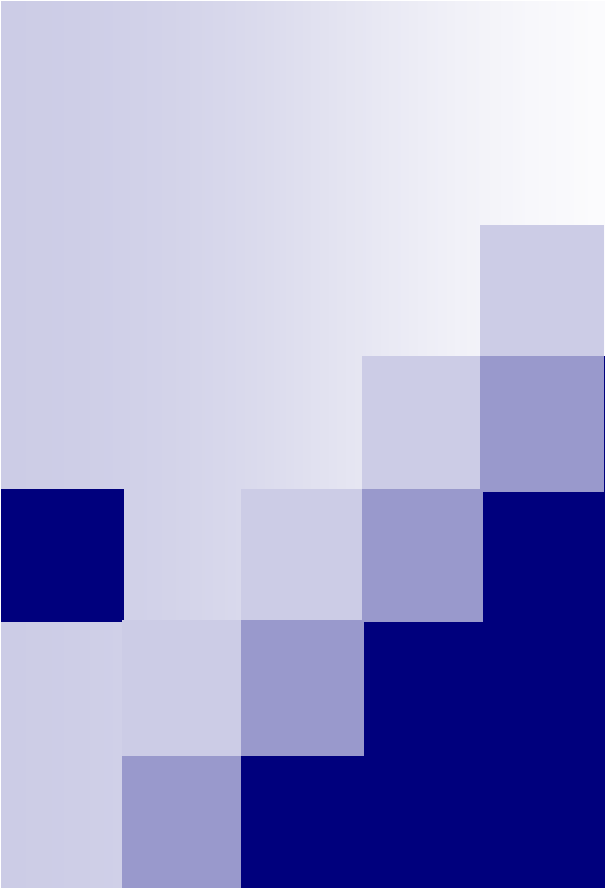




CHE 402 Kinetics & Reactor Design

Dr. Eid Al-Mutairi

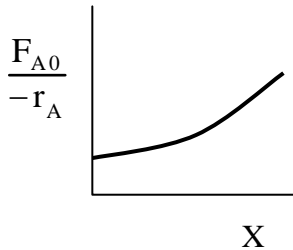


Chapter 3: Rate Laws and Stoichiometry

Dr. Eid Al-Mutairi

Why a Rate Law?

- If we have



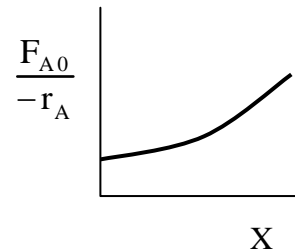
- Then we can size a number of CSTR and PFR reaction systems

Summary

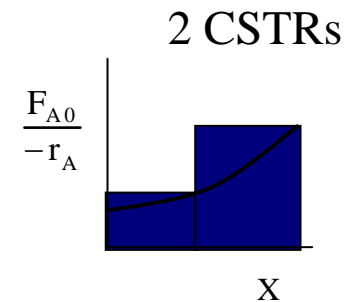
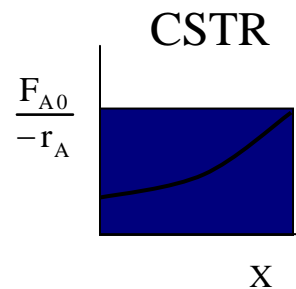
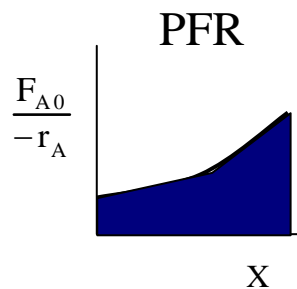
	<i>Differential Form</i>	<i>Algebraic Form</i>	<i>Integral Form</i>
Batch	$N_{A0} \frac{dX}{dt} = -r_A V$		$t = N_{A0} \int_0^X \frac{dX}{-r_A V}$ and $\int_0^t V(t) dt = N_{A0} \int_0^X \frac{dX}{-r_A}$
CSTR		$V = \frac{F_{A0}(X_{out} - X_{in})}{(-r_A)_{out}}$	
PFR	$F_{A0} \frac{dX}{dV} = -r_A$		$V = F_{A0} \int_{X_{in}}^{X_{out}} \frac{dX}{-r_A}$
PBR	$F_{A0} \frac{dX}{dW} = -r'_A$		$W = F_{A0} \int_{X_{in}}^{X_{out}} \frac{dX}{-r'_A}$

Why a Rate Law?

- If we have

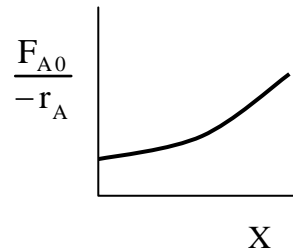


- Then we can size a number of CSTR and PFR reaction systems

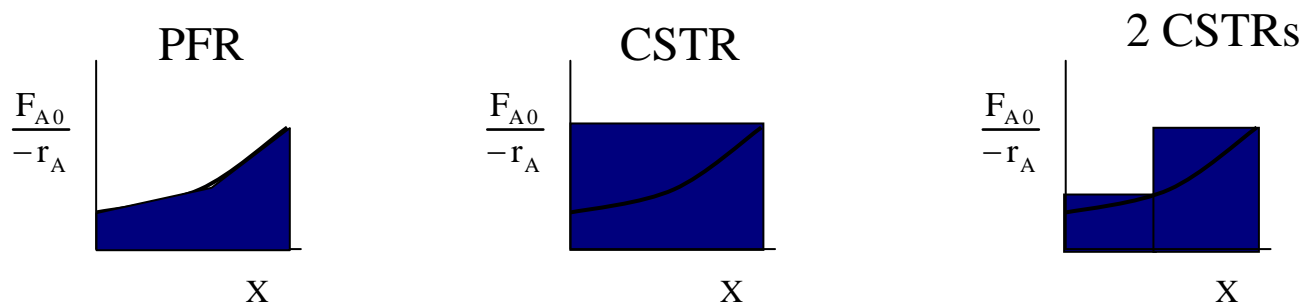


Why a Rate Law?

- If we have



- Then we can size a number of CSTR and PFR reaction systems



- To find $-r_A = f(X)$
 - 1) Need the rate law, $-r_A = f(C_A, C_B)$
 - 2) Need the reaction stoichiometry, $C_A = C_{A0}(1-X)$

Rate Law Basics

- A rate law describes the behavior of a reaction. The rate of a reaction is a function of temperature (through the rate constant) and concentration.

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- **Power Law Model**

$$-r_A = kC_A^\alpha C_B^\beta$$

α order in A
 β order in B
Overall Reaction Order = $\alpha + \beta$

- k is the specific reaction rate (constant)

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- **Power Law Model**

$$-r_A = kC_A^\alpha C_B^\beta$$

α order in A

β order in B

Overall Reaction Order = $\alpha + \beta$

k is the specific reaction rate (constant)

k is given by the Arrhenius Equation:

$$k = Ae^{-E/RT}$$

Where:

- E = activation energy (cal/mol)
- R = gas constant (cal/mol*K)
- T = temperature (K)
- A = frequency factor (units of A, and k, depend on overall reaction order)

Review

THE REACTION RATE CONSTANT

For irreversible chemical reactions, such as



the rate of disappearance of A, $-r_A$, may be written as:

$$\begin{aligned} \text{i.e.,} \quad -r_A &= \left[\begin{array}{c} \text{reaction rate} \\ \text{constant} \end{array} \right] * \left[\begin{array}{c} \text{function of the concentrations of the} \\ \text{species involved in the reaction} \end{array} \right] \\ -r_A &= k(T) * \text{function} (C_A, C_B, C_C \dots) \end{aligned}$$

The relationship between the **reaction rate constant** $k(T)$, also known as the **Arrhenius constant**, and temperature is given by the **Arrhenius equation**:

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

where

- A** = frequency factor [same units as $k(T)$, to be determined]
- E** = activation energy [J/mol or cal/mol]
- R** = gas constant [8.314 J/mol K or 1.987 cal/mol K]
- T** = absolute temperature [K]

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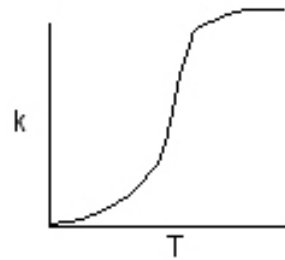
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Rate Law Basics

- To find the activation energy, plot k as a function of temperature:



Where:

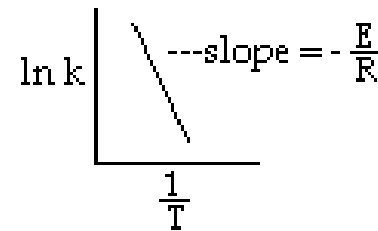
$$T \rightarrow \infty \quad k \rightarrow A$$

$$T \rightarrow 0 \quad k \rightarrow 0$$

$$A \approx 10^{13}$$

$$\mathbf{k = Ae^{-E/RT}}$$

$$\ln k = \ln A - \frac{E}{R} \left(\frac{1}{T} \right)$$



$$k(T_2) = k(T_1) \exp \left[\frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \right]$$

Review

THE REACTION RATE CONSTANT (cont.)

$$\ln k(T) = \ln (A e^{-E/RT}) = \ln A + (-E/R)(1/T)$$

$$\ln k(T) = (-E/R)(1/T) + \ln A$$

The **frequency factor** and **activation energy** can be obtained experimentally from a plot of $\ln k(T)$ vs. $1/T$:



Be careful!

- Make sure T is in absolute temperature units.
- If you use a **semilog scale** plot, don't read off the values on the y-axis in determining your slope! (That would be the slope of $k(T)$ vs. $1/T$). Make sure you measure the actual slope of the line.

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THE REACTION RATE CONSTANT (cont.)

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

Because the reaction rate, $-r_A$, is expressed in units of $\frac{\text{moles}}{\text{time} \cdot \text{reactor volume}}$, the units of $k(T)$ (and those of A) will depend on the form of the concentration function, as shown in the following examples:

RATE EXPRESSION :	$-r_A = k(T) C_A$	$-r_A = k(T) C_A C_B^2$
UNITS :	$\frac{\cancel{\text{moles}}}{\cancel{\text{time}} \cdot \cancel{\text{vol}}} = k(T) \frac{\cancel{\text{moles}}}{\cancel{\text{vol}}}$	$\frac{\cancel{\text{moles}}}{\cancel{\text{time}} \cdot \cancel{\text{vol}}} = k(T) \frac{\cancel{\text{moles}}}{\cancel{\text{vol}}} \frac{\text{moles}^2}{\text{vol}^2}$
UNITS OF $k(T)$:	$\frac{1}{\text{time}}$	$\frac{\text{vol}^2}{\text{time} \cdot \text{mol}^2}$

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Reaction Order

- You can tell the overall reaction order by the units of k

C_A	$-r_A$	Reaction Order	Rate Law	k
(mol/dm^3)	$(\text{mol}/\text{dm}^3\cdot\text{s})$	zero	$-r_A = k$	$(\text{mol}/\text{dm}^3\cdot\text{s})$

Reaction Order

- You can tell the overall reaction order by the units of k

C_A	$-r_A$	Reaction Order	Rate Law	k
(mol/dm^3)	$(\text{mol}/\text{dm}^3 \cdot \text{s})$	zero	$-r_A = k$	$(\text{mol}/\text{dm}^3 \cdot \text{s})$
		1st	$-r_A = kC_A$	s^{-1}

Reaction Order

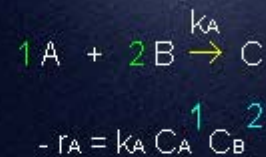
- You can tell the overall reaction order by the units of k

C_A	$-r_A$	Reaction Order	Rate Law	k
(mol/dm^3)	$(\text{mol}/\text{dm}^3 \cdot \text{s})$	zero	$-r_A = k$	$(\text{mol}/\text{dm}^3 \cdot \text{s})$
		1st	$-r_A = kC_A$	s^{-1}
		2nd	$-r_A = kC_A^2$	$(\text{dm}^3/\text{mol} \cdot \text{s})$

Review

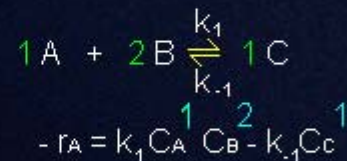
THE REACTION RATE LAW - elementary rate laws

For irreversible reactions that follow an elementary rate law, the reaction order for each reactant matches the **stoichiometric coefficient** of the reactant :



First order in A
Second order in B

If the reaction is **reversible** and follows an elementary rate law, the overall reaction rate is equal to the sum of the forward and reverse reaction rates :



Forward reaction: First order in A
Second order in B

Reverse reaction: First order in C

The reaction rate for the reversible reaction can also be expressed using the **concentration equilibrium constant** $K_c = k_1 / k_2$:

$$-r_A = k_1 C_A C_B^2 - k_{-1} C_C = k_1 \left(C_A C_B^2 - \frac{k_{-1} C_C}{k_1} \right) = k_1 \left(C_A C_B^2 - \frac{C_C}{K_c} \right)$$

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Review

THE REACTION RATE LAW - non-elementary reactions

For many catalyzed reactions, such as the **heterogeneous** reaction of carbon monoxide and nitrogen oxide gas (from automobile exhaust) over a solid catalyst yields harmless nitrogen and carbon dioxide,



the rate law is often not elementary. In addition, since the reactants are gases, it is often preferable to express the rate law in terms of **partial pressures**. At high temperatures, the **non-elementary** rate law for this **heterogeneous** reaction, $-r'_{\text{NO}}$, is:

$$-r'_{\text{NO}} = \frac{k P_{\text{NO}} P_{\text{CO}}}{(1 + K_1 P_{\text{NO}} + K_2 P_{\text{CO}})^2}$$

Note that $-r'_{\text{NO}}$ for the **heterogeneous** reaction (written with a prime to distinguish it from the homogeneous reaction rate term) has units of

$\frac{\text{moles}}{\text{sec} \cdot \text{grams of catalyst}}$ rather than $\frac{\text{moles}}{\text{sec} \cdot \text{reactor volume}}$

In this module we will focus on **homogeneous elementary** reactions.

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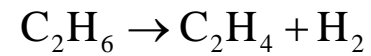
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Examples of Rate Laws

- First Order Reactions

(1) Homogeneous irreversible elementary gas phase reaction with



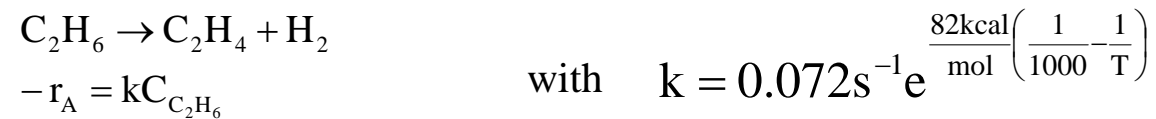
$$-r_A = kC_{\text{C}_2\text{H}_6}$$

$$k = 0.072\text{s}^{-1} e^{\frac{82\text{kcal}}{\text{mol}} \left(\frac{1}{1000} - \frac{1}{T} \right)}$$

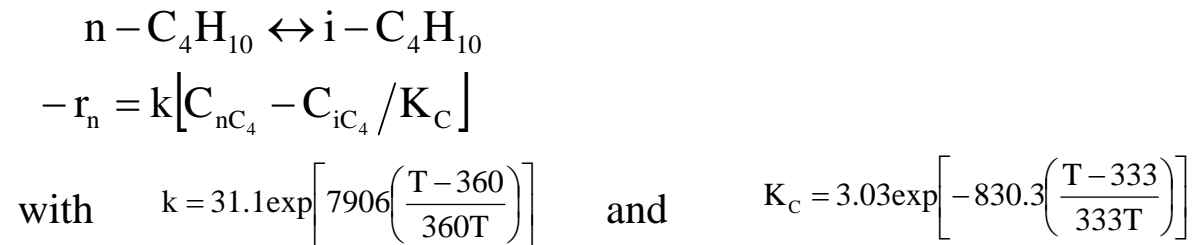
Examples of Rate Laws

- First Order Reactions

(1) Homogeneous irreversible elementary gas phase reaction



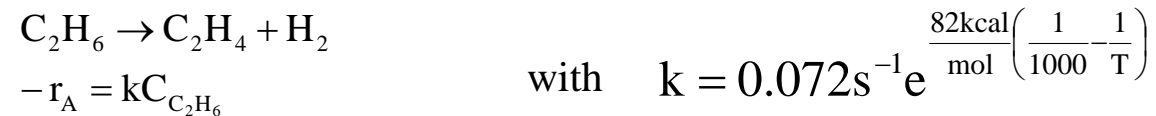
(2) Homogeneous reversible elementary reaction



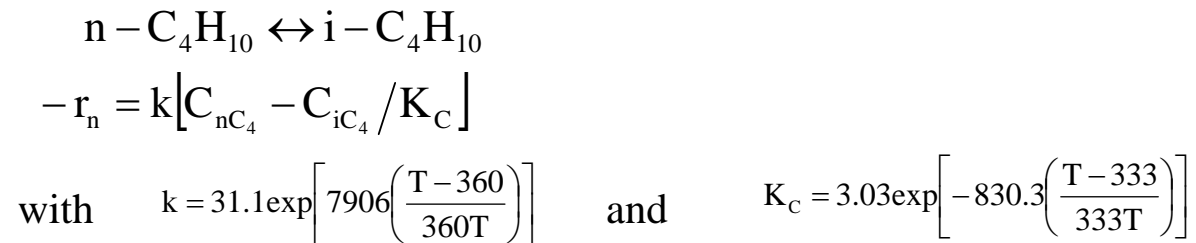
Examples of Rate Laws

- First Order Reactions

(1) Homogeneous irreversible elementary gas phase reaction

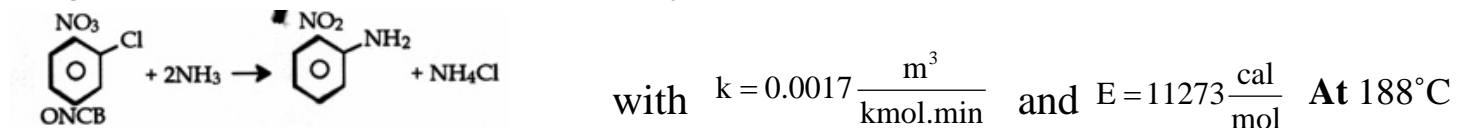


(2) Homogeneous reversible elementary reaction



- Second Order Reactions

(1) Homogeneous irreversible non-elementary reaction



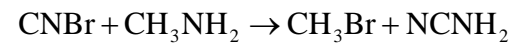
$$-r_A = kC_{\text{ONCB}}C_{\text{NH}_3}$$

This is first order in ONCB, first order in ammonia and overall second order.

Examples of Rate Laws

- Second Order Reactions

- (2) Homogeneous irreversible elementary reaction



$$-r_A = kC_{\text{CNBr}}C_{\text{CH}_3\text{NH}_2} \quad \text{with} \quad k = \frac{2.2\text{dm}^3}{\text{s.mol}}$$

Examples of Rate Laws

- Second Order Reactions

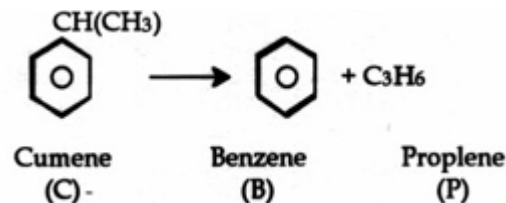
(2) Homogeneous irreversible elementary reaction



$$-r_A = k C_{\text{CNBr}} C_{\text{CH}_3\text{NH}_2}$$

This reaction is first order in CNBr, first order in CH₃NH₂ and overall second order.

(3) Heterogeneous catalytic reaction: The following reaction takes place over a solid catalyst:



$$-r_C = \frac{k[P_C - P_B P_P / K_P]}{1 + K_B P_B + K_C P_C}$$