

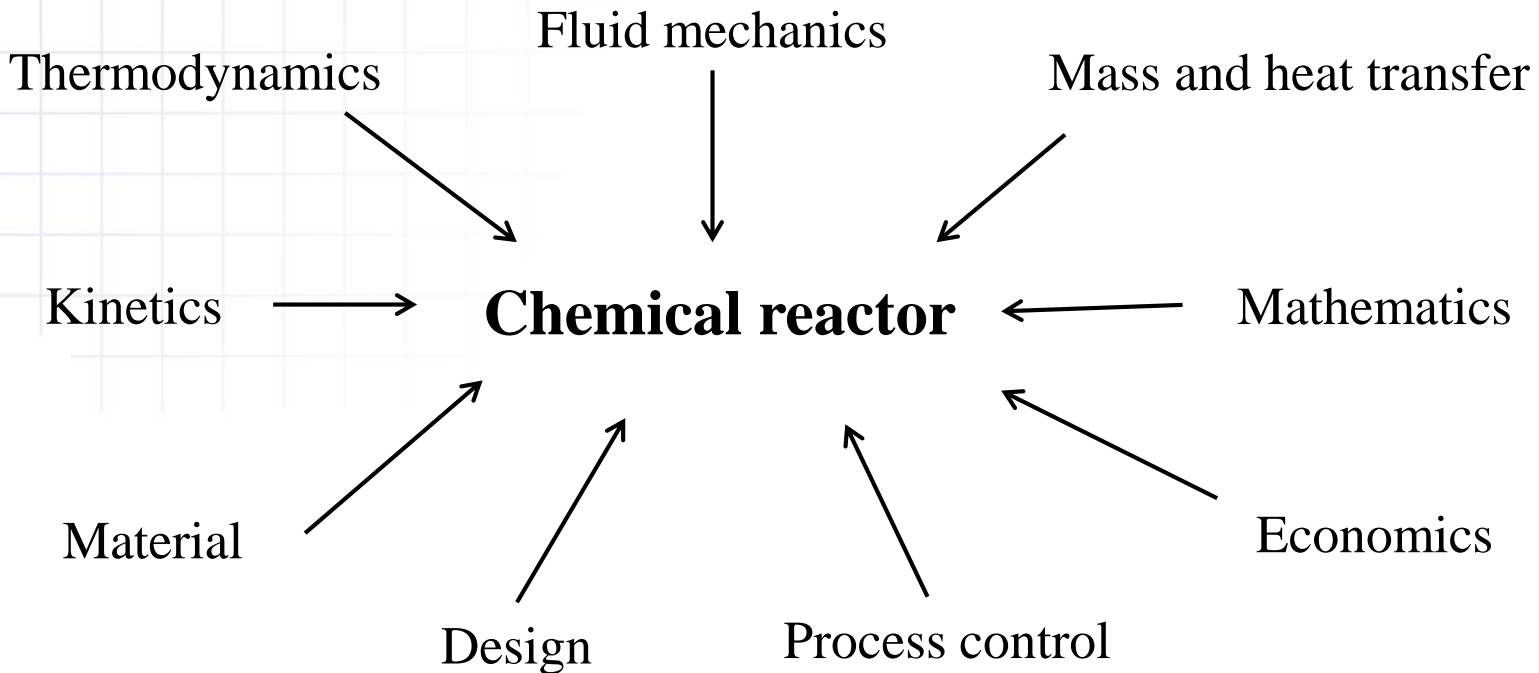
BAE 820 Physical Principles of Environmental Systems

Fundamentals of reaction kinetics

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Chemical reactor

- Chemical processes turn raw materials into valuable products.
- Chemical reactor is the “unit” in which chemical reactions occur.



Designing a chemical reactor

Logically, designing a chemical reactor for a given process might proceed as the following sequence of steps.

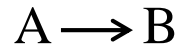
- Bench scale batch reactor
 - Conversions and kinetics are ideally obtained
- Bench scale continuous
 - Operating conditions are determined
- Pilot plant
 - Optimization
- Operating plant

Major challenges of engineers

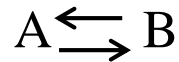
- Maintaining and operating a process
- Fixing some perceived problems
- Increasing capacity at minimum cost
- Searching for alternate processes or feedstock
- Reducing or eliminating a troublesome byproduct

Chemical reactions

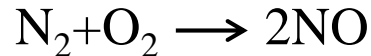
- Irreversible reaction with one reactant and one product



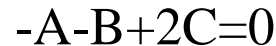
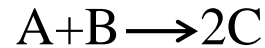
- Reversible reaction



- Consider the formation of nitric oxide



It can be generalized as



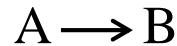
- The generalized equation for a single reaction

$$\sum_{j=1}^s v_j A_j = 0$$

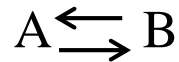
Where v_j is the stoichiometric coefficients of species j , and by convention $v_j < 0$ for a reactant and $v_j > 0$ for a product.

Chemical reactions

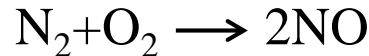
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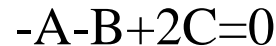
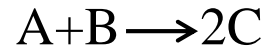
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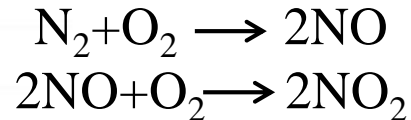
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Multiple reactions

- Consider the following reaction system



It can be generalized as

$$\begin{aligned} -A_1 - A_2 + 2A_3 &= 0 \\ -2A_3 - A_2 + 2A_4 &= 0 \end{aligned}$$

- The generalized equation for a set of reactions

$$\sum_{j=1}^s v_{ij} A_j = 0$$

Where $i=1, 2, \dots, R$, representing a set of R reactions.

The first order irreversible reaction

- Empirical expressions are usually used to describe reaction rates which are dependent on the parameters in the system.
- First order reaction:



$$r = \frac{dC_A}{dt} = -kC_A$$

$$\frac{dC_A}{C_A} = -kdt$$

$$\ln(C_A/C_{A0}) = -kt$$

$$C_A = C_{A0}\exp(-kt)$$

- Zero order reaction: reaction rate is independent of concentration of the species.

$$r = \frac{dC}{dt} = -k, \quad C_A = C_{A0} - kt$$

Example

- The reaction $A \rightarrow B$ has $k=0.01 \text{ sec}^{-1}$. For $C_{A0}=2.0$ moles/liter, what time is required for 90% conversion in a batch reactor? How about for 99%? For 99.9%?

- Solution:

For 90% conversion, $C_A=0.2$ moles/liter,

$$t = -\frac{1}{k} \ln \frac{C_A}{C_{A0}} = -\frac{1}{0.01} \ln \frac{0.2}{2} = 230 \text{ sec}$$

For 99% conversion, $C_A=0.02$ moles/liter,

$$t = -\frac{1}{k} \ln \frac{C_A}{C_{A0}} = -\frac{1}{0.01} \ln \frac{0.02}{2} = 460 \text{ sec}$$

For 99.9% conversion, $C_A=0.2$ moles/liter,

$$t = -\frac{1}{k} \ln \frac{C_A}{C_{A0}} = -\frac{1}{0.01} \ln \frac{0.002}{2} = 690 \text{ sec}$$

The residence time (usually proportional to reactor size) increases markedly as the required conversion increases.

The second order irreversible reaction

- For second order kinetics:



$$r = \frac{dC_A}{dt} = -kC_A^2$$

$$\frac{dC_A}{C_A^2} = -kdt$$

$$t = \frac{1}{k} \left(\frac{1}{C_A} - \frac{1}{C_{A0}} \right)$$

$$C_A = \frac{C_{A0}}{1 + C_{A0}kt}$$

Example

- The reaction $A \rightarrow B$ obeys second order kinetics with $k=0.01$ liter moles⁻¹ sec⁻¹. For $C_{A0}=2.0$ moles/liter, what time is required for 90% conversion in a batch reactor? How about for 99%? For 99.9%?
- Solution:

For 90% conversion, $C_A=0.2$ moles/liter,

$$t = \frac{1}{k} \left(\frac{1}{C_A} - \frac{1}{C_{A0}} \right) = \frac{1}{0.01} \left(\frac{1}{0.2} - \frac{1}{2} \right) = 450 \text{ sec}$$

For 99% conversion, $C_A=0.02$ moles/liter,

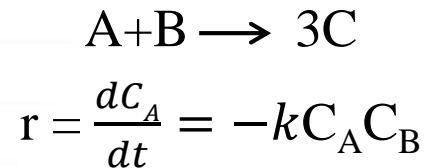
$$t = \frac{1}{k} \left(\frac{1}{C_A} - \frac{1}{C_{A0}} \right) = \frac{1}{0.01} \left(\frac{1}{0.02} - \frac{1}{2} \right) = 4950 \text{ sec}$$

For 99.9% conversion, $C_A=0.002$ moles/liter,

$$t = \frac{1}{k} \left(\frac{1}{C_A} - \frac{1}{C_{A0}} \right) = \frac{1}{0.01} \left(\frac{1}{0.002} - \frac{1}{2} \right) = 49950 \text{ sec}$$

Bimolecular reactions

- Consider a bimolecular reaction:



Which can not be solved without eliminating C_B

$$C_A - C_{A0} = C_B - C_{B0}$$
$$C_B = C_{B0} - C_{A0} + C_A$$

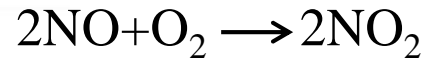
Substitution of C_B in terms of C_A yields

$$\frac{dC_A}{C_A(C_{B0} - C_{A0} + C_A)} = -kdt$$

If $C_{B0} = C_{A0}$, then $C_B = C_A$ at all times, and the expression is identical to a second order reaction.

Reaction rate of a single irreversible reaction

- For NO₂ formation from NO and O₂



$$r = k[\text{NO}]^2[\text{O}_2]$$

- The generalized equation for a single reaction

$$r = k \prod_{j=1}^s C_j^{m_j}$$

Where m_j is the order of the reaction with respect to the j th species; $m_j = 0$ for species that do not affect the rate of reaction.

Rate of formation of each species

- Consider the reaction



- Rate of production of species A, B, and C can be written as negative quantities for reactants and positive quantities for products for particular stoichiometry ($r_j = \nu_j r$)

$$r_A = k[A]^2 = -2r$$

$$r_B = k[A]^2 = r$$

$$r_C = k[A]^2 = 3r$$

Reversible reactions

- Rates of reversible reactions

If the reaction is reversible, we can write the rate as difference between the rate of the forward reaction r_f and the reverse (or back) reaction r_b .

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

- Consider the reaction



If at $t=0$, $C_A=C_{A0}$, $C_B=0$,

$$C_A(t) = C_{A0} \left\{ 1 - \frac{k_f}{k_f + k_b} [1 - \exp(-(k_f + k_b)t)] \right\}$$

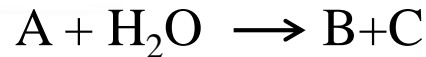
Elementary reaction

- On molecular level, reactions occur by collisions between molecules, and the rate is usually proportional to the density of each reacting molecule. Elementary reaction is defined when kinetics agree with their stoichiometry.
- In elementary reaction, the forward rates appear to be proportional to the concentrations of reactants raised to powers m_{fj} equal to their stoichiometric coefficients, while the backward rates appear to be proportional to the concentrations of products raised to powers m_{bj} equal to their stoichiometric coefficients.

$$\begin{array}{ll} m_{fj} = -v_j, & v_j < 0 \\ m_{fj} = 0, & v_j > 0 \\ m_{bj} = v_j, & v_j > 0 \\ m_{bj} = 0, & v_j < 0 \end{array}$$

Approximate reactions

- Consider the hydrolysis of species A



$$r = kC_A[H_2O]$$

- When the reaction is in dilute aqueous solution, the concentration of water is nearly constant (55 moles/liter for pure liquid water). It is common to omit water in the equation and redefine a new rate coefficient $k' = k[H_2O]$.

$$r = k'C_A$$

- Reaction rate expressions are always empirical, an engineer need to make whatever approximations are reasonable to find answers at the level of sophistication required for the problem at hand.

Reaction rate coefficients

- Reaction rate coefficient k describe the concentration dependences in reaction rate r . They are sometimes called rate constants.

Unit of reaction rate coefficients

Oder of reaction	Units of k
0	moles liter ⁻¹ time ⁻¹
1	time ⁻¹
2	liter moles ⁻¹ time ⁻¹
3	liter ² moles ⁻² time ⁻¹
0.5	moles ^{0.5} liter ^{-0.5} time ⁻¹
n	(liter/moles) ^{$n-1$} time ⁻¹

The Arrhenius temperature dependence

Reaction rate coefficients frequently depend on temperature as

$$k(T) = k_0 \exp(-E/RT)$$

Where

- k_0 is the pre-exponential factor;
- E is the activation energy;
- R is the ideal gas constant;
- T is temperature.
- k_0 and E can be empirically determined.

It is very rare to find reaction rate coefficients that are not described with fair accuracy by expression of this form. The equation predicts a very strong dependence of reaction rates on temperature.



Svante August Arrhenius
(1859-1972)

Winner of Nobel Prize in
Chemistry (1903)

Example

- How much does a reaction rate with an activation energy of 15000 cal/mole vary when temperature is increased from 300 to 310K? How about from 310 to 400K?
- Solution:

$$R = 8.31 \text{ J}/(\text{mol K}) \approx 2 \text{ cal}/(\text{mol K})$$

$$\frac{k_{310}}{k_{300}} = \frac{\exp[-15000/(2 \times 310)]}{\exp[-15000/(2 \times 300)]} = 2.24$$

$$\frac{k_{400}}{k_{300}} = \frac{\exp[-15000/(2 \times 400)]}{\exp[-15000/(2 \times 300)]} = 517$$

Thermodynamics and reactors

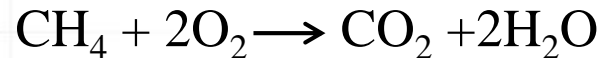
- Chemical reactions can liberate or absorb energy, and the handling of this energy is a major concern in reaction engineering.
 - When standard state enthalpies of reaction $\Delta H_R < 0$, the reaction liberates heat, and is called exothermic;
 - When standard state enthalpies of reaction $\Delta H_R > 0$, the reaction absorbs heat, and is called endothermic.
- In an adiabatic reactor (no heat is added or remove)

$$\Delta T = \frac{-\Delta H_R}{N C_{p, products}}$$

Where $C_{p, products}$ is the average heat capacity per mole of product, N is moles of product that are produced.

Example

- The methane combustion reaction is



And this reaction has a heat of reaction of -192 kcal/mole of methane. Suppose the room you are in now contains 9.5% CH₄. If someone turned on the light switch and create a spark, what would be the temperature and pressure in the room before the windows burst? How about if methane were 5% in air? Assuming the heat capacity C_p is equal to 7/2 R (a reasonable approximation for small molecules such as N₂).

- Solution:

For a basis of 1 mole of CH₄, before reaction, there are 2 moles of O₂ and 8 moles of N₂; after reaction, there are 1 moles of CO₂, 2 moles of H₂O and 8 moles of N₂ for a total 11 moles of product per mole of methane reacted.

$$\Delta T = \frac{-\Delta H_R}{NC_{p \text{ products}}} = \frac{192}{11 \times 7/2 \times R} = 2500 \text{ K}, \quad P_2/P_1 = T_2/T_1 = (2500+300)/300 = 9$$

For 5% CH₄, the products will be 1 moles of CO₂, 2 moles of H₂O, 2 moles of O₂ remaining, and 16 moles of N₂ for a total 21 moles, the temperature will be about half of that above.