

1.5 The steady state approximation (SSA)

1.5.1 Definitions

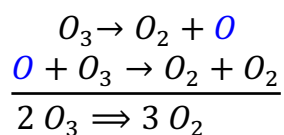
By definition, 1-step reactions between stable molecules are rare!

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 not reproduced after their reaction

Example: Ozone decomposition



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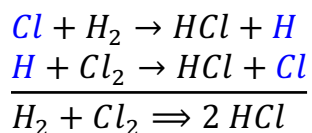
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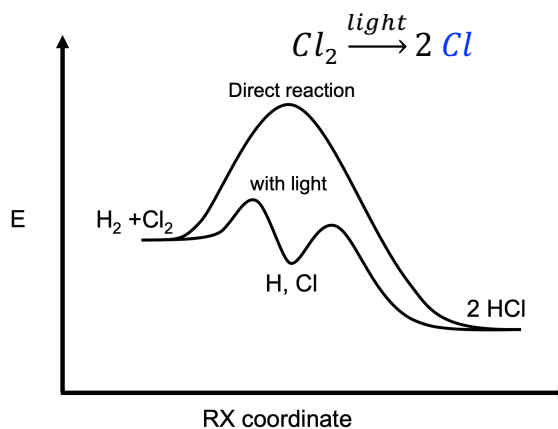
Cyclic reaction sequence: the reactive intermediates are reproduced after their reaction

The reaction is accelerated by initiating Cl_2 decomposition:

Example: HCl formation



In this example:
all reactive intermediates are part of the reactants and are part of the products
= **cyclic chain sequence**.



Cyclic reactions are significantly faster than direct reactions.

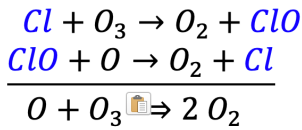
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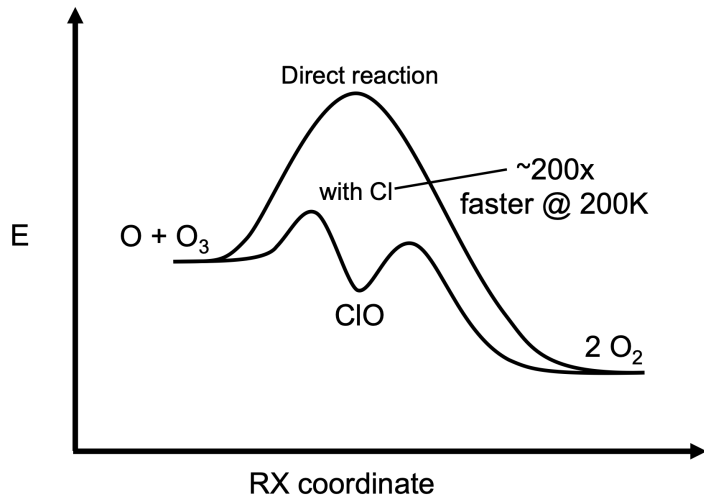
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Cyclic reaction sequence: the reactive intermediates are reproduced after their reaction

Second example: Cl catalyzed O₃ decomposition



In this example:
The cycled reactive intermediate is external
= cyclic catalytic sequence.

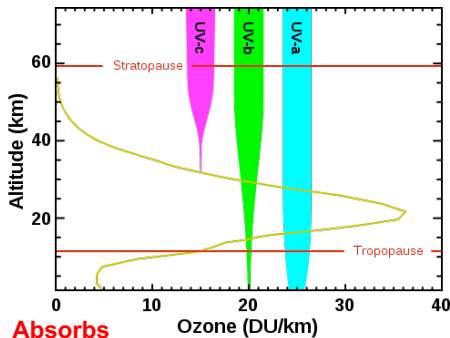


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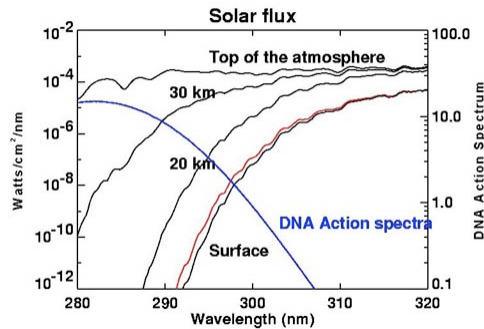
Side note: we just explained the depletion of the ozone layer!

UV spectra are blocked by O₃:



Absorbs radiation @:
<242 nm → $\text{O}_2 \xrightarrow{\text{UV}} 2 \text{O}$ (formation)
 $\text{O} + \text{O}_2 \rightarrow \text{O}_3$
280-320 nm → $\text{O}_3 \xrightarrow{\text{UV}} \text{O} + \text{O}_2$ (destruction)
 $\text{O} + \text{O}_3 \rightarrow 2 \text{O}_2$

Why is this important?



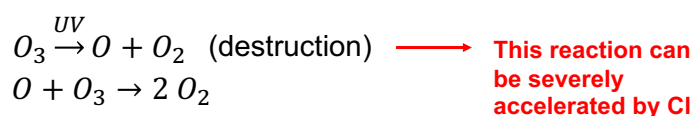
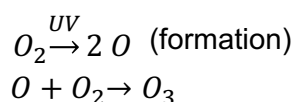
Blocking UV-B radiation is critical because it damages DNA!

Image source: wikipedia

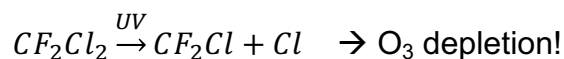
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The ozone layer depends on this delicate equilibrium:



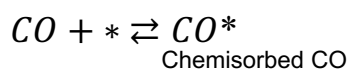
Humans have disrupted this equilibrium by using chlorofluorocarbons (CFCs):



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Relaxation methods: transient kinetic analysis

Reaction:

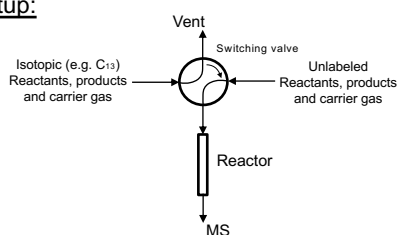


You want to estimate k_1 and k_{-1} , which are very fast.

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).

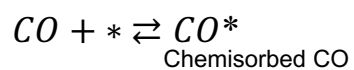
Setup:



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Relaxation methods: transient kinetic analysis

Reaction:

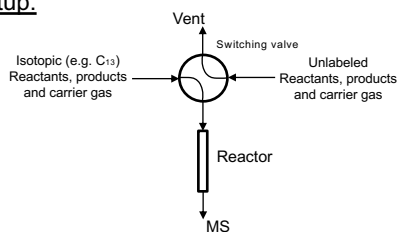


You want to estimate k_f and k_r , which are very fast.

Easiest possibility is to measure $t_r \sim k_f + k_r$

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

Setup:



MS signal after switch:

