Chemical Engineering of Heterogeneous Reactions

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Outline of the course

Objective: Be able to analyze and understand a heterogeneous reaction (mechanism, kinetics etc…) from experimental data .

- 1. Basic concepts (about 4 weeks)
  - Kinetics (elementary reactions and transition state theory) **Chapter 1 and 2 (partial)**
  - Ideal reactors **Chapter 3 (partial)**
  - Non-ideal reactors **Chapter 8 (most of it)**
  - **The Steady-State Approximation** (SSA) **Chapter 4 (most of it)**
- 2. Heterogeneous catalysis (about 4 weeks) — **Chapter 5**
  - What are heterogeneous catalysts?
  - Bulk and surface structures in heterogeneous catalysts
  - Surface reactivity
  - Elementary step kinetics
  - Kinetics of Overall Reactions
- 3. Transport effects in heterogeneous catalysis (about 4-5 weeks) — **Chapter 6**
  - External transport
  - Internal transport
  - Combined internal and external transport
  - Analyzing rate data

+ 1 week of computer exercises

1.5 The steady state approximation (SSA)

1.5.1 Definitions

By definition, 1-step reactions between stable molecules are rare!

Because of this, most reactions proceed through a **sequence** of elementary steps with reactive intermediates.

Let's define different kinds of reaction sequences:

Open reaction sequence: the reactive intermediates are <u>not</u> reproduced after their reaction

Example: Ozone decomposition

$$\begin{array}{r} O_3 \rightarrow O_2 + O \\ O + O_3 \rightarrow O_2 + O_2 \\ \hline 2\ O_3 \Longrightarrow 3\ O_2 \end{array}$$

1.5 The steady state approximation (SSA)

1.5.1 Definitions

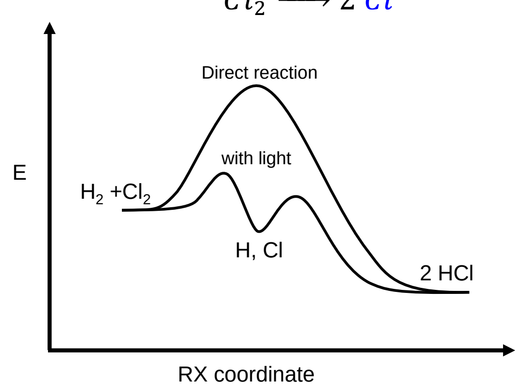
Cyclic reaction sequence: the reactive intermediates are reproduced after their reaction

The reaction is accelerated by initiating Cl_2 decomposition: $Cl_2 \xrightarrow{light} 2\ Cl$

Example: HCl formation

$$\begin{array}{r} Cl + H_2 \rightarrow HCl + H \\ H + Cl_2 \rightarrow HCl + Cl \\ \hline H_2 + Cl_2 \Longrightarrow 2\ HCl \end{array}$$

In this example:
reactive intermediates are systematically formed with products
= cyclic chain sequence.



Cyclic reactions are significantly faster than direct reactions.

1.5 The steady state approximation (SSA)

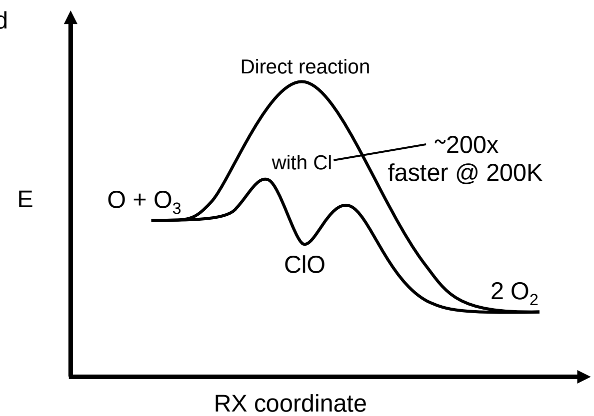
1.5.1 Definitions

Cyclic reaction sequence: the reactive intermediates are reproduced after their reaction

Second example: Cl catalyzed O_3 decompositon

$$\begin{aligned} Cl + O_3 &\rightarrow O_2 + ClO \\ ClO + O &\rightarrow O_2 + Cl \\ \hline O + O_3 &\Longrightarrow 2\,O_2 \end{aligned}$$

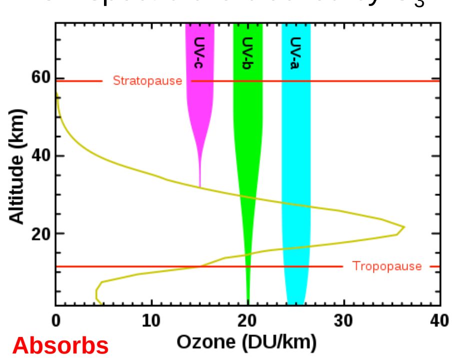
In this example:
The cycled reactive intermediate is <u>external</u>
= cyclic catalytic sequence.



1.5 The steady state approximation (SSA)

Side note: we just explained the depletion of the ozone layer!

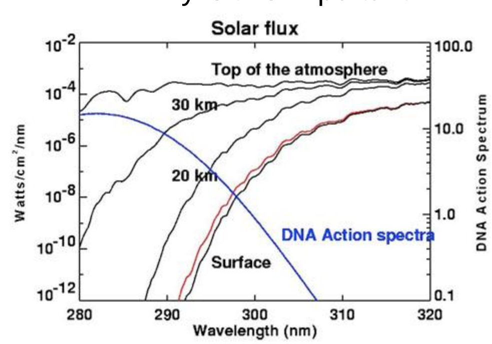
UV spectra are blocked by O_3:



Absorbs radiation @:
<242 nm $O_2 \xrightarrow{UV} 2\,O$ (formation)
$O + O_2 \rightarrow O_3$

280-320 nm $O_3 \xrightarrow{UV} O + O_2$ (destruction)
$O + O_3 \rightarrow 2\,O_2$

Why is this important?



Blocking UV-B radiation is critical because it damages DNA!

Image source: *wikipedia*

1.5 The steady state approximation (SSA)

The ozone layer depends on this delicate equilibrium:

$$O_2 \xrightarrow{UV} 2\ O \text{ (formation)}$$
$$O + O_2 \rightarrow O_3$$

$$O_3 \xrightarrow{UV} O + O_2 \text{ (destruction)}$$
$$O + O_3 \rightarrow 2\ O_2$$

This reaction can be severely accelerated by Cl

Humans have disrupted this equilibrium by using chlorofluorocarbons (CFCs):

$$CF_2Cl_2 \xrightarrow{UV} CF_2Cl + Cl \rightarrow O_3 \text{ depletion!}$$

ChE-403 Problem Set 1.4

Week 4

Problem 1

Consider the decomposition of N_2O_5:

$$2\ \ _2\ \ _5 \Rightarrow 4\ \ _2 + \ \ _2$$

Experimentally, we observe that the rate of oxygen formation is consistent with the following expression:

$$\frac{[\ \ _2]}{\quad} = \ [\ \ _2\ \ _5]$$

With *k* being a constant.

Is this compatible with the following suggested mechanism?

$$2(N_2O_5 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO_2 + NO_3)$$
$$NO_2 + NO_3 \xrightarrow{k_2} NO_2 + O_2 + NO$$
$$NO + NO_3 \xrightarrow{k_3} 2NO_2$$
$$2N_2O_5 \Rightarrow 4NO_2 + O_2$$

Relaxation methods: transient kinetic analysis

Reaction:

$$CO + * \rightleftarrows CO^*$$

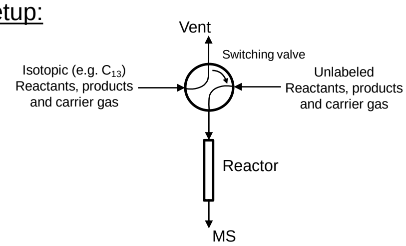
Chemisorbed CO

You want to estimate k_1 and k_{-1}, which are very fast.

Easiest possibility is to measure $t_r \sim k_1 + k_{-1}$

t_r represents how long a system takes to reach "steady-state" (i.e. to equilibrate).

Setup:



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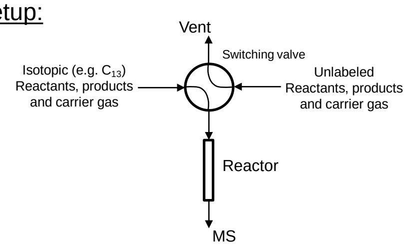
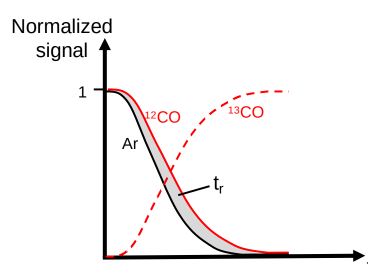


MS signal after switch:



Problem 2
Consider the decomposition of ozone catalyzed by *Cl*:

$$Cl + O_3 \xrightarrow{k_1} O_2 + ClO$$

$$\underline{ClO + O \xrightarrow{k_2} O_2 + Cl}$$
$$O + O_3 \Rightarrow 2O_2$$

Can you use the steady state approximation on reactive intermediate *ClO* to show that the rate of ozone disappearance can be written as:

$$\frac{d[O_3]}{dt} = -\frac{k_1 k_2 [O][O_3][Cl]_0}{k_2[O] + k_1[O_3]}$$

Where $[Cl]_0$ is the Cl loaded/present in the system at t=0.