

Introduction to Chemical Reactors

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1. Introduction and Basic Concepts

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Course outline

- 8 chapters
 1. Introduction and basic concepts
 2. Design of isothermal reactors
 3. Multiple reactions
 4. Design of non-isothermal reactors
 5. Design of catalytic reactors
 6. Non-ideal reactors

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Recommended texts

Textbook

- Schmidt, L.D. “***The Engineering of Chemical Reactions***”, Second edition, Oxford University Press, 2005.
Well explained and integrated.

Recommended

- Metcalfe, I.S. “***Chemical Reaction Engineering. A First Course***”, Oxford University Press, 2000.
Covers most of the material (but not catalytic reactors), often offering an alternative viewpoint and useful examples.

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More recommended texts

Further reading

- Fogler, H.S. “***Elements of Chemical Reaction Engineering. 4th ed.***”, Prentice Hall, international edition, 2005.
Access to web resources and full of examples and exercises.
- Levenspiel, O. “***Chemical Reaction Engineering. 3rd ed.***”, John Wiley & Sons, 1998.
Very didactic.
- Smith, J.M. “***Chemical Engineering Kinetics. 3rd ed.***”, McGraw-Hill, 1981.
Specialised in kinetics but with chapters on reaction design, etc..
- Denbigh, K.G. and Turner, J.C.R. “***Chemical Reactor Theory: An Introduction. 3rd ed.***”, 1984.
A classic book with in-depth treatment of some of the topics.

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1. Introduction and Basic concepts

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Objectives

- review some of the **fundamental concepts** around the subject of chemical reactions
- construct an **Stoichiometric Table in terms of the conversion** of the basis species
- express **concentrations in terms of conversion**

Sources for the introduction

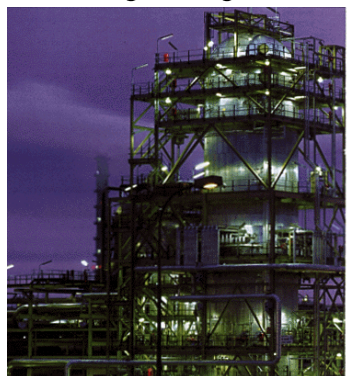
- Schmidt: Chapter 2
- Fogler: Sections 1.1, 2.1, 3.1, 3.3

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Context

Reaction Kinetics and Reactor Engineering form the basis for the production of most industrial chemicals and distinguishes Chemical Engineering from other branches of engineering.



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Sasol Advanced Synthol (SAS) reactor
(from [Fogler 05])

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Context (2)

The selection of a *reaction system* and the design of a *reaction process*, i.e. the reactor(s), condition the design and operation of the whole chemical process in terms of cost and safety.



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Reactor system used at BP
(from [Fogler 05])

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Context (3)

The “building blocks” of the area are:

- mass and energy balances
- stoichiometry
- rate laws
- heat and mass transfer

1.1 Stoichiometry and Reaction rate

The two basic concepts of reaction engineering are:

- ***Stoichiometry***, from *stoicheion* (element) and *metron* (measure), is the calculation of the relation between reactants and products in a chemical reaction, i.e. a Material Balance of the reaction.
- ***Reaction rate*** refers to the speed at which reactants transform into products.

Reaction stoichiometry

Relates the number/proportion of molecules involved in a reaction.

Generalised single reaction: $\sum_{j=1}^S \nu_j A_j = 0$

ν_j is the stoichiometric coefficient of species j

$\nu_j < 0$ for a reactant

$\nu_j > 0$ for a product

A_j is the species j

e.g. $N_2 + O_2 \rightarrow 2 NO$ ($A_1 + A_2 \rightarrow 2 A_3$)

$$-A_1 - A_2 + 2 A_3 = 0$$

Reaction rate: r

The reaction rate is the **speed** at which a species loses its chemical identity (changes in kind, number or configuration of its atoms) per unit volume. It is an **empirical expression**.

The rate of reaction, r_j , can be expressed as the number of moles that react per unit of time and volume, e.g. [mole s⁻¹ m⁻³].

In general it can be expressed as

- the rate of disappearance of a reactant, or
- the rate of appearance of a product,

so, for reaction $a A + b B \rightarrow c C + d D$

the rate of formation of each species is $-\frac{1}{a}r_A = -\frac{1}{b}r_B = \frac{1}{c}r_C = \frac{1}{d}r_D$

Reaction rate: r (2)

I find the notation used in Schmidt clearer and more general; he defines the rate of reaction as a positive rate of change for a particular stoichiometry.

We can describe r as: $r = k(T) \prod_{j=1}^S C_j^{m_j}$ [mole m⁻³ s⁻¹]

“rate-law” or
“power-law kinetics”

where m_j is the order of the reaction with respect to the j^{th} species;
 Σm_j is the overall reaction order; and

C_j is the concentration $C_j = \frac{N_j}{V} = \frac{F_j}{v}$ [moles m⁻³]

For example, for $2A \rightarrow B + 3C$ $r = kC_A^2$

$$\begin{aligned} r_A &= -2kC_A^2 = -2r \\ r_B &= kC_A^2 = r \\ r_C &= 3kC_A^2 = 3r \end{aligned}$$

$$r_j = \nu_j r$$

Reaction rate: r (3)

$$r = k(T) \prod_{j=1}^S C_j^{m_j}$$

- r is a **function of concentration, T, P and catalyst type**, in particular, r is expressed in terms of concentrations and T.
- r is **independent of reactor type** (batch, PFR, CSTR, ...)
- r is an **algebraic equation**, not a differential equation!

A good first guess of the reaction order can be made from its stoichiometry: $m_j = -\nu_j$ for $\nu_j < 0$ (reactants)

$m_j = 0$ for $\nu_j > 0$ (products)

but this guess is only valid for *elementary reactions* (when the reaction also describes the mechanism by which the process occurs, this will be clearer later ...).

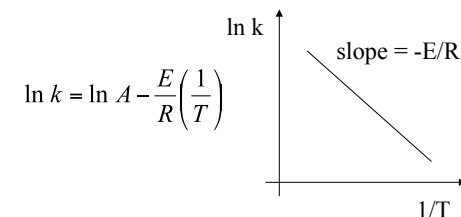
Rate Law. Arrhenius equation

In a reaction rate, $r = k(T) f_n(C_A, C_B, \dots)$,

$k(T)$ –the **specific reaction rate** or **rate coefficient**– is given by the Arrhenius equation:

$$k(T) = A e^{-E/RT}$$

The activation energy, E , can be found by plotting $\ln k$ vs. $1/T$



$$\frac{k_{T_2}}{k_{T_1}} = \frac{\exp\left(\frac{-E}{RT_2}\right)}{\exp\left(\frac{-E}{RT_1}\right)}$$

Reversible reactions and their reaction rate

A reversible reaction $A \rightleftharpoons B$ is equivalent to $A \rightarrow B$ and $A \leftarrow B$

The overall rate is the difference between the forward reaction rate, r_f , and the reverse reaction rate, r_b :

$$r = r_f - r_b = k_f \prod_{j=1}^S C_j^{m_{fj}} - k_b \prod_{j=1}^S C_j^{m_{bj}}$$

where

k_f, k_b : rate coefficients for the forward/reverse reactions

m_{fj}, m_{bj} : orders of the forward/reverse reactions with respect to the j th species

An “irreversible” reaction is an approximation for the situation where $r_f \gg r_b$

1.2 Reaction equilibrium and Thermodynamics

Thermodynamics can predict, from first principles, whether a reaction is going to occur or not (its equilibrium). However, it is unable to predict how fast a feasible reaction is going to proceed; this is the subject of **Kinetics**.

There is a link (constraint) between Thermodynamics and Kinetics: the relationship between the **Equilibrium Constant**, K , and the ratio of the forwards and backwards **reaction rate coefficients**, k_f and k_b .

Derivation of the Arrhenius equation (from [Smith 81])

From the van't Hoff equation $\frac{d \ln K_{eq}}{dT} = \frac{\Delta H^o}{RT^2}$

and recalling that $K_{eq} = \frac{k_f}{k_b}$ and $\Delta H = \Delta H_f - \Delta H_b$

$$\begin{aligned} \frac{d \ln k_f}{dT} - \frac{d \ln k_b}{dT} &= \frac{\Delta H_f}{RT^2} - \frac{\Delta H_b}{RT^2} \\ \text{separate and integrate} \quad \frac{d \ln k_f}{dT} &= \frac{\Delta H_f}{RT^2} \quad \frac{d \ln k_b}{dT} = \frac{\Delta H_b}{RT^2} \\ \text{Set } C = \ln A \quad \ln k_f &= \frac{-\Delta H_f}{RT} + C \\ k_f &= A e^{-\Delta H_f/RT} \quad \dots \text{ sounds familiar?} \end{aligned}$$

Thermodynamics: equilibrium constant (K_{eq})

The free energy change in a system of reacting chemical species is

$$\Delta G = \sum_{j=1}^S \nu_j \mu_j = \sum_{j=1}^S \nu_j (\mu_j^o + RT \ln a_j)$$

At chemical equilibrium (and constant T, P) G is a minimum and $\Delta G = 0$

$$0 = \sum_{j=1}^S \nu_j \mu_j^o + \sum_{j=1}^S \nu_j RT \ln a_j$$

$$\exp\left(-\sum_{j=1}^S \frac{\nu_j \mu_j^o}{RT}\right) = \prod_{j=1}^S a_j^{\nu_j} \equiv K_{eq}$$

$$K_{eq} = \exp\left(-\frac{\Delta G_R^o}{RT}\right)$$

liquid solns. $\rightarrow \prod_{j=1}^S C_j^{\nu_j}$

gases $\rightarrow \prod_{j=1}^S P_j^{\nu_j}$

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K_{eq} and the rate constants

For a reversible reaction at equilibrium the reaction rate is 0

$$r = r_f - r_b = k_f \prod_{j=\text{reactants}} C_j^{m_{fj}} - k_b \prod_{j=\text{products}} C_j^{m_{bj}} = 0$$

$$\frac{k_f}{k_b} = \frac{\prod_j C_j^{m_{bj}}}{\prod_j C_j^{m_{fj}}} = \prod_{j=1}^S C_j^{m_{bj} - m_{fj}} \quad \leftarrow \text{rearranging}$$

and from the definition of K_{eq} :

$$K_{eq} = \prod_{j=1}^S C_j^{\nu_j}$$

$$\nu_j = m_{bj} - m_{fj}$$

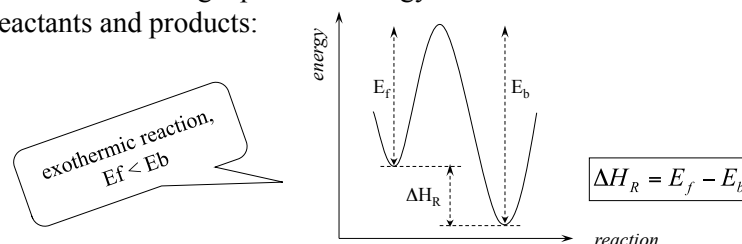
$$K_{eq} = \frac{k_f}{k_b}$$

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Physical interpretation of the Arrhenius equation

M. Polanyi and E. Wigner proposed to describe reactions as the process of crossing a potential energy surface between reactants and products:



From statistical mechanics the rates can be described by a Boltzmann factor, $\exp(-E/RT)$, which is the probability of crossing a potential energy barrier.

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Heat of reaction (ΔH_R)

Recall that

$$K_{eq} = \exp\left(-\frac{\Delta G_R^o}{RT}\right) = \exp\left(-\frac{(\Delta H_R^o - T\Delta S_R^o)}{RT}\right)$$

$\Delta G_R^o = \Delta H_R^o - T\Delta S_R^o$
from thermo

$$K_{eq} = \frac{k_f}{k_b} = \frac{A_f \exp\left(-\frac{E_f}{RT}\right)}{A_b \exp\left(-\frac{E_b}{RT}\right)}$$

$$K_{eq} = \exp\left(\frac{\Delta S_R^o}{R}\right) \exp\left(-\frac{\Delta H_R^o}{RT}\right)$$

$$K_{eq} = \frac{A_f}{A_b} \exp\left(-\frac{(E_f - E_b)}{RT}\right)$$

equating and comparing

$$\Delta H_R^o = E_f - E_b$$

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1.3 Conversion and Stoichiometric Tables

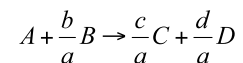
Reaction rates are expressed in terms of reactant concentrations which, by definition, vary as the reaction takes place.

A convenient way to express this variation is through the concept of **conversion**, X . Generally simple for *constant volume systems*, it gets a bit more complicated in the case of *variable volume systems*.

For even the most complicated reactions, expressions for the concentrations in terms of conversion are conveniently derived through a ***Stoichiometric Table***.

Conversion

The general reaction equation can be expressed using A as a basis (the **limiting reactant** is chosen as a basis)



Define **conversion** of species A, X_A , as the number of moles of reacted A per moles of A fed:

- for batch regime $X = \frac{(N_{A0} - N_A)}{N_{A0}} ; \quad N_A = N_{A0}(1 - X)$
- for flow regime $X = \frac{(F_{A0} - F_A)}{F_{A0}} ; \quad F_A = F_{A0}(1 - X)$

In the simplest case ...



first order reaction: $r = k C_A$ with feed at C_{A0}

and since $X = \frac{C_{A0} - C_A}{C_{A0}}$

$$C_A = C_{A0}(1 - X)$$

$$C_B = C_{A0}X$$

Stoichiometric Table for reaction $A + \frac{b}{a}B \rightarrow \frac{c}{a}C + \frac{d}{a}D$

Species	Initial	Change	Remaining
A	F_{A0}	$-F_{A0}X$	$F_A = F_{A0}(1-X)$
B	$F_{B0} = F_{A0}\Theta_B$	$-\frac{b}{a}F_{A0}X$	$F_B = F_{A0}\left(\Theta_B - \frac{b}{a}X\right)$
C	$F_{C0} = F_{A0}\Theta_C$	$+\frac{c}{a}F_{A0}X$	$F_C = F_{A0}\left(\Theta_C + \frac{c}{a}X\right)$
D	$F_{D0} = F_{A0}\Theta_D$	$+\frac{d}{a}F_{A0}X$	$F_D = F_{A0}\left(\Theta_D + \frac{d}{a}X\right)$
I (inert)	$F_{I0} = F_{A0}\Theta_I$	no change	$F_I = F_{A0}\Theta_I$
TOTAL	$\sum F_i = F_{T0}$		$F_T = F_{T0} + \delta F_{A0}X$

where $\Theta_j = \frac{F_{j0}}{F_{A0}} = \frac{C_{j0}v_0}{C_{A0}v_0} = \frac{C_{j0}}{C_{A0}} = \frac{y_{j0}}{y_{A0}}$
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$$\delta = \frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1$$

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Concentration

To design reactors we need to express concentrations in terms of conversion X (because $r = k(T) \cdot f_n(C_A, C_B, \dots)$, but the Stoichiometric Table is in terms of X).

Recall that $C_j = \frac{N_j}{V} = \frac{F_j}{v}$ [moles m^{-3}] also $C_j = \frac{N_j}{V} = \frac{y_j P}{RT}$
 ideal gas, $PV = NRT$

We have to distinguish between two types of systems:

- constant volume
- variable volume

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Concentration: constant volume systems

Reactions in liquid phase, or in gas phase without variation of volume or density (e.g. $N_{\text{reactants}} = N_{\text{products}}$ hence $v = v_0$).

$$C_A = \frac{F_A}{v} = \frac{F_{A0}(1-X)}{v_0} = C_{A0}(1-X)$$

$$C_B = \frac{F_B}{v} = \frac{F_{A0}\left(\Theta_B - \frac{b}{a}X\right)}{v_0} = C_{A0}\left(\Theta_B - \frac{b}{a}X\right)$$

$$C_C = C_{A0}\left(\Theta_C + \frac{c}{a}X\right)$$

$$C_D = C_{A0}\left(\Theta_D + \frac{d}{a}X\right)$$

$$C_I = C_{A0}\Theta_I$$

from Stoichiometric Table

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Concentration: variable volume systems

Reactions in gas phase with $N_{\text{reactants}} < \text{neq} > N_{\text{products}}$.

Volume and # of moles are related by an equation of state:

$$\frac{Pv}{P_0 v_0} = \frac{ZF_T RT}{Z_0 F_{T0} R T_0} \rightarrow v = v_0 \left(\frac{F_T}{F_{T0}} \right) \left(\frac{P_0}{P} \right) \left(\frac{T}{T_0} \right) \left(\frac{Z}{Z_0} \right)$$

(assume $Z = Z_0$)

$$\frac{F_T}{F_{T0}} = 1 + X y_{A0} \delta = (1 + \epsilon X)$$

$\epsilon \equiv y_{A0} \delta$

$$C_A = \frac{F_A}{v} = \frac{F_{A0}(1-X)}{v_0(1+\epsilon X)} \left(\frac{T_0}{T} \right) \left(\frac{P}{P_0} \right) = C_{A0} \frac{(1-X)}{(1+\epsilon X)} \left(\frac{T_0}{T} \right) \left(\frac{P}{P_0} \right)$$

in general ...

$$C_j = C_{A0} \frac{(\Theta_j + y_j X)}{(1 + \epsilon X)} \left(\frac{T_0}{T} \right) \left(\frac{P}{P_0} \right)$$

note that v_j has been normalised wrt to v_A (see general Stoichiometric Table)

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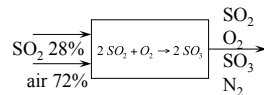
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1.4 An example of a variable volume system

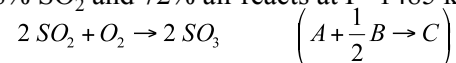
This example develops expressions
for the concentrations in terms of conversion,
of all the reaction species (reactants and products),
in the case of a variable volume system,
through a Stoichiometric Table.

As a result, we can predict the concentration of all the
species given a value of conversion.

Example: oxidation of SO₂



Mixture of 28% SO₂ and 72% air reacts at P=1485 kPa, T=227 C



Calculate its Stoichiometric Table and plot C_j as a function of X

$$\left. \begin{array}{l} F_{A0} = (0.28)F_{T0} \\ F_{B0} = (0.72)(0.21)F_{T0} \\ F_{C0} = 0 \\ F_{I0} = (0.72)(0.79)F_{T0} \end{array} \right\} \quad \begin{array}{l} \Theta_B = \frac{F_{B0}}{F_{A0}} = \frac{(0.72)(0.21)}{0.28} = 0.54 \\ \Theta_C = \frac{F_{C0}}{F_{A0}} = 0 \\ \Theta_I = \frac{F_{I0}}{F_{A0}} = \frac{(0.72)(0.79)}{0.28} = 2.03 \end{array}$$

$$C_{A0} = \frac{y_{A0}P_0}{RT_0} = \frac{(0.28)(1485)}{(227 + 273)(8.314)} = 0.1 \frac{\text{mol}}{\text{lt}}$$

$$\varepsilon = y_{A0} \delta = (0.28) \left(-\frac{1}{2} \right) = -0.14 \quad [kPa \text{ dm}^3 \text{ mole}^{-1} \text{ K}^{-1}]$$

Stoichiometric Table for $\text{SO}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{SO}_3$

Species	Initial	Change	Remaining
A (SO ₂)	$(0.28)F_{T0}$	$-F_{A0}X$	$(0.28)F_{T0}(1 - X)$
B (O ₂)	$(0.54)(0.28)F_{T0}$	$-\frac{1}{2}F_{A0}X$	$(0.28)F_{T0}\left(0.54 - \frac{1}{2}X\right)$
C (SO ₃)	0	$F_{A0}X$	$(0.28)F_{T0}X$
I (N ₂)	$(2.0314)(0.28)F_{T0}$	no change	$(2.0314)(0.28)F_{T0}$
TOTAL	F_{T0}		$F_{T0} - \frac{1}{2}(0.28)F_{T0}X$

$$\Theta_B = 0.54$$

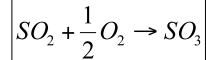
$$\Theta_C = 0$$

$$\Theta_I = 2.0314$$

$$\delta = \frac{1}{1} - \frac{\frac{1}{2}}{1} - 1 = -\frac{1}{2}$$

$$\varepsilon = -0.14$$

Example: oxidation of SO₂ (2)



$$C_A = C_{A0} \frac{(1-X)}{(1+\varepsilon X)}$$

$$C_B = C_{A0} \frac{(\Theta_B - \frac{1}{2}X)}{(1+\varepsilon X)}$$

$$C_C = C_{A0} \frac{X}{(1+\varepsilon X)}$$

$$C_I = C_{A0} \frac{\Theta_I}{(1+\varepsilon X)}$$

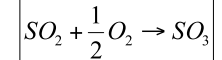
$$\begin{aligned} \varepsilon &= -0.14; \\ C_{A0} &= 0.1 \frac{\text{mol}}{\text{l}}; \\ \Theta_B &= 0.54; \\ \Theta_I &= 2.03 \end{aligned}$$

equations from slide
for concentrations for
variable volume systems
with
 $P_0=P$ and $T_0=T$

Note that it is usual
to express gas
concentrations in
terms of partial
pressures, P_j :

$$C_j = \frac{y_j P}{RT} = \frac{P_j}{RT}$$

Example: oxidation of SO₂ (3)

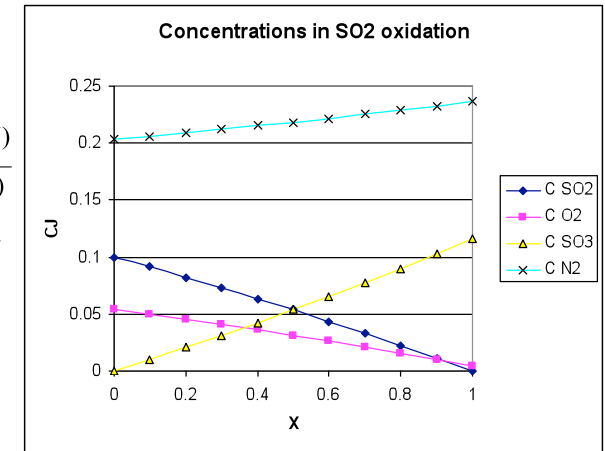


$$C_A = 0.1 \frac{(1-X)}{(1-0.14X)}$$

$$C_B = 0.1 \frac{(0.54 - \frac{1}{2}X)}{(1-0.14X)}$$

$$C_C = 0.1 \frac{X}{(1-0.14X)}$$

$$C_I = 0.1 \frac{2.0314}{(1-0.14X)}$$



1.5 Residence time

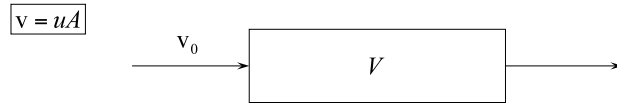
An important concept is that of *residence time*.

In general, residence time is an indication of how fast a material flows through the system.

In the case of chemical reactors, it can be interpreted as the *time required to process the feed stream given a reactor volume*.

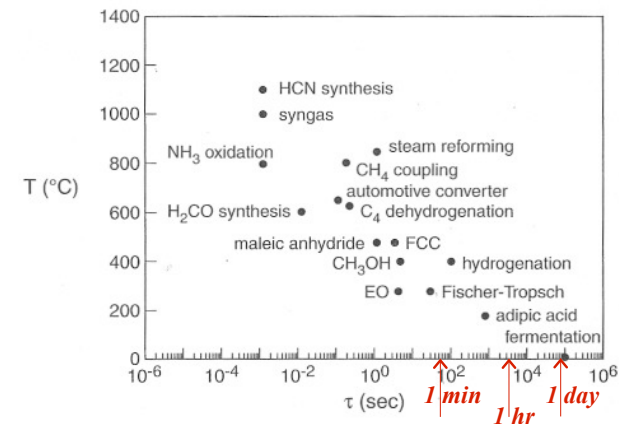
Residence time is a convenient and popular way to characterise reactions in industry.

Residence time



- Residence time (τ) $\tau = \frac{V}{v} = \frac{L}{u} \quad [\text{s}]$
- Space-Time $SpaceTime = \frac{V}{v_0} \quad [\text{s}]$
- Space Velocity (SV) $SV = \frac{v_0}{V} \quad [\text{s}^{-1}]$

Typical τ for several important industrial reactors (Figure 3-7, Schmidt)



1.6 Summary and Nomenclature

Summary (1)

- generalised reaction $\sum_{j=1}^S \nu_j A_j = 0$
- reaction rate $r = k(T) \, fn(C_A, C_B, \dots)$
- rate law $r = k(T) \prod_{j=1}^S C_j^{m_j}$
- Arrhenius equation $k(T) = A e^{-E/RT}$
- Equilibrium constant $\left\{ \begin{array}{l} K_{eq} = \exp\left(-\frac{\Delta G_R^o}{RT}\right) \\ K_{eq} = \prod_{j=1}^S C_j^{\nu_j} \quad K_{eq} = \frac{k_f}{k_b} \end{array} \right.$

Summary (2)

- Conversion $X = \frac{\text{moles reacted}}{\text{moles fed}} = \frac{F_{J0} - F_J}{F_{J0}} \Rightarrow F_J = F_{J0}(1 - X)$
- Stoichiometric Table (for reaction $A + \frac{b}{a}B \rightarrow \frac{c}{a}C + \frac{d}{a}D$)
- concentration in terms of X
 - constant volume systems
 - variable volume systems

- Residence time $\tau = \frac{V}{v} = \frac{L}{u}$

Nomenclature

a_j : activity of species J	δ : Δ of N_T per mole of A reacted
A: pre-exponential factor	ϵ : fraction Δ in V per mole reacted A
E: activation energy [J/mole]	μ_j : chemical potential of species J
F_j : molar flowrate of species J [gmole/s]	Θ_j : ratio of input moles of J per input moles of A
G: Gibbs free energy	
k: specific reaction rate; rate coefficient	
N_j : number of moles of species J [gmole]	<u>subscripts</u>
R: gas constant, 8.314 [kPa dm ³ /(mole K)]	0: input or initial condition
T: absolute temperature [K]	T: total
V: reactor volume [m ³]	f: forward
v: volumetric flowrate [m ³ /s]	b: backward
y_j : vapour mole fraction of J	<u>superscripts</u>
Z: compressibility factor	°: standard state