

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

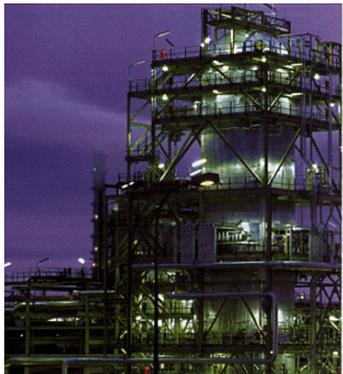
- Schmidt: Chapter 2
- Fogler: Sections 1.1, 2.1, 3.1, 3.3

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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.



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.



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 $aA + bB \rightarrow cC + dD$

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 $2A \rightarrow B + 3C$ $r = kC_A^2$ $\left\{ \begin{array}{l} r_A = -2kC_A^2 = -2r \\ r_B = kC_A^2 = r \\ r_C = 3kC_A^2 = 3r \end{array} \right.$

$$r_j = \nu_j r$$

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)

$$m_j = 0 \quad \text{for } \nu_j > 0 \quad (\text{products})$$

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 ...).

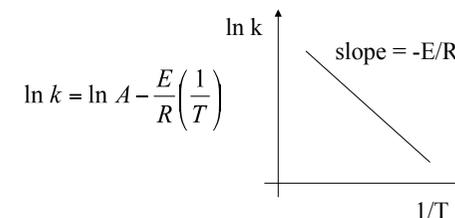
Rate Law. Arrhenius equation

In a reaction rate, $r = k(T) \text{fn}(C_A, C_B, \dots)$,

$k(T)$ –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. $1/T$



$$\frac{k_{r_2}}{k_{r_1}} = \frac{\exp\left(\frac{-E}{RT_2}\right)}{\exp\left(\frac{-E}{RT_1}\right)}$$

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 $\Delta H = \Delta H_f - \Delta H_b$

$$\frac{d \ln k_f}{dT} - \frac{d \ln k_b}{dT} = \frac{\Delta H_f}{RT^2} - \frac{\Delta H_b}{RT^2}$$

separate and integrate

$$\frac{d \ln k_f}{dT} = \frac{\Delta H_f}{RT^2} \quad \frac{d \ln k_b}{dT} = \frac{\Delta H_b}{RT^2}$$

$$\ln k_f = \frac{-\Delta H_f}{RT} + C$$

Set $C = \ln A$

$$k_f = A e^{-\Delta H_f/RT} \quad \dots \text{ sounds familiar?}$$

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

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

K_{eq} and the rate constants

For a reversible reaction at equilibrium the reaction rate is 0

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

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

and from the definition of K_{eq} :

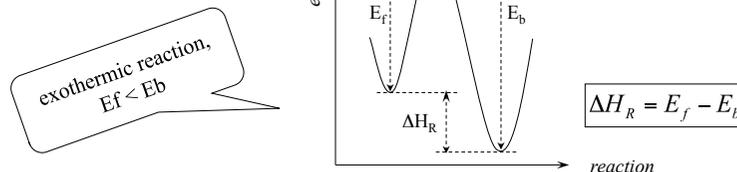
$$K_{eq} = \prod_{j=1}^S C_j^{\nu_j}$$

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

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

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.

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

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

1.3 Conversion and Stoichiometric Tables

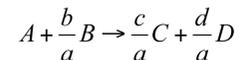
Reaction rates are expressed in terms of reactant concentrations which, by definition, vary as the reaction takes place.

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

In the simplest case ...



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

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

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

$$C_B = C_{A0}X$$

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 $\Theta_i = \frac{F_{i0}}{F_{A0}} = \frac{C_{i0}v_0}{C_{A0}v_0} = \frac{C_{i0}}{C_{A0}} = \frac{y_{i0}}{y_{A0}}$ $\delta = \frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1$ 1-29
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Concentration

To design reactors we need to express concentrations in terms of conversion X (because $r = k(T) \text{fn}(C_A, C_B, \dots)$, 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

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 $v = v_0$).

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

from Stoichiometric Table

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

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

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

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

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 $Z = Z_0$)

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

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

in general ... $C_J = C_{A0} \frac{(\Theta_J + v_J X)}{(1 + \epsilon X)} \left(\frac{T_0}{T}\right) \left(\frac{P}{P_0}\right)$

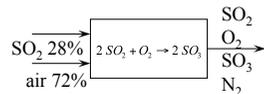
note that v_j has been normalised wrt to v_A (see general Stoichiometric Table)

1.4 An example of a variable volume system

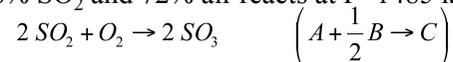
This example develops expressions
for the concentrations in terms of conversion,
of all the reaction species (reactants and products),
in the case of a variable volume system,
through a Stoichiometric Table.

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

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

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

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

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} - $\frac{1}{2}(0.28)F_{T0}X$

$$\Theta_B = 0.54$$

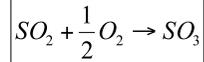
$$\Theta_C = 0$$

$$\Theta_I = 2.0314$$

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

$$\varepsilon = -0.14$$

Example: oxidation of SO₂ (2)



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

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

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

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

$$\varepsilon = -0.14;$$

$$C_{A0} = 0.1 \frac{\text{mol}}{\text{l}};$$

$$\Theta_B = 0.54;$$

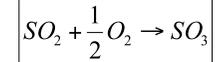
$$\Theta_I = 2.03$$

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)

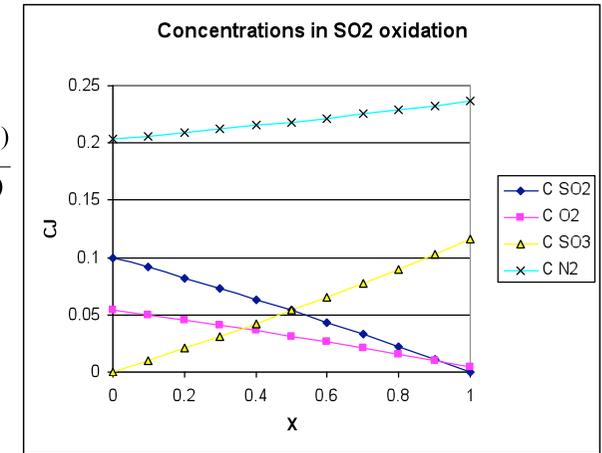


$$C_A = 0.1 \frac{(1-X)}{(1-0.14X)}$$

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

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

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



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*.

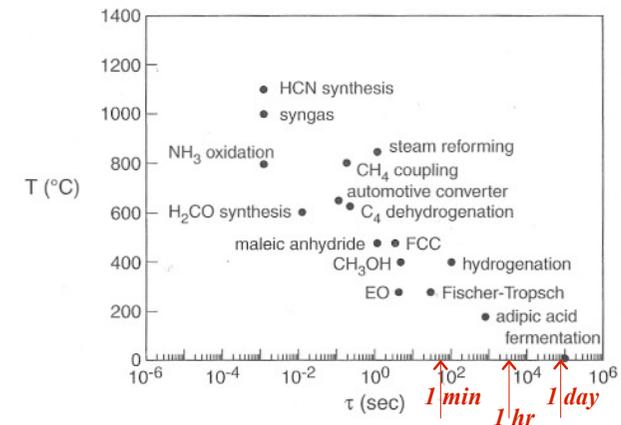
Residence time is a convenient and popular way to characterise reactions in industry.

Residence time



- Residence time (τ) $\tau = \frac{V}{v} = \frac{L}{u}$ [s]
- Space-Time $SpaceTime = \frac{V}{v_0}$ [s]
- Space Velocity (SV) $SV = \frac{v_0}{V}$ [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 $r = k(T) f_n(C_A, C_B, \dots)$
- 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
- A: pre-exponential factor
- E: activation energy [J/mole]
- F_J : molar flowrate of species J [gmole/s]
- G: Gibbs free energy
- k: specific reaction rate; rate coefficient
- N_j : number of moles of species J [gmole]
- R: gas constant, 8.314 [kPa dm³/(mole K)]
- T: absolute temperature [K]
- V: reactor volume [m³]
- v: volumetric flowrate [m³/s]
- y_j : vapour mole fraction of J
- Z: compressibility factor
- δ : Δ of N_T per mole of A reacted
- ϵ : fraction Δ in V per mole reacted A
- μ_j : chemical potential of species J
- Θ_j : ratio of input moles of J per input moles of A
- subscripts
- 0: input or initial condition
- T: total
- f: forward
- b: backward
- superscripts
- °: standard state