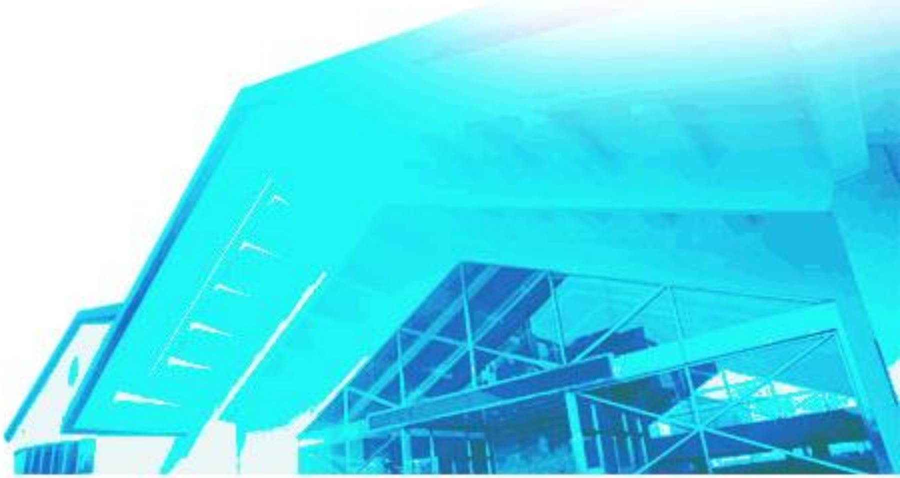
Mole Balances



Chemical Identity

A chemical species is said to have reacted when it has lost its chemical identity. The identity of a chemical species is determined by the kind, number, and configuration of that species' atoms.

Three ways a chemical species can lose its chemical identity:

decomposition

$$CH_3CH_3 \rightarrow H_2 + H_2C = CH_2$$

combination

$$N_2 + O_2 \rightarrow 2NO$$

isomerization

$$C_2H_5CH = CH_2 \rightarrow CH_2 = C(CH_3)$$

Reaction Rate

The reaction rate is the rate at which a species looses its chemical identity per unit volume.

The rate of a reaction can be expressed as the rate of disappearance of a reactant or as the rate of appearance of a product.

Consider species A:

$$A \rightarrow B$$

r_A = the rate of formation of species A per unit volume

$-r_A$ = the rate of a disappearance of species A per unit volume mol/dm$^3\cdot$s

r_B = the rate of formation of species B per unit volume

$\longrightarrow -r_A = r_B$

For a catalytic reaction, we refer to $-r_A'$, which is the rate of disappearance of species A on a per mass of catalyst basis. mol/s·g catalyst

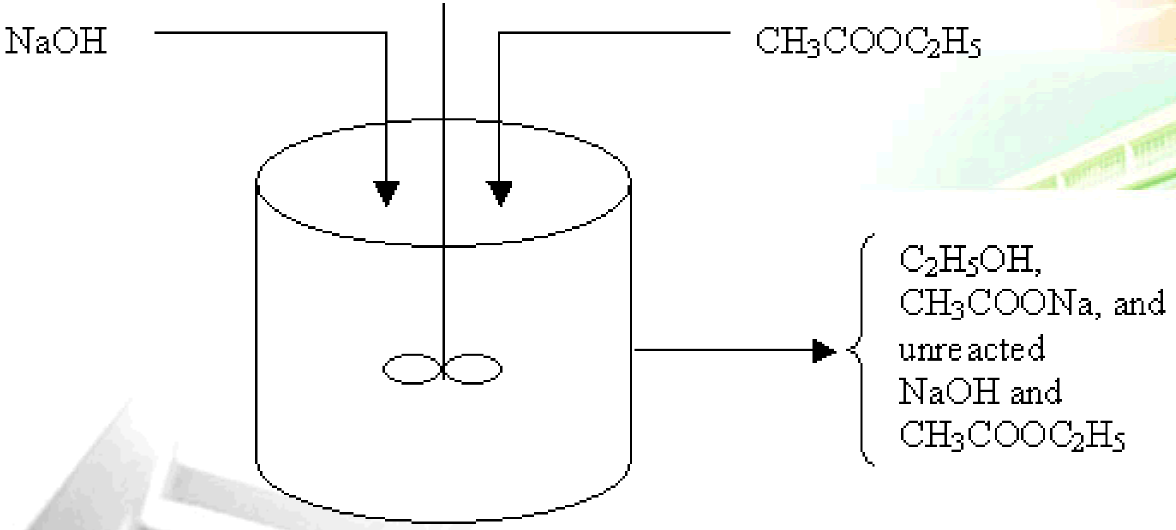
Note: dC_A/dt is not the rate of reaction $\longrightarrow$ $r_A = \frac{dC_A}{dt}$ for a constant-volume batch reactor

Example~Is sodium hydroxide reacting?

Sodium hydroxide and ethyl acetate are continuously fed to a rapidly stirred tank in which they react to form sodium acetate and ethanol:

$$NaOH + CH_3COOC_2H_5 \rightarrow CH_3COONa + C_2H_5OH$$

The product stream, containing sodium acetate and ethanol, together with the unreacted sodiium hydroxide and ethyl acetate, is continuously withdrawn from the tank at a rate equal to the total feed rate. The contents of the tank in which this reaction is taking place may be considered to be perfectly mixed. Because the system is operated at steady state, if we were to withdraw liquid samples at some location in the tank at various times and analyze them chemically, we would find that the concentrations of the individual species in the different samples were identical. That is, the concentration of the sample taken at 1 P.M. is the same as the that of the sample taken at 3 P.M.



Well mixed reaction vessel

Because the species concentrations are constant and therefore do not change with time,

$$\frac{dC_A}{dt} = 0 \quad \text{where A is NaOH.} \longrightarrow r_A = 0$$

Which is <u>incorrect</u> because C_2H_5OH and CH_3COONa are being formed from NaOH and $CH_3COOC_2H_5$ at a finite rate.

Consequently, the rate of reaction as defined by $r_A = \frac{dC_A}{dt}$ cannot apply to a flow system and is <u>incorrrect</u> if it is defined in this manner.

Note:

Consider species j:

r_j is the rate of formation of species j per unit volume [e.g. $mol/dm^3 \cdot s$]

r_j is <u>a function of concentration, temperature, pressure, and the type of catalyst</u> (if any)

r_j is <u>independent of the type of reaction system</u> (batch, plug flow, etc.)

r_j is an algebraic equation, <u>not</u> a differential equation

We use an algebraic equation to relate the rate of reaction, $-r_A$, to the concentration of reacting species and to the temperature at which the reaction occurs. [e.g. $-r_A = k(T)C_A^2$].

Convention for Rates of Reaction

Consider the reaction

$$A+2B \rightarrow 3C$$

in which the rate of disappearance of A is 5 moles of A per dm^3 per second at the start of the reaction.

At the start of the reaction

(a) What is $-r_A$?

(b) What is the rate of formation of B?

(c) What is the rate of formation of C?

(d) What is the rate of disappearance of C?

(e) What is the rate of formation of A, r_A?

(f) What is $-r_B$?

Solution

(a) Rate of disappearance of A = $-r_A$ = 5 mole/dm^3/s

(b) Rate of formation of B = r_B = -5*2 = -10 mole/dm^3/s

(c) Rate of formation of C = r_C = 5*3 = 15 mole/dm^3/s

(d) Rate of disappearance of C = $-r_C$ = -15 mole/dm^3/s

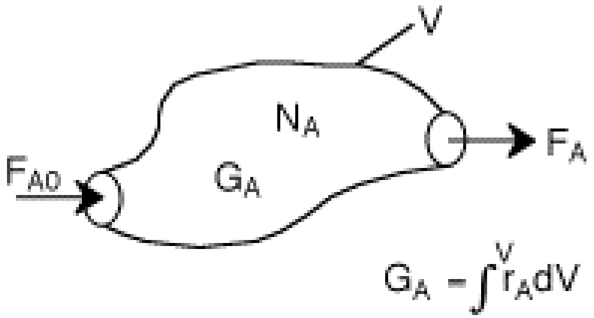
(e) Rate of formation of A = r_A = -5 mole/dm^3/s

(f) Rate of disappearance of B = $-r_B$ = 10 mole/dm^3/s

→ rate of reaction=?

General Mole Balance Equation

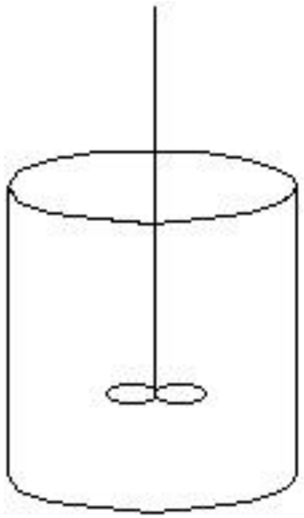
IN - OUT + GENERATION = ACCUMULATION



$$F_{A0} - F_A + G_A = \frac{dN_A}{dt} \longrightarrow F_{A0} - F_A + \int^V r_A dV = \frac{dN_A}{dt}$$

Batch Reactor

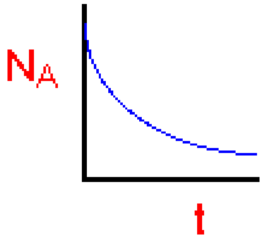
General mole balance on system volume V



No inflow or outflow $\longrightarrow$ $F_{A0} = F_A = 0$

$$F_{A0} - F_A + \int^{V} r_A \, dV = \frac{dN_A}{dt} \longrightarrow r_A V = \frac{dN_A}{dt}$$

well mixed



Example~Constant Volume or Constant Pressure

Write the mole balance for dimethyl ether in terms of the reactor volume, concentration, and rate of formation of dimethyl ether for both a constant-pressure and a constant-volume batch reactor.

Solution

$A \rightarrow M + H + C$ **M is methane, H is hydrogen, and C is carbon monoxide.**

For both batch reactor, the mole balance on A is

$$r_A V = \frac{dN_A}{dt} \longrightarrow \frac{1}{V}\frac{dN_A}{dt} = r_A$$

Constant-volume batch reactor $\longrightarrow$ $\dfrac{d(N_A/V)}{dt} = \dfrac{dC_A}{dt} = r_A$

Constant-pressure batch reactor $\longrightarrow$ $\dfrac{1}{V}\dfrac{dN_A}{dt} = \dfrac{1}{V}\dfrac{d(C_A V)}{dt} = \dfrac{dC_A}{dt} + \dfrac{C_A}{V}\dfrac{dV}{dt} = r_A$

$$r_A = \frac{dC_A}{dt} + \frac{C_A \, d\ln V}{dt}$$

Example~Batch Reactor Times

Consider the reaction

$$A \rightarrow B$$

Calculate the time to reduce the number of moles by a factor of 10 in a batch reactor for the above reaction with $-r_A = kC_A$, when $k = 0.046\ \mathrm{min}^{-1}$.

Solution

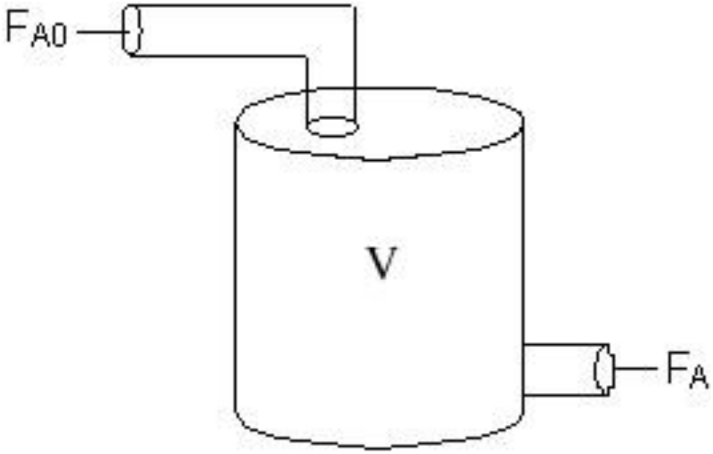
$$F_{A0} - F_A + \int^V r_A\,dV = \frac{dN_A}{dt} \xrightarrow[-r_A = kC_A = k\frac{N_A}{V}]{F_{A0} = F_A = 0} \frac{dN_A}{dt} = -kN_A$$

$$\xrightarrow[N_A = N_A \bullet\bullet\bullet t \quad = t]{N_A = N_{A0} \bullet\bullet t \quad = 0} t = \int_{N_{A0}}^{N_A} \frac{dN_A}{-kN_A} \longrightarrow t = \frac{1}{k}\ln\frac{N_{A0}}{N_A}$$

$$\longrightarrow t = \frac{1}{k}\ln\frac{N_{A0}}{N_A} = \frac{1}{0.046}\ln(10) = 50 \bullet \mathrm{min}$$

Continuous-Stirred Tank Reactor, CSTR

General mole balance on system volume V



$$F_{A0} - F_A + \int^{V} r_A dV = \frac{dN_A}{dt}$$

Steady state

$$\frac{dN_A}{dt} = 0$$

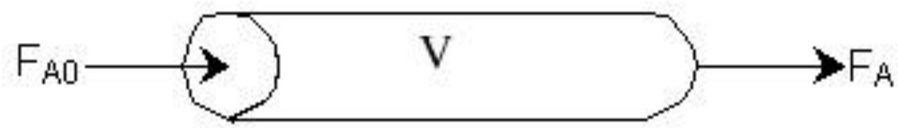
Well mixed

$$\int^{V} r_A dV = r_A V$$

$$\left.\begin{matrix} \frac{dN_A}{dt} = 0 \\ \int^{V} r_A dV = r_A V \end{matrix}\right\} \longrightarrow F_{A0} - F_A + r_A V = 0 \longrightarrow V = \frac{F_{A0} - F_A}{-r_A}$$

Plug-Flow Reactor, PFR

General mole balance on system volume V



No radial variation in concentration
The reactants are continuously consumed as they flow down the length of the reactor.

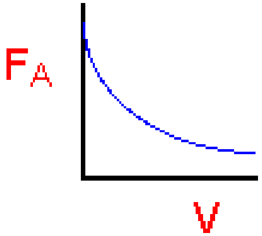
$$F_{A0} - F_A + \int^{V} r_A dV = \frac{dN_A}{dt}$$

Steady state

$$\frac{dN_A}{dt} = 0 \longrightarrow F_{A0} - F_A + \int^{V} r_A dV = 0$$

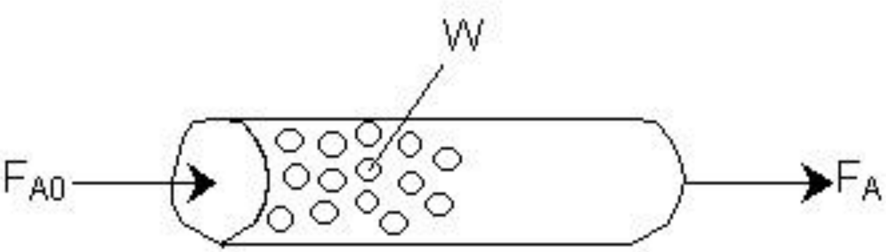
Differentiate with respect to V

$$\longrightarrow 0 - \frac{dF_A}{dV} = -r_A \longrightarrow \frac{dF_A}{dV} = r_A$$



Packed Bed Reactor, PBR

General mole Balance on system volume V



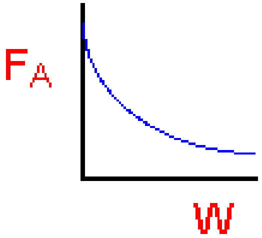
$$F_{A0} - F_A + \int^{v} r_A' dW = \frac{dN_A}{dt}$$

Steady state

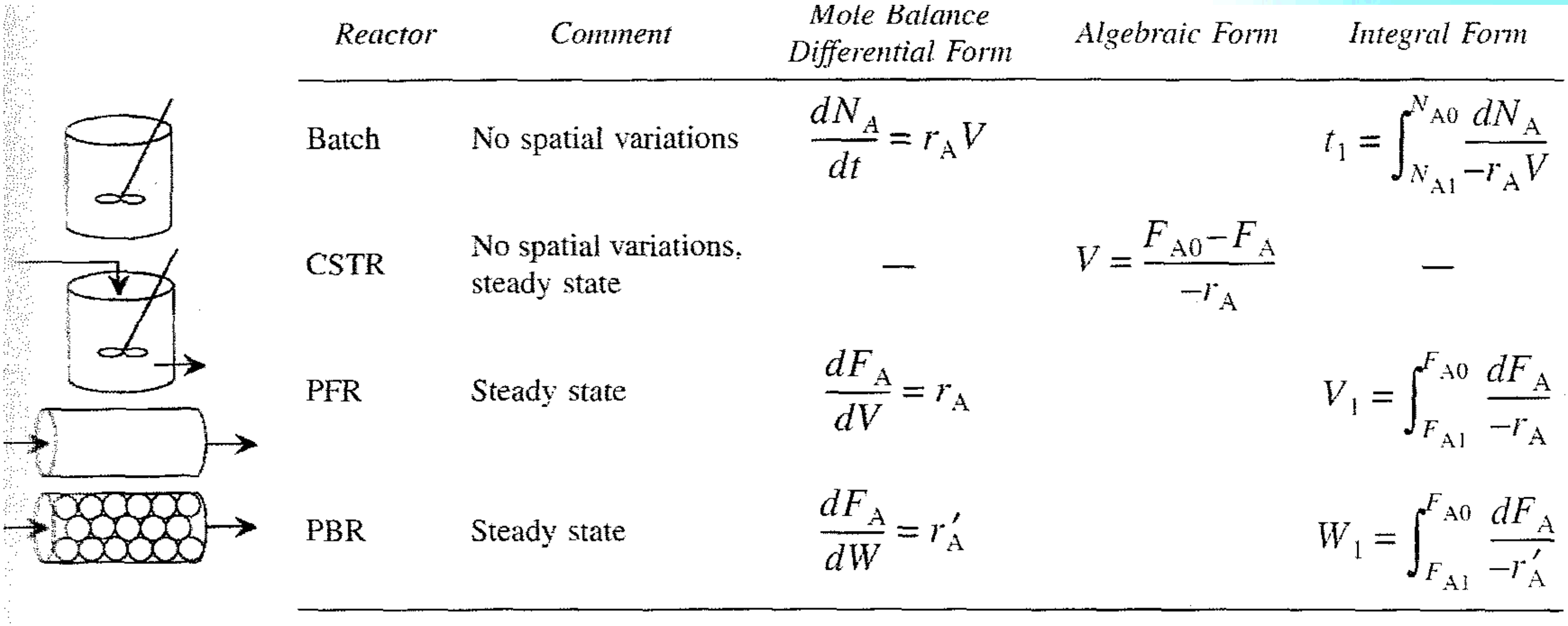
$$\frac{dN_A}{dt} = 0 \longrightarrow F_{A0} - F_A + \int^{v} r_A' dW = 0$$

Differentiate with respect to W

$$\longrightarrow 0 - \frac{dF_A}{dW} = -r_A' \longrightarrow \frac{dF_A}{dW} = r_A'$$



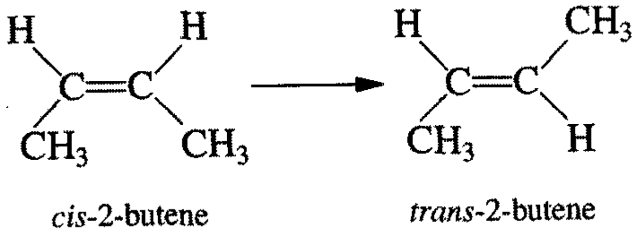
Summary of Reactor Mole Balances



Reactor	Comment	Mole Balance Differential Form	Algebraic Form	Integral Form
Batch	No spatial variations	$\frac{dN_A}{dt} = r_A V$		$t_1 = \int_{N_{A1}}^{N_{A0}} \frac{dN_A}{-r_A V}$
CSTR	No spatial variations, steady state	—	$V = \frac{F_{A0} - F_A}{-r_A}$	—
PFR	Steady state	$\frac{dF_A}{dV} = r_A$		$V_1 = \int_{F_{A1}}^{F_{A0}} \frac{dF_A}{-r_A}$
PBR	Steady state	$\frac{dF_A}{dW} = r'_A$		$W_1 = \int_{F_{A1}}^{F_{A0}} \frac{dF_A}{-r'_A}$

Example~How Large Is It?

Consider the liquid phase cis-trans isomerization of 2-butene



which we will write symbolically as

$$A \rightarrow B$$

The first order ($-r_A=kC_A$) reaction is carried out in a tubular reactor in which the volumetric flow rate, v, is constant, i.e., $v=v_0$.

1.Sketch the concentration profile.

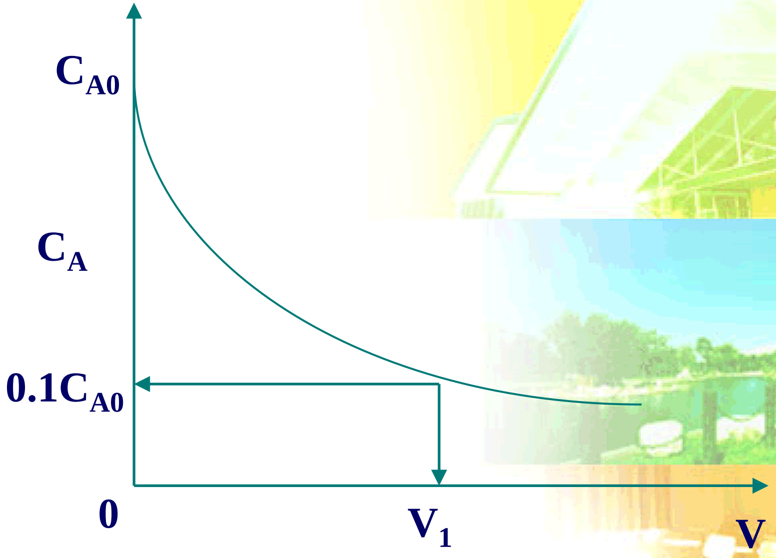
2.Derive an equation relating the reactor volume to the entering and exiting concentration of A, the rate constant k, and the volumetric flow rate v.

3.Determine the reactor volume necessary to reduce the exiting concentration to 10% of the entering concentration when the volumetric flow rate is 10 dm^3/min (i.e., liters/min) and the specific reaction rate, k, is 0.23 min^{-1}.

Solution

1.

$$\frac{dF_A}{dV} = r_A \xrightarrow{F_A = C_A v_0} \frac{dC_A}{dV} = \frac{r_A}{v_0}$$



2.

$$\frac{dC_A}{dV} = \frac{r_A}{v_0} \xrightarrow{-r_A = kC_A} -\frac{v_0}{k}\left(\frac{dC_A}{C_A}\right) = dV \xrightarrow[\text{when } V = 0]{C_A = C_{A0}} -\frac{v_0}{k}\int_{C_{A0}}^{C_A}\frac{dC_A}{C_A} = \int_0^V dV$$

$$\longrightarrow V = \frac{v_0}{k}\ln\frac{C_{A0}}{C_A}$$

3.

$$V = \frac{v_0}{k}\ln\frac{C_{A0}}{C_A} = \frac{10\ dm^3/min}{0.23\ min^{-1}}\ln\frac{C_{A0}}{0.1C_{A0}} = \frac{10\ dm^3}{0.23}\ln 10 = 100\ dm^3 = 0.1\ m^3$$

A reactor volume of 0.1m³ is necessary to convert 90% of species A entering into product B for the parameter given.

Industrial Reactors

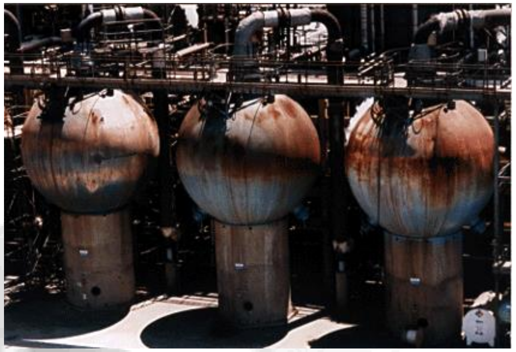
Batch Reactor

Cutaway View of CSTR

Reactor System Used at Amoco

Spherical Reactor

Three Spherical Reactors



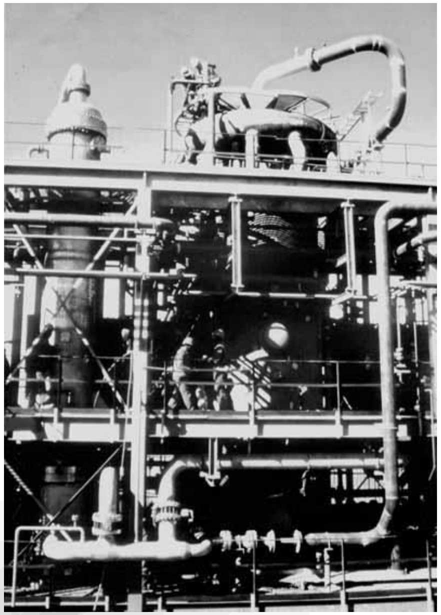
Spherical Reactors Connected in Series

Reactors Used at SASOL plants

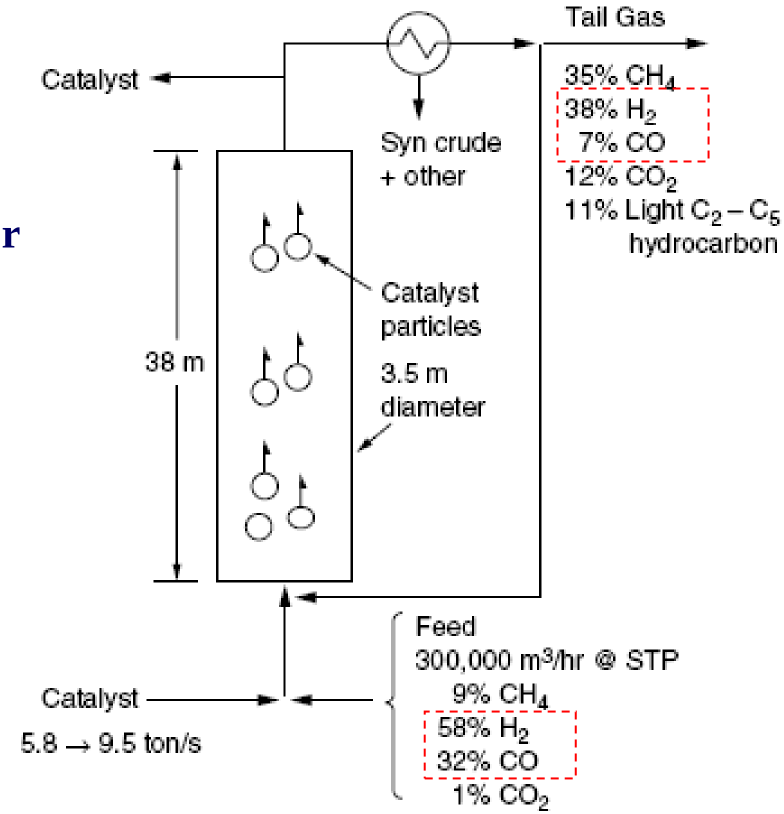
Fisher-Tropsch synthesis reaction

$$nCO + (2n+1)H_2 \rightarrow C_nH_{2n+2} + nH_2O$$

Packed Bed Reactor



Straight Though Transport Reactor



Closure

The goal of this section is to weave the fundamentals of chemical reaction engineering into a structure or algorithm that is easy to use and apply to a variety of problems.

We have just finished the first building block of this algorithm: mole balances.

This algorithm and its corresponding building blocks will be developed and discussed in the following section:

~ Conversion and Reactor Sizing

~ Rate Laws and Stoichiometry

~ Isothermal Reactor Design

~ Nonisothermal Reactor Design

With this algorithm, one can approach and solve chemical reaction engineering problems through logic rather than memorization.