)\ V_f = 2500$

$(26)\ F_{A0} = 200$

$(28)\ F_{B0} = 200$

$(26)\ \upsilon_0 = 100$

Example B: Liquid Phase CSTR

Same reactions, rate laws, and rate constants as Example A

$$(1)\quad A + 2B \rightarrow C \qquad\qquad -r_{1A} = k_{1A} C_A C_B^2$$

NOTE: The specific reaction rate k_{1A} is defined with respect to species A.

$$(2)\quad 3C + 2A \rightarrow D \qquad\qquad -r_{2C} = k_{2C} C_C^3 C_A^2$$

NOTE: The specific reaction rate k_{2C} is defined with respect to species C.

Example B: Liquid Phase CSTR

The complex liquid phase reactions take place in a 2,500 dm^3 CSTR. The feed is equal molar in A and B with F_{A0}=200 mol/min, the volumetric flow rate is 100 dm^3/min and the reaction volume is 50 dm^3.

Find the concentrations of A, B, C and D existing in the reactor along with the existing selectivity.

Plot F_A, F_B, F_C, F_D and $S_{C/D}$ as a function of V

Example B: Liquid Phase CSTR

(1) $A + 2B \rightarrow C$ (2) $2A + 3C \rightarrow D$

$$r_{1A} = -k_{1A}C_A C_B^2$$

$$r_{2C} = -k_{2C}C_A^2 C_C^3$$

1) Mole Balance

(1) A $\upsilon_0 C_{A0} - \upsilon_0 C_A + r_A V = 0$

(2) B $\upsilon_0 C_{B0} - \upsilon_0 C_B + r_B V = 0$

(3) C $0 - \upsilon_0 C_C + r_C V = 0$

(4) D $0 - \upsilon_0 C_D + r_D V = 0$

Example B: Liquid Phase CSTR

2) Rate Laws: (5)-(14) same as PFR

3) Stoichiometry: (15)-(18)
same as Liquid Phase PFR

$$(19)\ S_{C/D} = \frac{F_C}{F_D + 0.0001} = \frac{\upsilon_0 C_C}{\upsilon_0 C_D + 0.0001}$$

4) Parameters:

$$k_{1A},\quad k_{2C},\quad C_{A0},\quad C_{B0},\quad V,\quad \upsilon_0$$

Example B: Liquid Phase CSTR

In terms of molar flow rates

(1) A + 2B → C   (2) 2A + 3C → D

$$r_{1A} = -k_{1A} C_A C_B^2$$

$$r_{2C} = -k_{2C} C_A^2 C_C^3$$

1) Mole Balance (1–4)

$$(1)\ f\left(F_A\right) = F_{A0} - F_A + r_A V \quad (=0)$$

$$(2)\ f\left(F_B\right) = F_{B0} - F_B + r_B V \quad (=0)$$

$$(3)\ f\left(F_C\right) = 0 - F_C + r_C V \quad (=0)$$

$$(4)\ f\left(F_D\right) = 0 - F_D + r_D V \quad (=0)$$

2) Rates (5–14)

Same as Example A

3) Stoichiometry: (15–19)

$$(15)\quad C_A = F_A / \upsilon_0$$

$$(16)\quad C_B = F_B / \upsilon_0$$

$$(17)\quad C_C = F_C / \upsilon_0$$

$$(18)\quad C_D = F_D / \upsilon_0$$

$$(19)\quad S_{C/D} = \frac{F_C}{F_D + 0.00001}$$

Example B: Liquid Phase CSTR

In terms of concentration

(1) A + 2B →C   (2) 2A + 3C → D

$$r_{1A} = -k_{1A} C_A C_B^2$$

$$r_{2C} = -k_{2C} C_A^2 C_C^3$$

1) Mole Balance (1–4)

$$(1)\ f(C_A) = \upsilon_0 C_{A0} - \upsilon_0 C_A + r_A V$$ (=0)

$$(2)\ f(C_B) = \upsilon_0 C_{B0} - \upsilon_0 C_B + r_B V$$ (=0)

$$(3)\ f(C_C) = 0 - \upsilon_0 C_C + r_C V$$ (=0)

$$(4)\ f(C_D) = 0 - \upsilon_0 C_D + r_D V$$ (=0)

2) Rates (5–14)

Same as
Example A

3) Stoichiometry: (15–19)

$$(15)\ S_{C/D} = \frac{F_C}{F_D + 0.00001}$$

Example C: Gas Phase PFR, No ΔP

Same reactions, rate laws, and rate constants as Example A:

$$(1)\quad A + 2B \rightarrow C \qquad\qquad -r_{1A} = k_{1A} C_A C_B^2$$

NOTE: The specific reaction rate k_{1A} is defined with respect to species A.

$$(2)\quad 3C + 2A \rightarrow D \qquad\qquad -r_{2C} = k_{2C} C_C^3 C_A^2$$

NOTE: The specific reaction rate k_{2C} is defined with respect to species C.

Example C: Gas Phase PFR, No ΔP

1) Mole Balance

$$(1)\quad \frac{dF_A}{dV} = r_A \qquad (3)\quad \frac{dF_C}{dV} = r_C$$

$$(2)\quad \frac{dF_B}{dV} = r_B \qquad (4)\quad \frac{dF_D}{dV} = r_D$$

2) Rate Laws: (5)-(14) same as CSTR

Example C: Gas Phase PFR, No ΔP

3) Stoichiometry:

Gas: Isothermal $T = T_0$

$$(15)\ C_A = C_{T0}\frac{F_A}{F_T}y \qquad (16)\ C_B = C_{T0}\frac{F_B}{F_T}y$$

$$(17)\ C_C = C_{T0}\frac{F_C}{F_T}y \qquad (18)\ C_D = C_{T0}\frac{F_D}{F_T}y$$

$$(19)\ F_T = F_A + F_B + F_C + F_D$$

Packed Bed with Pressure Drop

$$\frac{dy}{dW} = -\frac{\alpha}{2y}\left(\frac{F_T}{F_{T0}}\right)\left(\frac{T}{T_0}\right) = -\frac{\alpha}{2y}\frac{F_T}{F_{T0}}$$

Example C: Gas Phase PFR, No ΔP

4) Selectivity

$$S = \frac{F_C}{F_D} = \text{if } (V > 0.00001) \text{ then } \left(\frac{F_C}{F_D}\right) \text{ else}(0) \quad (20)$$

$$y = 1 \quad (21)$$

Example D: Membrane Reactor with ΔP

Same reactions, rate laws, and rate constants as Example A:

$$(1)\quad A + 2B \rightarrow C \qquad\qquad -r_{1A} = k_{1A}C_A C_B^2$$

NOTE: The specific reaction rate k_{1A} is defined with respect to species A.

$$(2)\quad 3C + 2A \rightarrow D \qquad\qquad -r_{2C} = k_{2C}C_C^3 C_A^2$$

NOTE: The specific reaction rate k_{2C} is defined with respect to species C.

Example D: Membrane Reactor with ΔP

Because the smallest molecule, and the one with the lowest molecular weight, is the one diffusing out, we will neglect the changes in the mass flow rate down the reactor and will take as first approximation: $\dot{m}_0 = \dot{m}$

1) Mole Balances

$$A \qquad \frac{dF_A}{dV} = r_A \quad (1) \qquad C \quad \frac{dF_C}{dV} = r_C - R_C \quad (3)$$

$$B \qquad \frac{dF_B}{dV} = r_B \quad (2) \qquad D \quad \frac{dF_D}{dV} = r_D \quad (4)$$

We also need to account for the molar rate of desired product C leaving in the sweep gas F_{Csg} $\frac{dF_{Csg}}{dV} = R_C$

Example D: Membrane Reactor with ΔP

We need to reconsider our pressure drop equation.

When mass diffuses out of a membrane reactor there will be a decrease in the superficial mass flow rate, G. To account for this decrease when calculating our pressure drop parameter, we will take the ratio of the superficial mass velocity at any point in the reactor to the superficial mass velocity at the entrance to the reactor.

$$\alpha = \alpha_0 \frac{G}{G_0} = \alpha_0 \left[\frac{\sum F_i \cdot MW_i}{\sum F_{i0} \cdot MW_i} \right]$$

Example D: Membrane Reactor with ΔP

The superficial mass flow rates can be obtained by multiplying the species molar flow rates, F_i, by their respective molecular weights, Mw_i, and then summing over all species:

$$\frac{G}{G_0} = \frac{m / A_{C_1}}{m_0 / A_{C_1}} = \frac{\sum F_i \cdot (MW_i) / A_{C_1}}{\sum F_{i0} \cdot (MW_i) / A_{C_1}} = \frac{\sum F_i (MW_i)}{\sum F_{i0} (MW_i)}$$

Example D: Membrane Reactor with ΔP

2) Rate Laws: (5)-(14) same as Examples A, B, and C.

3) Stoichiometry: (15)-(20) same as Examples A and B (T=T_0)

$$\frac{dy}{dW} = -\frac{\alpha}{2y}\frac{F_T}{F_{T0}} \qquad \frac{dy}{dV} = -\frac{\rho\alpha}{2y}\frac{F_T}{F_{T0}} \quad (21)$$

$$R_C = k_C\left(C_C - C_{CSweep}\right)$$

4) Sweep Gas Balance:

$$F_{Csg}\Big|_V - F_{Csg}\Big|_{V+\Delta V} + R_C \Delta V = 0$$

$$\frac{dF_{Csg}}{dV} = R_C$$

Example E: Liquid Phase Semibatch

Same reactions, rate laws, and rate constants as Example A:

$$(1)\quad A + 2B \rightarrow C \qquad\qquad -r_{1A} = k_{1A} C_A C_B^2$$

NOTE: The specific reaction rate k_{1A} is defined with respect to species A.

$$(2)\quad 3C + 2A \rightarrow D \qquad\qquad -r_{2C} = k_{2C} C_C^3 C_A^2$$

NOTE: The specific reaction rate k_{2C} is defined with respect to species C.

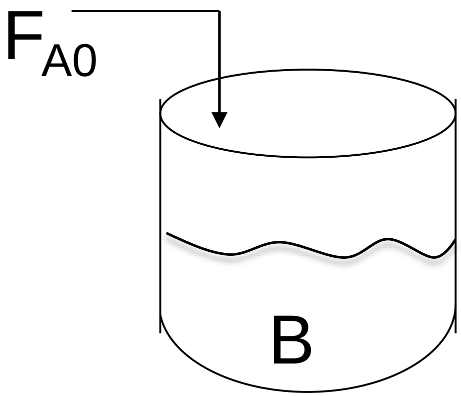
Example E: Liquid Phase Semibatch

The complex liquid phase reactions take place in a **semibatch reactor** where A is fed to B with F_{A0}= 3 mol/min. The volumetric flow rate is 10 dm^3/min and the initial reactor volume is 1,000 dm^3.

The maximum volume is 2,000 dm^3 and C_{A0}=0.3 mol/dm^3 and C_{B0}=0.2 mol/dm^3. Plot C_A, C_B, C_C, C_D and $S_{S/D}$ as a function of time.

Example E: Liquid Phase Semibatch

(1) $A + 2B \rightarrow C$ (2) $2A + 3C \rightarrow D$



1) Mole Balances:

$$\frac{dN_A}{dt} = r_A V + F_{A0} \qquad N_{A0} = 0$$

$$\frac{dN_B}{dt} = r_B V \qquad N_{B0} = C_{B0} V_0 = 2.000$$

$$\frac{dN_C}{dt} = r_C V \qquad N_{C0} = 0$$

$$\frac{dN_D}{dt} = r_D V \qquad N_{D0} = 0$$

Example E: Liquid Phase Semibatch

2) Rate Laws: (5)-(14)

Net Rate, Rate Laws and relative rate – are the same as Liquid and Gas Phase PFR and Liquid Phase CSTR

$$V = V_0 + v_0 t \quad (15)$$

$$C_A = \frac{N_A}{V} \quad (16) \qquad C_B = \frac{N_B}{V} \quad (17)$$

$$C_C = \frac{N_C}{V} \quad (18) \qquad C_D = \frac{N_D}{V} \quad (19)$$

3) Selectivity and Parameters:

$$S_{C/D} = \text{if } (t > 0.0001) \text{ then} \left(\frac{N_C}{N_D} \right) \text{else} (0) \quad (20)$$

$$\upsilon_0 = 10 \text{dm}^3/\text{min} \quad \text{V}_0 = 100 \text{dm}^3 \quad \text{F}_{\text{A0}} = 3 \text{mol}/\text{min}$$

End of Lecture 13