CHEM 3310

Chemical Kinetics

Reaction Mechanism

What is a Reaction Mechanism?

Reaction mechanism is a collection of steps that account for the way the reactants become products.

This is not the same as a balanced chemical equation.

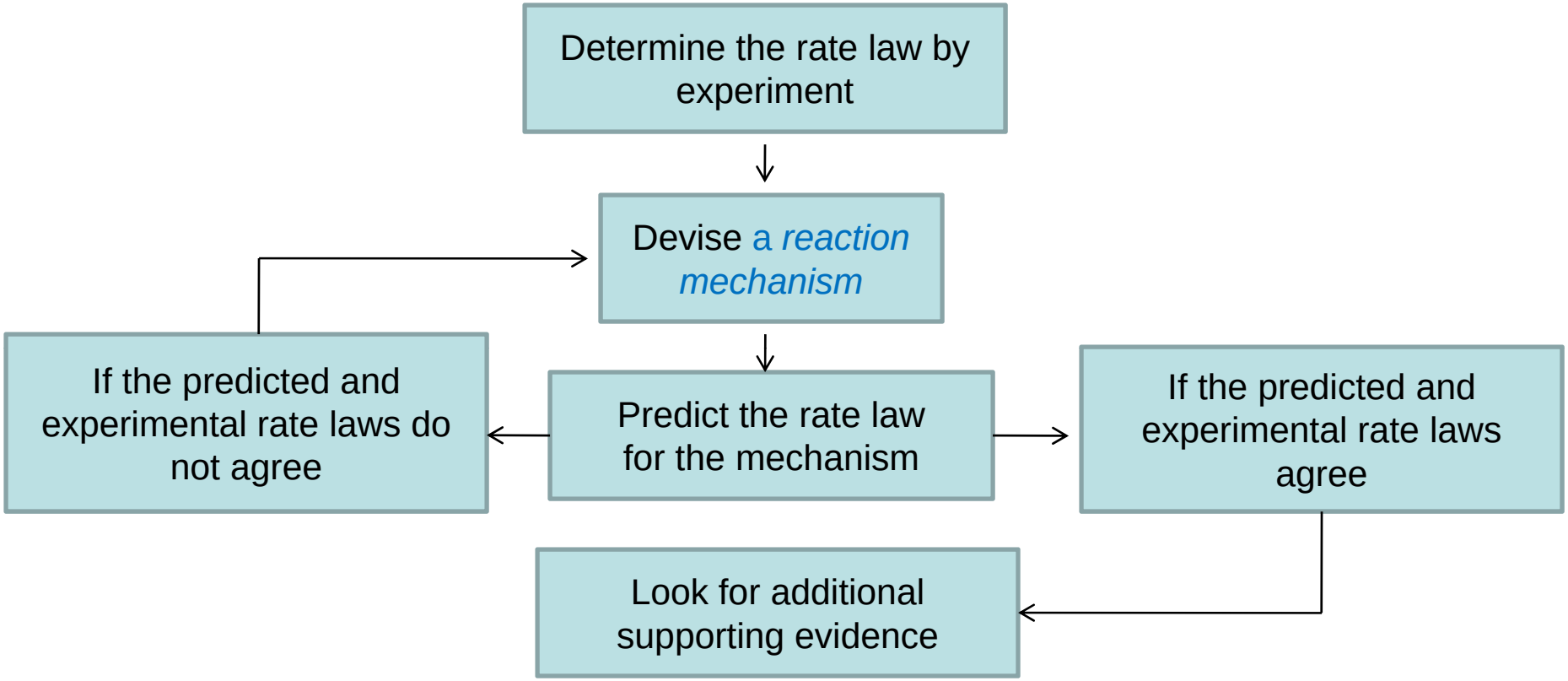
A balanced chemical equation does not tell us how the reactants become the products. It tells us the before (reactants) and the after (products) states of the overall process.

Example: Photosynthesis

$$6\,CO_2 + 6\,H_2O \xrightarrow{\text{light}} C_6H_{12}O_6 + 6\,O_2$$

This reaction occurs in many steps!

What is a Reaction Mechanism?



What is a Reaction Mechanism?

- Reaction mechanism is a collection of steps that account for the way the reactants become products. These steps are called *elementary steps*.

- The reaction steps involve the breaking of chemical bonds and/or the making of new bonds.

- Each step in a reaction mechanism is a description of the chemical reaction.

- Reactions may occur all at once or through several discrete steps. Each of these processes is known as an *elementary reaction* or *elementary step*.

What is a Reaction Mechanism?

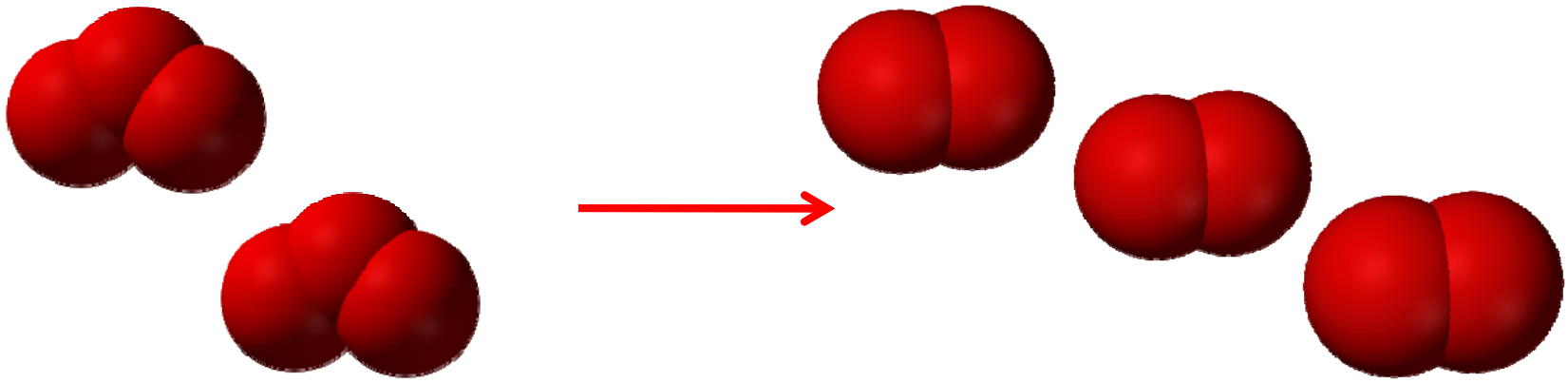
- Each elementary step occurs at different rates.
- Elementary step could be reversible (i.e. equilibrium is reached). When this is present in a reaction mechanism, this is usually the fast step.
- The step(s) in a reaction mechanism must add to give the overall balanced chemical reaction.
- The proposed mechanism must be consistent with the observed rate law of the reaction.

What is a Reaction Mechanism?

Example:

$$2\ O_3\ (g) \longrightarrow 3\ O_2\ (g)$$

(balanced reaction)



This is NOT a reaction mechanism.

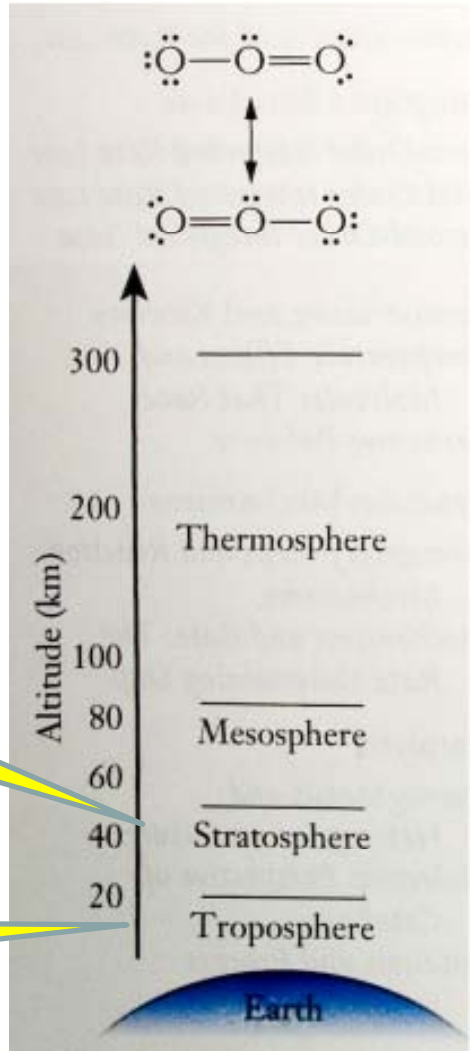
Reaction Mechanism

The Chapman Cycle

the **natural** creation and destruction of ozone in the stratosphere

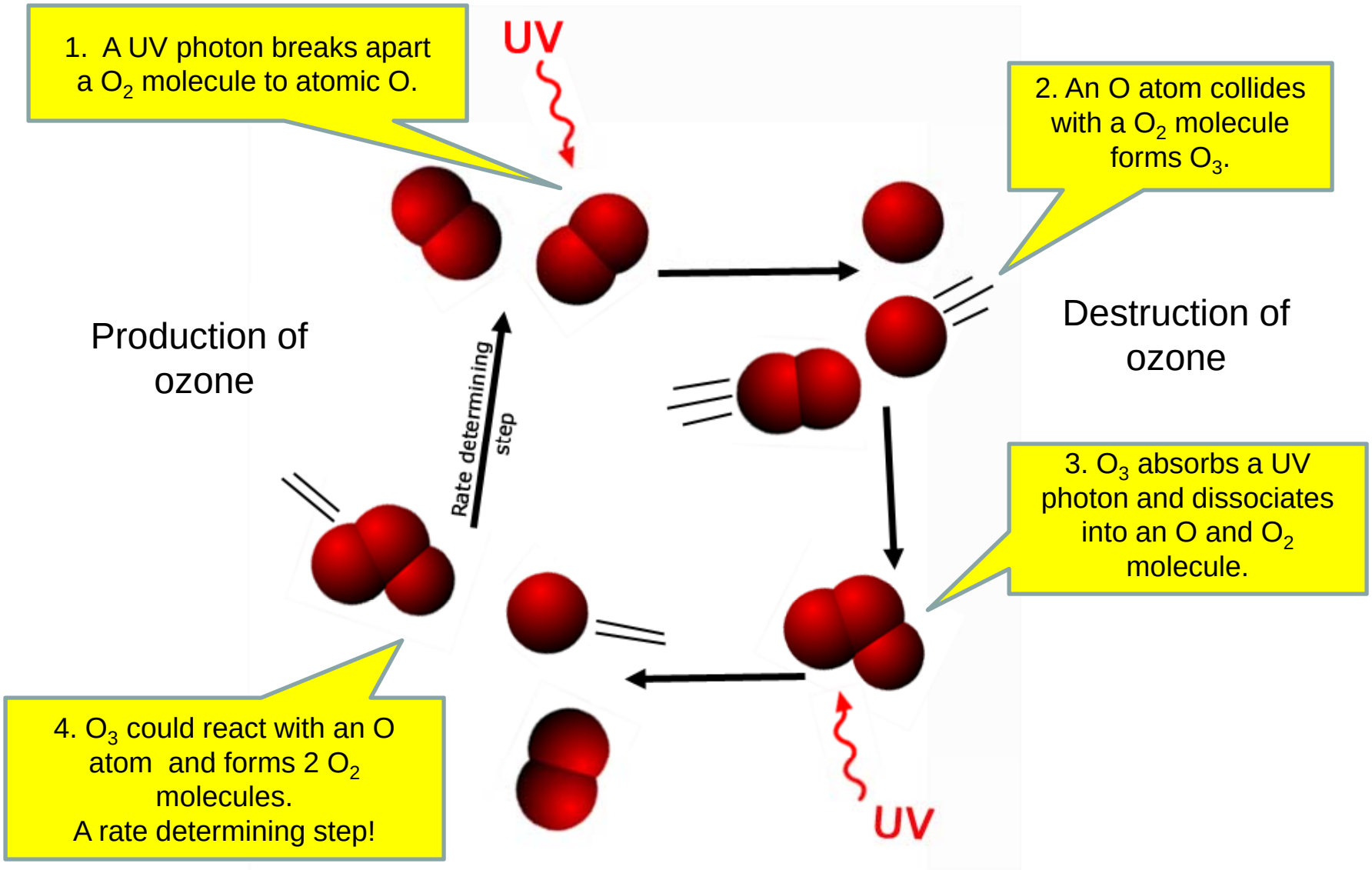
Ozone in the stratosphere is good. It absorbs solar UV and protects us.

Ozone in the troposphere is smog, concentrated around urban areas.



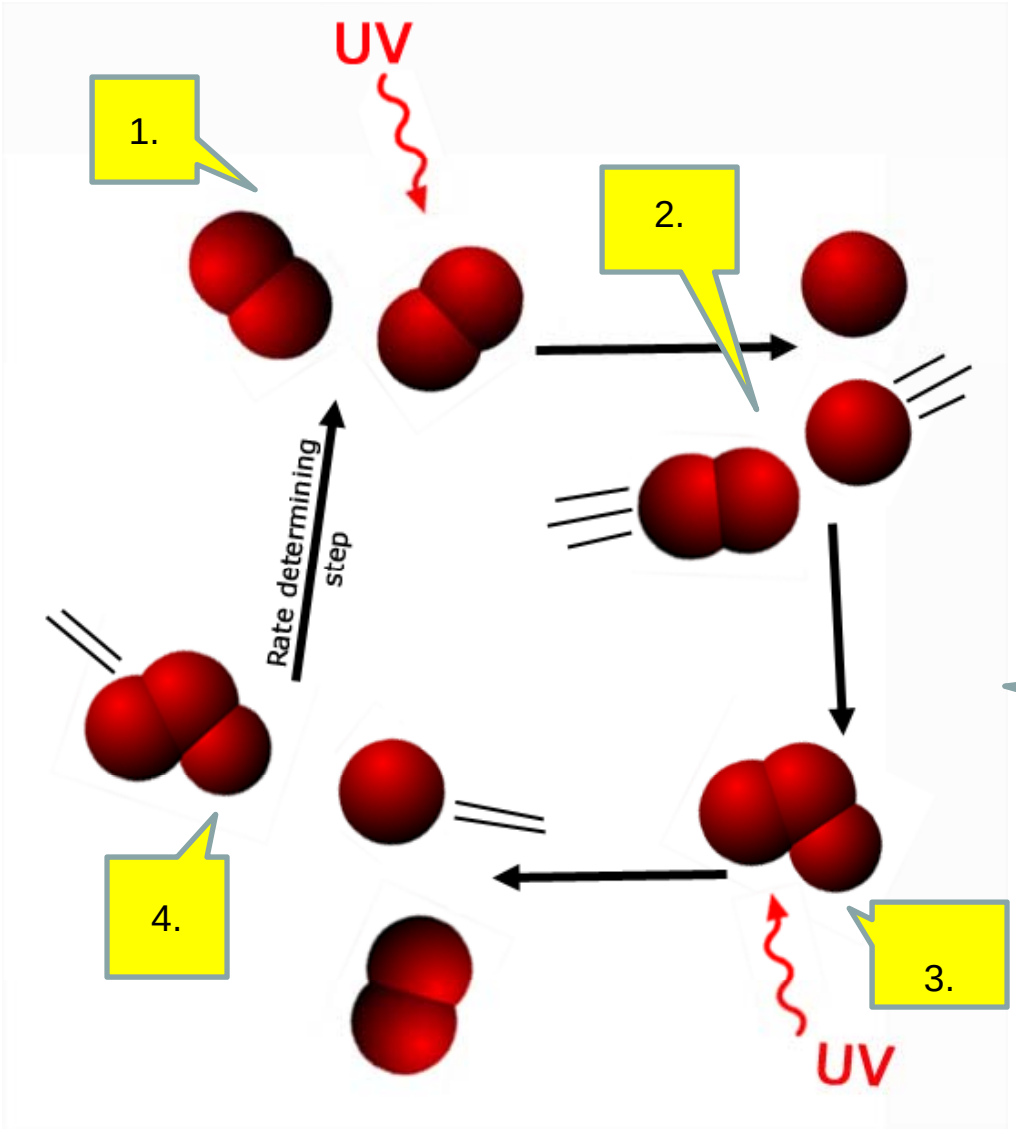
Reaction Mechanism

The Chapman Cycle is a set of reaction mechanism that describes the **natural** creation and destruction of ozone in the stratosphere.



What is a Reaction Mechanism?

The Chapman Cycle



1. $2\,O_2 \rightarrow 4\,O$
2. $4\,O + O_2 \rightarrow 2\,O_3$

Source of O_3

3. $O_3 \rightarrow O_2 + O$
4. $O_3 + O \rightarrow 2\,O_2$

Use up of O_3

Add up the steps

Nothing to add up; nothing really happens

Chapman Cycle: null cycle
A steady-state concentration of ozone is produced.

Reaction Mechanism

Depletion of ozone

Ozone depletion in the stratosphere is caused by chemicals that are used in refrigerators and air conditioners, chlorofluorocarbons (CFCs).

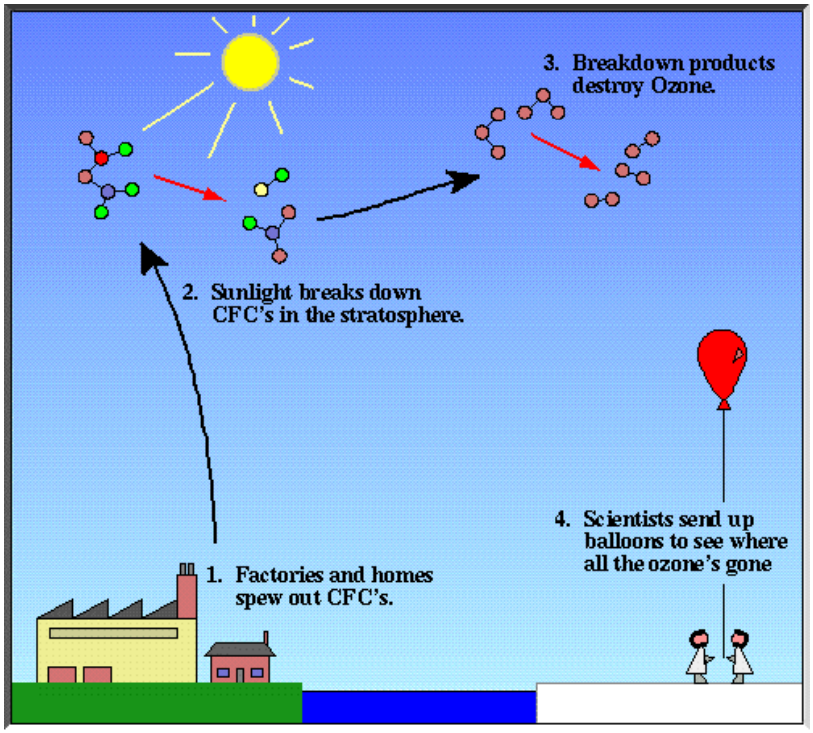


Image credit:
http://australia.jrn.msu.edu/2000/work/projects/environment/ozonepage.html

The set-up for launch of the instrument payloads took place in September under clear skies in Antarctica. (Courtesy Concordiasi team)

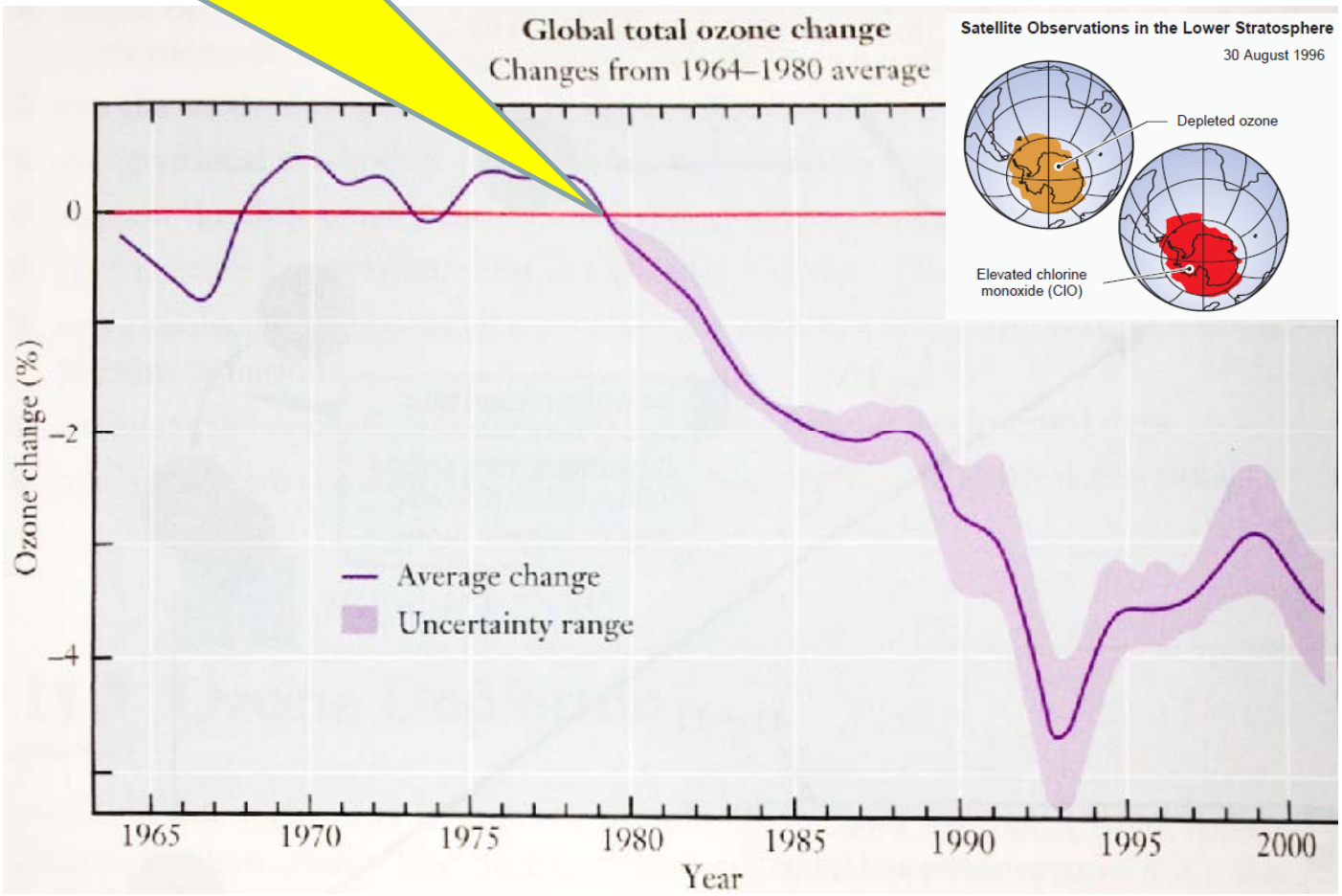
LASP (Laboratory for Atmospheric and Space Physics)

Image credit:
http://lasp.colorado.edu/home/blog/2010/09/30/lasp-researchers-launch-balloons-to-study-ozone-over-antarctica/

Reaction Mechanism – ozone depletion

Observe a decrease in the overall levels of ozone in the stratosphere in the past decades. We are losing protection from UV light.

$$2\ O_3\ (g) \rightarrow 3\ O_2\ (g)$$

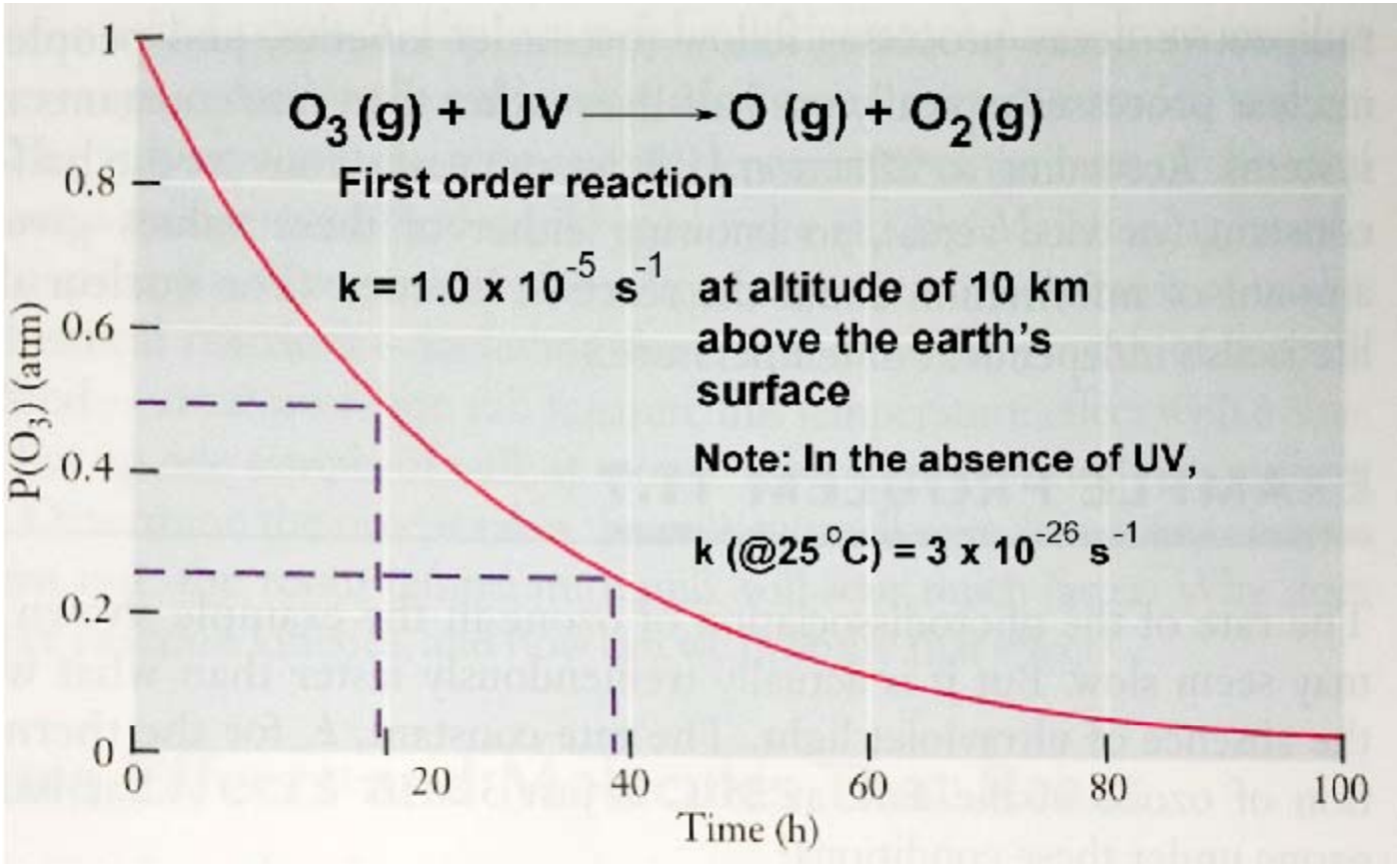


Reaction Mechanism

Experimental evidence shows that *k* is large for the step

$$O_3\,(g) + UV \rightarrow O\,(g) + O_2\,(g)$$ (destruction step in Chapman cycle)

in the presence of UV.



Reaction Mechanism

The rate law that governs the depletion of ozone

$$2\ O_3\ (g) \rightarrow 3\ O_2\ (g)$$

is experimentally determined to be overall first order.

$$Rate = k\frac{[O_3]^2}{[O_2]} = k[O_3]^2[O_2]^{-1}$$

Increase $[O_3]$ increases the reaction rate.
Increase $[O_2]$ decreases the reaction rate.

- 2^{nd} order with respect to O_3.
- Negative 1^{st} order with respect to O_2.
- Overall reaction order = 1^{st} order.

Negative exponent!

Not a simple reaction mechanism.

Reaction Mechanism

Reaction mechanism is a collection of steps that account for the way the reactants become products.

A proposed reaction mechanism for ozone destruction:

Step 1a: $O_3 \rightarrow O_2 + O$ (fast)

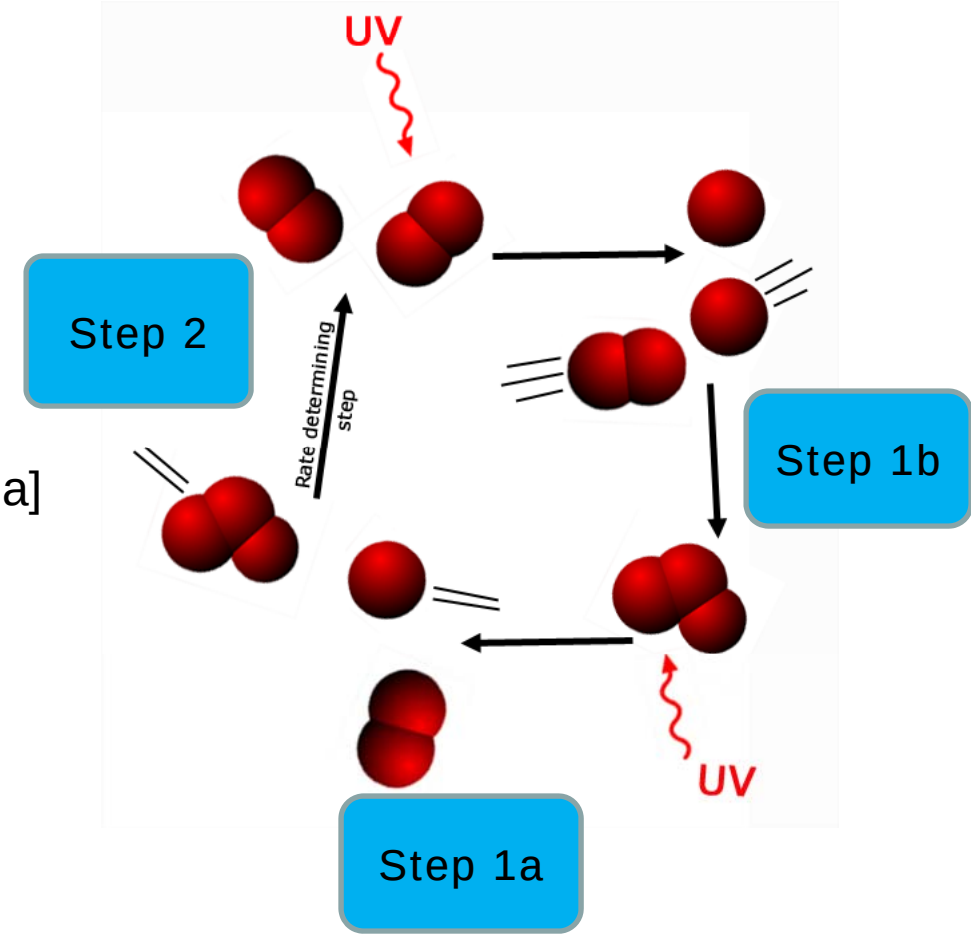
Step 1b: $O_2 + O \rightarrow O_3$ (fast)

[reverse of Step 1a]

Step 2: $O_3 + O \rightarrow 2\ O_2$ (slow)

Step 2 is a slow step because there are relatively few O atoms around.

The Chapman Cycle – the natural creation and destruction of ozone in the Stratosphere



Reaction Mechanism

Proposed reaction mechanism for ozone destruction:

Step 1a: $O_3 \rightarrow O_2 + O$ (fast)

Step 1b: $O_2 + O \rightarrow O_3$ (fast)
[reverse of Step 1a]

Step 2: $O_3 + O \rightarrow 2\ O_2$ (slow)

Step 1: $O_3 \rightleftharpoons O_2 + O$

Step 2: $O_3 + O \rightarrow 2\ O_2$

Add up the steps

Overall reaction is $2\ O_3\ (g) \rightarrow 3\ O_2\ (g)$

Is this mechanism consistent with the experimentally determined rate law?

Reaction Mechanism

Some terminologies:

Step 1: $O_3 \rightleftharpoons O_2 + O$ (fast)

Step 2: $O_3 + O \rightarrow 2\ O_2$ (slow)

- Intermediate – These are species that are formed in one elementary step and consumed in the subsequent step.

  Atomic O is an intermediate

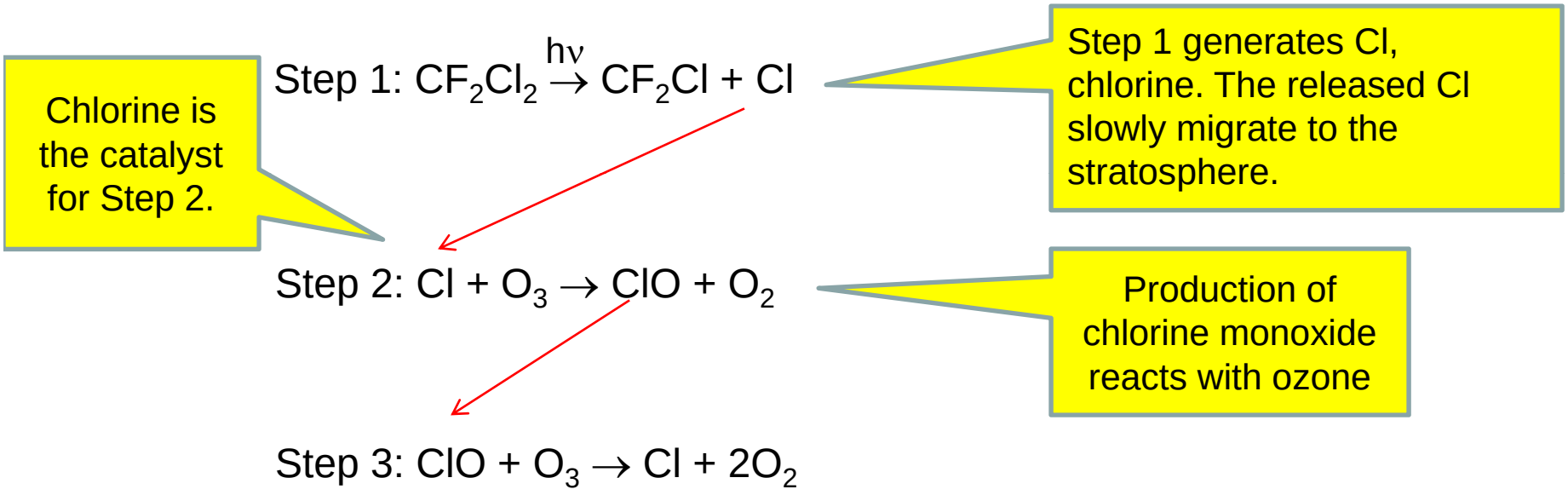
- Rate determining step – Elementary steps do not occur at the same rate. The slowest step is called the *rate determining step.* It determines the overall rate of the reaction.

  Step 2 is the rate determining step

Reaction Mechanism

The catalytic destruction of ozone in the stratosphere involves chlorine as a catalyst.

Upon absorption of UV light, the CFCs initiate a catalyzed reaction mechanism.



Overall reaction for Step 2 & Step 3

$$2\ O_3\ (g) \rightarrow 3\ O_2\ (g)$$

- Cl is a catalyst
- ClO is an intermediate

Reaction Mechanism

The catalytic destruction of ozone in the stratosphere involves nitrogen oxides as a catalyst.

Step 1: $NO + O_3 \rightarrow NO_2 + O_2$

NO is the Catalyst.

Step 2: $NO_2 + O \rightarrow NO + O_2$

- NO is a catalyst
- NO_2 is an intermediate

Overall reaction for Step 1 and Step 2

$$O_3\,(g) + O \rightarrow 2\,O_2\,(g)$$

The high temperature reaction of N_2 and O_2 in supersonic airplane engines produces NO. The airplanes' exhaust injects additional nitrogen oxide into the stratosphere results in accelerating ozone depletion.

Different destruction mechanisms can predominate under special circumstances.

Reaction Mechanism