

# Chemical reactors

- chemical transformation of **reactants** into **products**

## Classification:

- according to the type of equipment
  - o **batch** stirred tanks – small-scale production, mostly liquids
  - o **continuous** stirred tank reactors (CSTR) – medium to large-scale production, arrangement into **cascades** (liquids)
  - o **tubular** continuous reactors – gases or liquids flow through a pipe, which may be containing a fixed bed of granular material → catalyst, large-scale production
- according to number of phases
  - o **homogeneous** – just one phase (gas or liquid)
  - o **heterogeneous** – fixed bed of catalyst particles

## General mass and enthalpy balance

inflow + source/sink = outflow + accumulation

- mass of component k:  $\dot{m}_{k,i} + \frac{dm_{kR}}{d\tau} = \dot{m}_{k,e} + \frac{dm_{kS}}{d\tau}$
- mass of all components:  $\dot{m}_i + 0 = \dot{m}_e + \frac{dm_S}{d\tau}$
- enthalpy:  $\dot{H}_i + 0 = \dot{H}_e + \frac{dN_S}{d\tau}$

$\dot{H}$  has **thermal** contribution, **pressure** contribution (often negligible) and **reaction** contribution (“source”-like)

## Stoichiometry

- chemical reaction is written as:  $\sum v_k M_k = 0$ 
  - $v_k$  ... stoichiometric coefficient, negative for reactants, positive for products
  - $M_k$  ... molar mass of component k

## Conservation of stoichiometric ratios

$\frac{n_{kr}}{n_{lr}} = \frac{v_k}{v_l}$ ; l and k are two components taking part in a reaction (reactants or products)

it follow that

$$\frac{n_{kr}}{v_k} = \frac{n_{lr}}{v_l} = \xi \text{ ... extent}$$

Extent is independent of the choice of component, it is a measure of the reaction.

If  $n_{k0}$  is amount of k at the beginning and  $n_k$  is amount of k at the end of the reaction then

$$\xi = \frac{n_{kr}}{\nu_k} = \frac{n_k - n_{k0}}{\nu_k} = \frac{m_k - m_{k0}}{M_k \nu_k}$$

unit of  $\xi$ : [moles of reaction turnover]

For constant volume (liquids):  $\xi = V_S \frac{c_k - c_{k0}}{\nu_k}$

### Conversion of a reactant k

$$\zeta_k = -\frac{n_{kr}}{n_{k0}} = \frac{n_{k0} - n_k}{n_{k0}} = \frac{m_{k0} - m_k}{m_{k0}}$$

- for constant volume:  $\zeta_k = \frac{c_{k0} - c_k}{c_{k0}}$

- relation between  $\xi$  and  $\zeta_k$ :  $\xi = -\frac{n_{k0} \zeta_k}{\nu_k}$

- another relation:

$$\frac{n_l - n_{l0}}{\nu_l} = \frac{n_k - n_{k0}}{\nu_k} \rightarrow n_l = n_{l0} + \frac{\nu_l}{\nu_k} (n_k - n_{k0})$$

- for  $V_S = const$

$$c_l = c_{l0} + \frac{\nu_l}{\nu_k} (c_k - c_{k0})$$

also

$$n_l = n_{l0} + \frac{\nu_l}{\nu_k} n_{k0} \zeta_k; \quad \text{for } V_S = const: \quad c_l = c_{l0} + \frac{\nu_l}{\nu_k} c_{k0} \zeta_k$$

### Thermodynamics

Enthalpy of the reaction mixture is:

$$dH = n c_p dT + \left( \frac{\partial H}{\partial p} \right)_{T, \xi} dp + \Delta h_r d\xi$$

$n$  ... number of moles

$c_p$  ... molar thermal capacity

$\Delta h_r$  ... **molar reaction enthalpy**

For liquids and ideal gases  $\left( \frac{\partial H}{\partial p} \right)_{T, \xi} = 0$

Standard molar reaction enthalpy is:

$$\Delta h_{r0} = \sum \nu_k \Delta h_{fk0} = - \sum \nu_k \Delta h_{ck0}$$

where

$\Delta h_{fk0}$  ... standard molar enthalpy of formation of component k ( )

$\Delta h_{ck0}$  ... standard molar combustion enthalpy of k

can be found in tables

$\Delta h_r$  varies with temperature:

$$\Delta h_r = \Delta h_{r0} + \int_{T_0}^T v_k c_{pk} dT$$

**The Gibbs free energy is**

$$dG = -SdT + V_S dp + \Delta g_r d\xi$$

$S$  ... entropy

$\Delta g_r$  ... molar reaction Gibbs energy

$$\Delta g_r = \Delta g_{r0} + RT \ln \left( \prod_{k=1}^K a_k^{v_k} \right)$$

$a_k$  ... activity of k

$K$  ... equilibrium constant

At equilibrium  $\Delta g_r$  and  $\Delta g_{r0}$  is found in tables

**Calculation of  $K$ :**

$$\ln K = -\frac{\Delta g_{r0}}{RT}$$

$K$  ... true equilibrium constant

$K_C$  ... concentration equilibrium constant  $K_C = \prod_{k=1}^K c_k^{v_k}$

**$K$  depends on temperature:**

$$\left( \frac{\partial \ln K}{\partial T} \right)_{p,\xi} = \frac{\Delta h_{r0}}{RT^2}$$

## Kinetics

source/sink:

$$\frac{dn_{kr}}{d\tau} = v_k R = v_k \int_{V_S} r dV$$

$R$  ... extensive reaction rate [moles of reaction turnover/s]

$r$  ... intensive reaction rate [moles of reaction turnover/s/m<sup>3</sup>]

reaction rate of component k

$$R_K = \nu_k R$$

$$r_K = \nu_k r$$

From the definition:

$$R = \frac{1}{\nu_k} \frac{dn_{kr}}{d\tau} = \frac{d}{d\tau} \left( \frac{n_{kr}}{\nu_k} \right) = \frac{d\xi}{d\tau}$$

For **ideally mixed** systems  $r$  does not depend on position  $dV \rightarrow R = rV_S$

Reaction rate  $r$  depends on molar concentration of reactants

For example  $aA + bB \rightarrow \dots r = kc_A^a c_B^b$

where

$$k = \underbrace{k_0}_{\substack{\text{frequency} \\ \text{factor}}} \exp\left(-\frac{\overset{\text{activation}}{\text{energy}}}{RT}\right) \dots \text{Arrhenius relation}$$

For reversible reactions:  $r = r_+ - r_-$

For example:  $aA + bB \rightleftharpoons pP + qQ$

$$r = k_+ c_A^a c_B^b - k_- c_P^p c_Q^q$$

at equilibrium

$$r = 0 \rightarrow k_+ c_A^a c_B^b = k_- c_P^p c_Q^q$$

and

$$K = \frac{k_+}{k_-} = \frac{c_P^p c_Q^q}{c_A^a c_B^b}$$

### Batch reactor

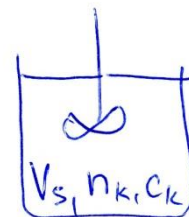
Assumptions:

- one reaction only
- ideal mixing  $R = rV_S$
- constant density  $V_S = \text{const}$

**Balance on moles of k** (no inflow, no outflow)

source = accumulation

$$\frac{dn_{kr}}{d\tau} = \frac{dn_{ks}}{d\tau}$$



for  $\tau=0, c_k = c_{k0}$

$$v_k r V_S = V_S \frac{dc_k}{d\tau}$$

**Reaction time:**

$$\tau = \int_0^\tau d\tau = \int_{c_{k0}}^{c_k} \frac{dc_k}{v_k r}$$

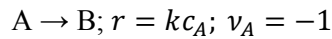
The use of conversion:

$$\zeta_k = \frac{c_{k0} - c_k}{c_{k0}} \rightarrow c_k = c_{k0}(1 - \zeta_k) \rightarrow dc_k = -c_{k0} d\zeta_k$$

$$\tau = -c_{k0} \int_0^{\zeta_k} \frac{d\zeta_k}{v_k r}$$

$r$  must be expressed in terms of either  $c_k$  or  $\zeta_k$

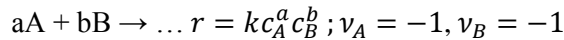
**Example 1:** isothermal reaction of first order



$$\tau = \int_{c_{A0}}^{c_A} \frac{dc_A}{-kc_A} = \frac{1}{k} \ln \frac{c_{A0}}{c_A}$$

$$\tau = -c_{A0} \int_0^{\zeta_A} \frac{d\zeta_A}{-kc_{A0}(1 - \zeta_A)} = \frac{1}{k} \ln \frac{1}{1 - \zeta_A}$$

**Example 2:** isothermal reaction of second order



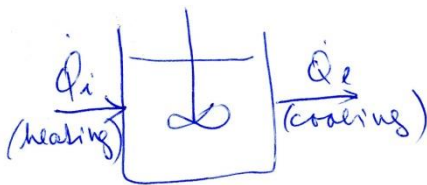
$c_B$  is expressed via  $c_A$ :

$$c_B = c_{B0} + \frac{v_B}{v_A} (c_A - c_{A0})$$

and then:

$$\tau = \int_{c_{A0}}^{c_A} \frac{dc_A}{-kc_A(c_{B0} + \frac{-1}{-1}(c_A - c_{A0}))} = \frac{1}{(c_{A0} - c_{B0})k} \ln \left( \frac{c_{B0}}{c_{A0}} \frac{c_A}{c_{B0} - c_{A0} + c_A} \right)$$

**Enthalpy balance** (neglecting pressure term)



$$Q_i = Q_e + \frac{dH}{d\tau}$$

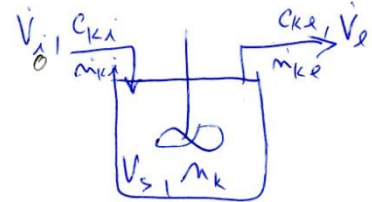
$$Q_i - Q_e = \frac{d}{d\tau} (nc_p dT) + \frac{d}{d\tau} (\Delta h_r d\xi)$$

$$Q_i - Q_e + (-\Delta h_r) \frac{d\xi}{d\tau} = n c_p \frac{dT}{d\tau}$$

Mass and enthalpy balances must be solve together since  $R = rV_S$  depends on molar concentrations.

### Continuous stirred tank reactor – CSTR

- assumptions:
  - o one reaction
  - o ideal mixing ( $R = rV_S$ )
  - o constant density:  $\dot{V}_i = \dot{V}_e = \dot{V} = \text{const}$  (liquids)
  - o steady state



**Balance on moles of k:**

$$\dot{n}_{ki} + v_k r V_S = \dot{n}_{ke}$$

$$\dot{V} c_{ki} + v_k r V_S = \dot{V} c_{ke}$$

$$\bar{\tau} = \frac{V_S}{\dot{V}} = \frac{c_{ke} - c_{ki}}{v_k r}$$

$\bar{\tau}$  ... mean residence time

Using conversion:

$$\zeta_k = \frac{c_{ki} - c_{ke}}{c_{ki}} \rightarrow \bar{\tau} = -\frac{c_{ki} \zeta_k}{v_k r}$$

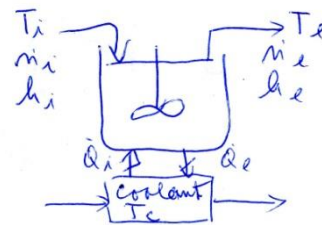
Again  $r$  is expressed in terms of  $c_k$  or  $\zeta_k$ .

### Enthalpy balance

$$\dot{n}_i h_i = \dot{n}_e h_e + \dot{Q}_e - \dot{Q}_i$$

$h_i$  and  $h_e$  include thermal and reaction terms!

$$\dot{Q}_e - \dot{Q}_i = K(T_e - T_c)A \quad \dots \text{heat transfer equation}$$

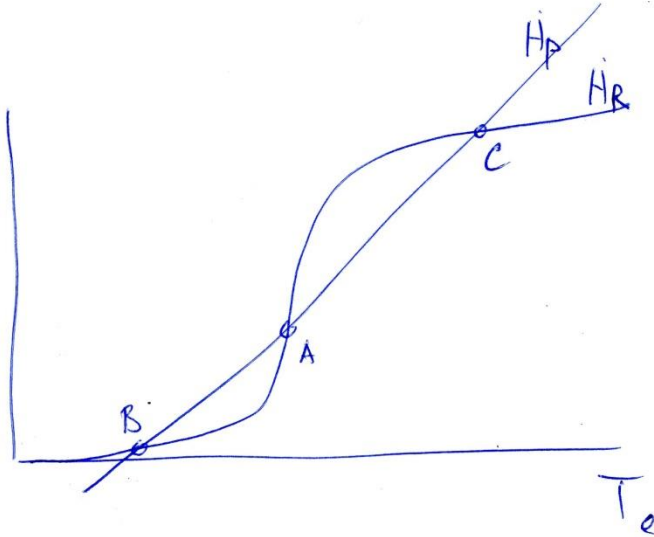


After some algebra it can be shown that the enthalpy balance is:

$$\dot{n}_i c_{pi} (T_i - T_0) + (-\Delta h_{r0}) r V_S = \dot{n}_e c_{pe} (T_e - T_0) + K(T_e - T_c)A$$

By choosing standard temperature  $T_0 = T_i$ :

$$\underbrace{(-\Delta h_{ri}) r V_S}_{\substack{\text{for exothermic} \\ \text{reaction this is} \\ \text{sigmoidal function} \\ \text{of } T_e \dots H_R}} = \underbrace{\dot{n}_e c_{pe} (T_e - T_i) + K(T_e - T_c)A}_{\text{linear function of } T_e \dots H_P}$$

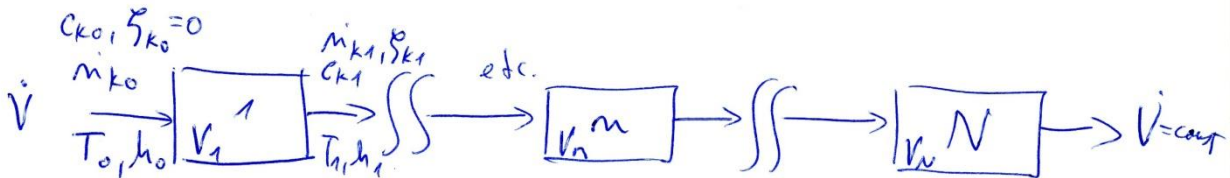


Intersection of the line  $\rightarrow$  steady states – three

A ... unstable state

B, C ... stable states with low and high temperature respectively (high temperatures  $\rightarrow$  operational limits, explosions!)

### Cascade of CSTRs



- assumptions as for one CSTR
- conversion in n-th reactor:  $\zeta_{kn} = \frac{c_{k0} - c_{kn}}{c_{k0}}$
- molar flow:  $\dot{n}_{kn} = \dot{V} c_{kn}$
- reactors may have different volumes:  $V_n; n = 1, \dots, N$

### Balance on moles of k in the n-th reactor

$$\begin{aligned} \dot{n}_{k,n-1} + v_k r_n V_n &= \dot{n}_{k,n} \\ c_{k,n-1} - c_{k,n} + v_k r_n \bar{\tau}_n &= 0 \\ c_{k0} (\zeta_{k,n} - \zeta_{k,n-1}) + v_k r_n \bar{\tau}_n &= 0 \end{aligned}$$

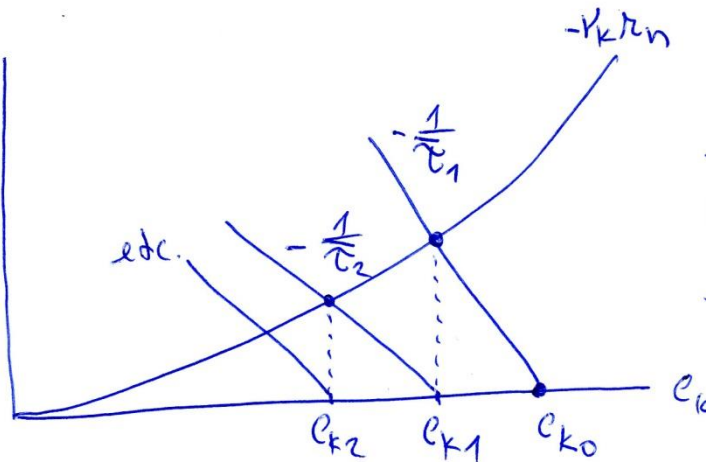
Convenient calculation is from reactor N to reactor 1 because  $r_n$  depends on  $c_{k,n}$  and  $c_{k,n-1}$  is easy to evaluate

### Graphical solution

It does not matter if from reactor 1 to reactor N or vice versa.

Rewrite mass balance:

$$\underbrace{-\nu_k r_n}_{\substack{>0 \text{ for} \\ \text{reactant,} \\ \text{generally} \\ \text{a curve}}} = \underbrace{-\frac{1}{\bar{t}_n} (c_{k,n} - c_{k,n-1})}_{\substack{\text{straight line with} \\ \text{slope } -\frac{1}{\bar{t}_n} \text{ passing} \\ \text{through point } [c_{k,n-1}; 0]}}$$



The straight lines are parallel if the reactors have constant volume ( $\rightarrow \bar{t} = \text{const}$ )

**Analytical solution** for isothermal 1<sup>st</sup> order reaction  $A \rightarrow \dots$ ;  $r_n = k c_{A,n}$ ;  $\nu_A = -1$ ;  $\bar{t} = \text{const}$ .

**Mass balance:**

$$c_{A,n-1} - c_{A,n} + (-1)k c_{A,n} \bar{t} = 0$$

$$\frac{c_{A,n-1}}{c_{A,n}} = 1 + k\bar{t}$$

Then

$$\frac{c_{A,0}}{c_{A,1}} \frac{c_{A,1}}{c_{A,2}} \dots \frac{c_{A,N-1}}{c_{A,N}} = \frac{c_{A,0}}{c_{A,N}} = (1 + k\bar{t})^N$$

**Enthalpy balance:** (reference state at  $T = T_0$ )

$$\frac{\dot{Q}_{in} - \dot{Q}_{en}}{K(T_n - T_c)A_n} + \dot{n}_{n-1} c_{p,n-1} (T_{n-1} - T_0) + (-\Delta h_{r0}) r_n V_n = \dot{n}_n c_{pn} (T_n - T_0)$$

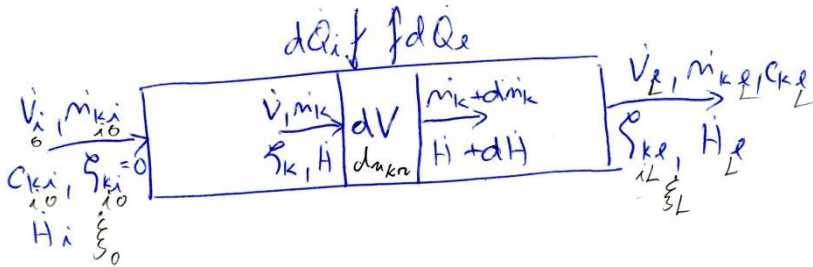
Can be used to calculate heat exchange area  $A_n$ .

**Tubular reactor** (continuous, for gases or liquids)

- assuming:
  - o one reaction



- turbulent flow → approximation by **plug flow**
- density may not be constant for gases
- steady state



Conversion is defined as:

$$\zeta_k = \frac{\dot{n}_{ki} - \dot{n}_k}{\dot{n}_{ki}} \rightarrow d\dot{n}_k = -\dot{n}_{ki} d\zeta_k$$

**Balance on moles of k in dV**

$$\dot{n}_k + v_k \frac{rdV}{\frac{d}{dt}(d\zeta_k)} = \dot{n}_k + d\dot{n}_k$$

Reaction volume is:

$$V = \int_0^V dV = \int_{\dot{n}_{ki}}^{\dot{n}_{ke}} \frac{d\dot{n}_k}{v_k r} = -\dot{n}_{ki} \int_0^{\zeta_{ke}} \frac{d\zeta_k}{v_k r}$$

- a) **liquids:**  $density = const \rightarrow \dot{V} = const \rightarrow \bar{\tau} = \frac{V}{\dot{V}}$  is well defined

mean residence time:

$$\bar{\tau} = \frac{V}{\dot{V}} = \int_{c_{ki}}^{c_{ke}} \frac{dc_k}{v_k r}$$

Formally the same formula that is for calculation of reaction time in a **batch** reactor

- b) **gases:** instead of  $\bar{\tau}$  we define a spacetime at input  $\tau_i = \frac{V}{\dot{V}_i}$

then

$$\tau_i = \frac{V}{\dot{V}_i} = -c_{ki} \int_0^{\zeta_{ke}} \frac{d\zeta_k}{v_k r}$$

Now we need to express r in terms of the conversion.

We know that:

- 1)  $\dot{n}_l = \dot{n}_{li} - \frac{v_l}{v_k} \dot{n}_{ki} \zeta_k$
- 2) gas follows the equation  $p\dot{V} = \dot{n}RT = \sum_l \dot{n}_l RT$

r depends on  $c_l$ ;  $l = 1, \dots$  and  $c_l$  is expressed as

$$c_l = \frac{\dot{n}_l}{\dot{V}} = \frac{\dot{n}_l}{\frac{\dot{n}RT}{p}} = \frac{p}{RT} \frac{\dot{n}_l}{\dot{n}} = c \frac{\frac{\dot{n}_l}{\sum_l \dot{n}_l}}{\frac{\dot{n}_l - \frac{v_l}{v_k} \dot{n}_{ki} \zeta_k}{\sum_l \dot{n}_l}} = \frac{y_{li} - \frac{v_l}{v_k} y_{ki} \zeta_k}{1 - \frac{y_{ki} \zeta_k}{v_k} \sum_l v_l}$$

$c$  ... molar density

Thus  $r$  is expressed in terms of  $y_{li}$ ,  $y_{ki}$  and  $\zeta_k$ .

### Enthalpy balance

$$d\dot{Q}_i + \dot{H} = \dot{H} + d\dot{H} + d\dot{Q}_e$$

where

$$d\dot{H} = \underbrace{\dot{n}c_p}_{\dot{m}c_{pm}} dT + \Delta h_r d\left(\frac{d\xi}{d\tau}\right)_{dR=r dV}$$

Thus

$$-\Delta h_r r dV = \dot{m}c_{pm} dT + d\dot{Q}_e - d\dot{Q}_i$$