Determination of Pathways in Chemical Reaction Systems:

An Algorithm and its Application to Atmospheric Chemistry

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Algorithm for the automatic determination of pathways in chemical reaction systems:

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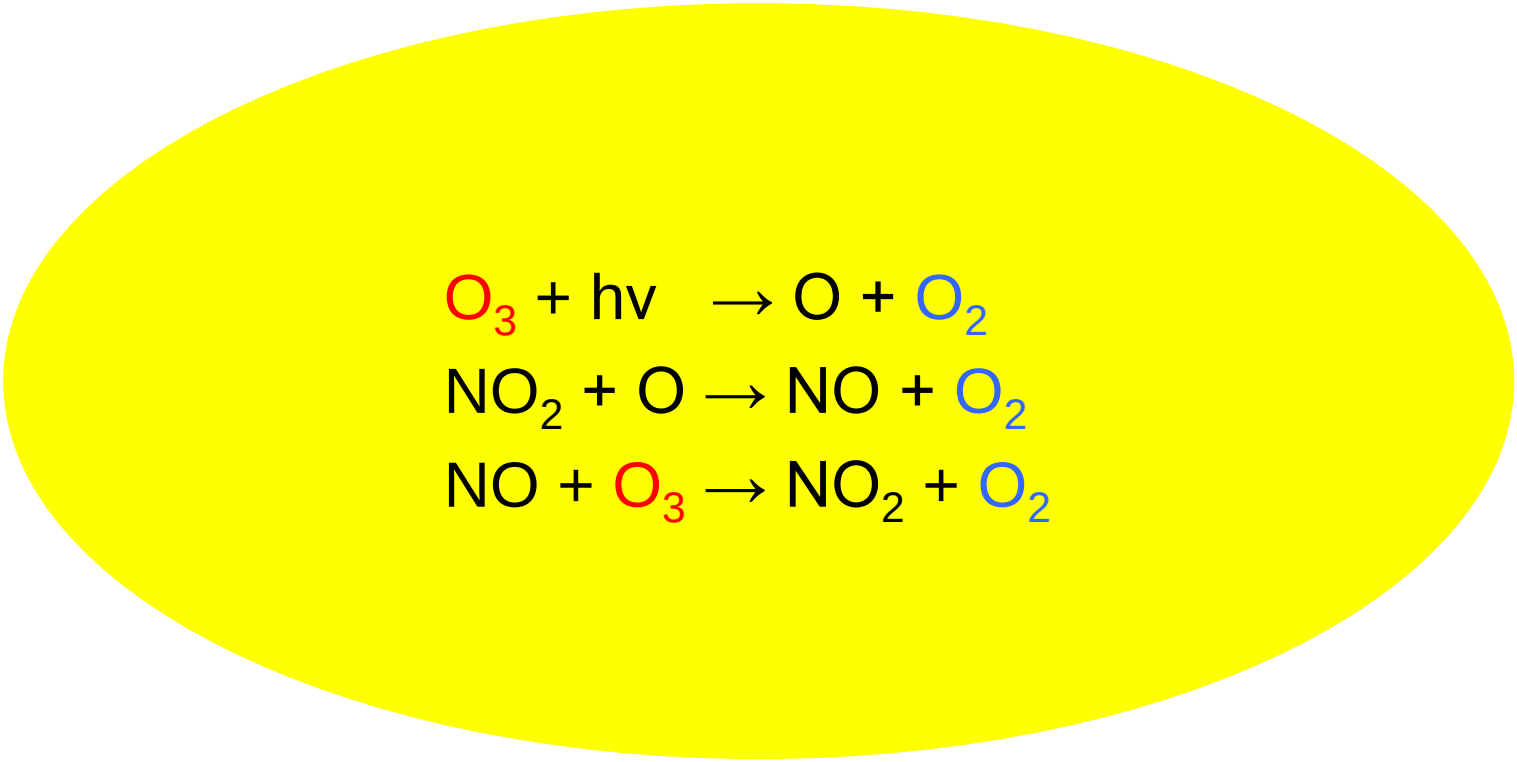


Motivation: Stratospheric ozone chemistry

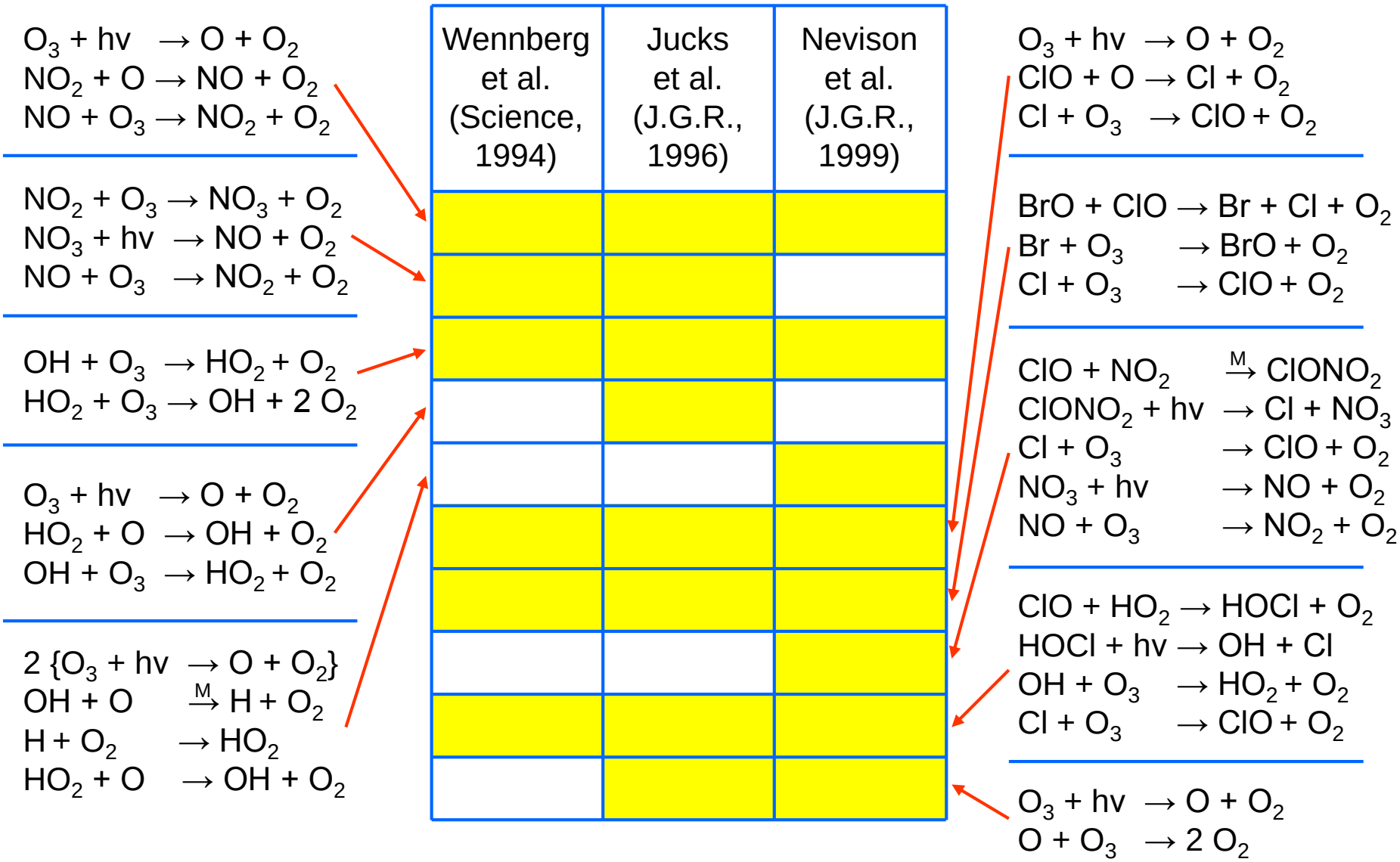
Motivation: Catalytic ozone destruction

$$O_3 + h\nu \rightarrow O + O_2$$
$$NO_2 + O \rightarrow NO + O_2$$
$$NO + O_3 \rightarrow NO_2 + O_2$$

Net: $2\ O_3 \rightarrow 3\ O_2$

Pathway = set of reactions:

Ozone destruction: Complete list of cycles?



Net: $2\ O_3 \rightarrow 3\ O_2$

Motivation

Reaction system (list of ≈ 150 reactions):

List of all catalytic ozone destruction cycles?

No! (Too many ← very small rates)

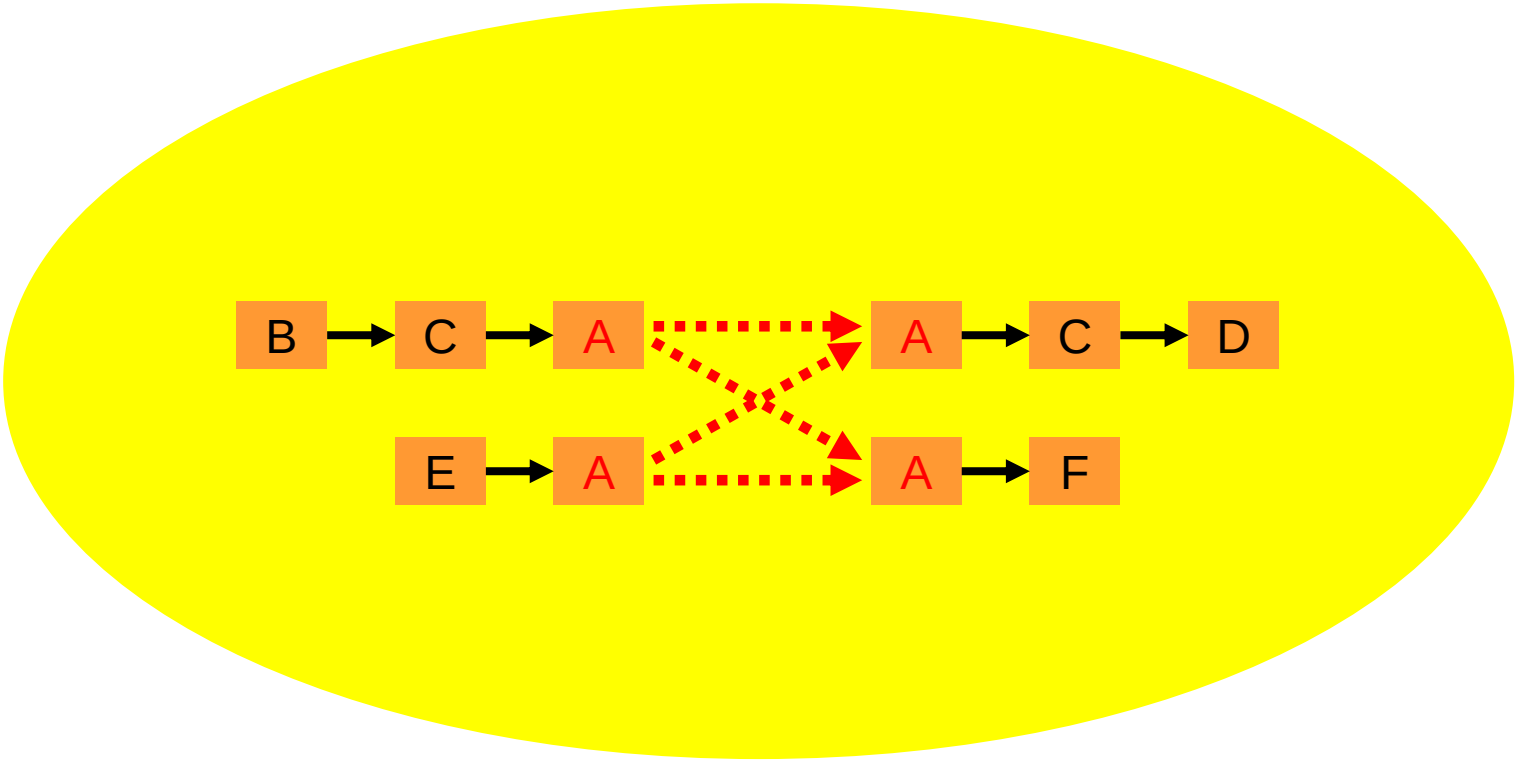
Reaction rates

List of important cycles?

Algorithm

Pathways that produce / destroy an *arbitrary species* of interest

(Lehmann, J. Atmos. Chem., 2004)



Algorithm: Overview

What does the algorithm yield?

Input:

- Reaction system
- Reaction rates

  (averaged over time interval [0,T])
- Concentrations

  (at times 0 and T & mean)

Output:

- All significant pathways

  (e.g. catalytic ozone destruction cycles,

  CH_4 oxidation pathways)
- Rates

$O_3 + hv \rightarrow O + O_2$ 71 ppm/h

$O + O_2 + M \rightarrow O_3 + M$ 72 ppm/h

$O_3 + NO \rightarrow NO_2 + O_2$ 280 ppb/h

$NO_2 + hv \rightarrow NO + O$ 400 ppb/h

$O + NO_2 \rightarrow NO + O_2$ 1 ppb/h

…

O_3: 3000 ppb ► 2996 ppb

…

$ClO + ClO + M \rightarrow Cl_2O_2 + M$

$Cl_2O_2 + hv \rightarrow Cl + Cl + O_2$

2 x $\{ Cl + O_3 \rightarrow ClO + O_2 \}$

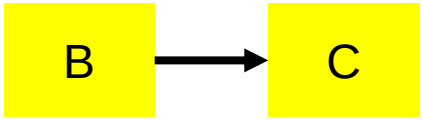
$2\ O_3 \rightarrow 3\ O_2$ 0.1 ppb/h

…

How does the algorithm work?

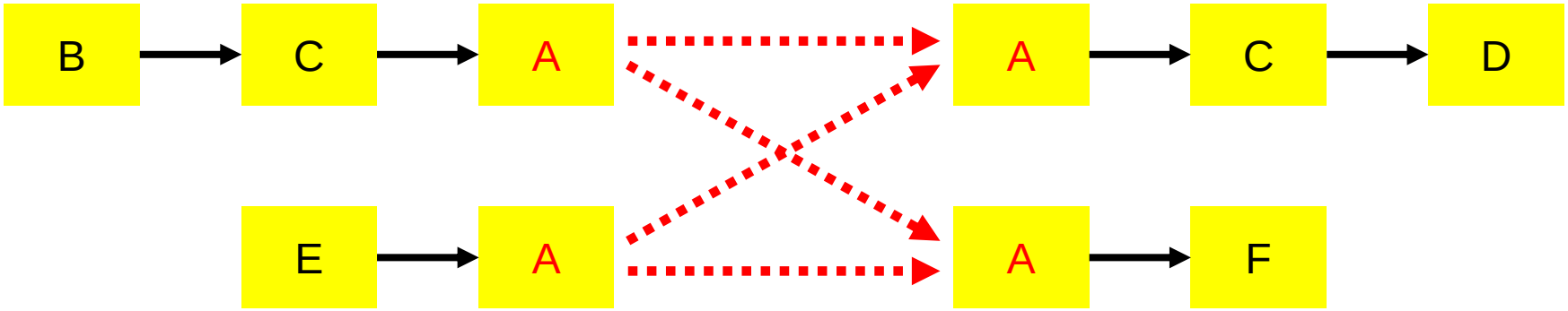
Construction of the pathways

- Start: Pathways := individual reactions



For each intermediate species A (beginning with short-lived ones):

- Connect all pathways P_i^+ forming A with all pathways P_k^- consuming A



Rate of new pathway

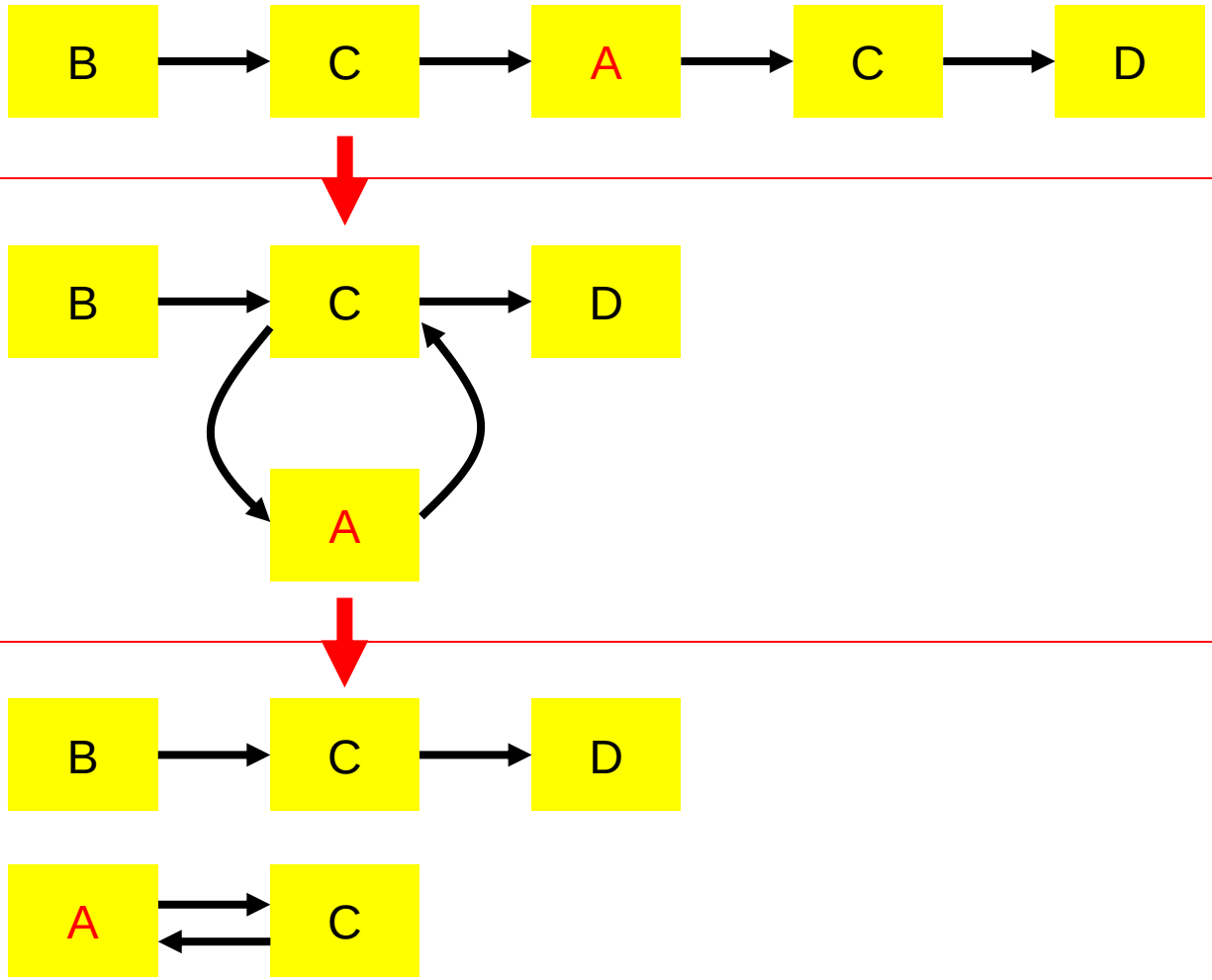
= Rate of P_i^+ · probability of consumption of A by P_k^-

= Rate of P_i^+ · Rate of P_k^- / total consumption of A

- Take stoichiometric coefficients into account!

Splitting into sub-pathways

- Determine sub-pathways (e.g. zero cycles);
  Split pathways into their sub-pathways (if existent):

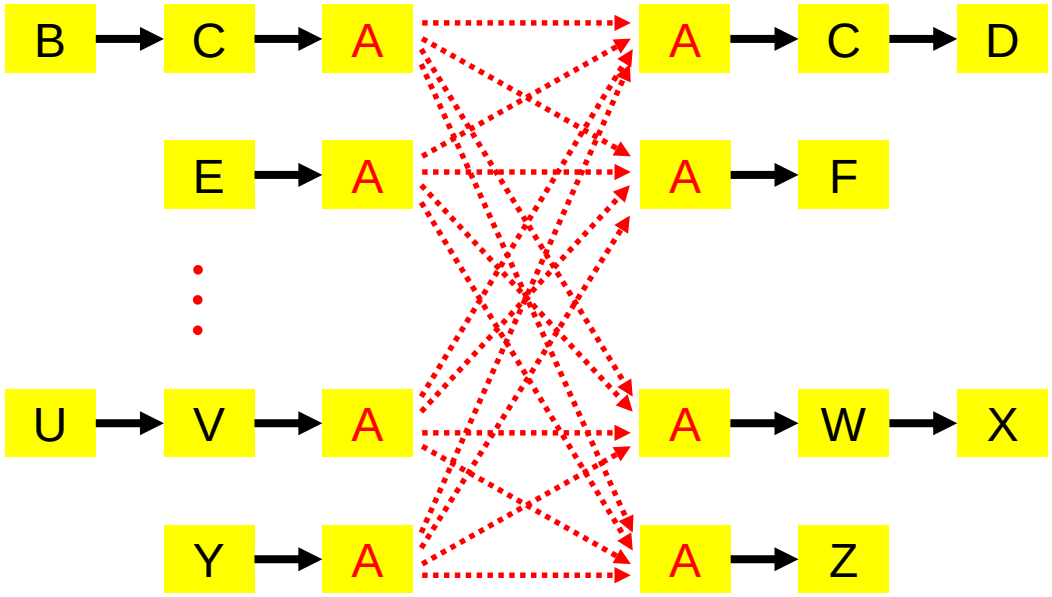


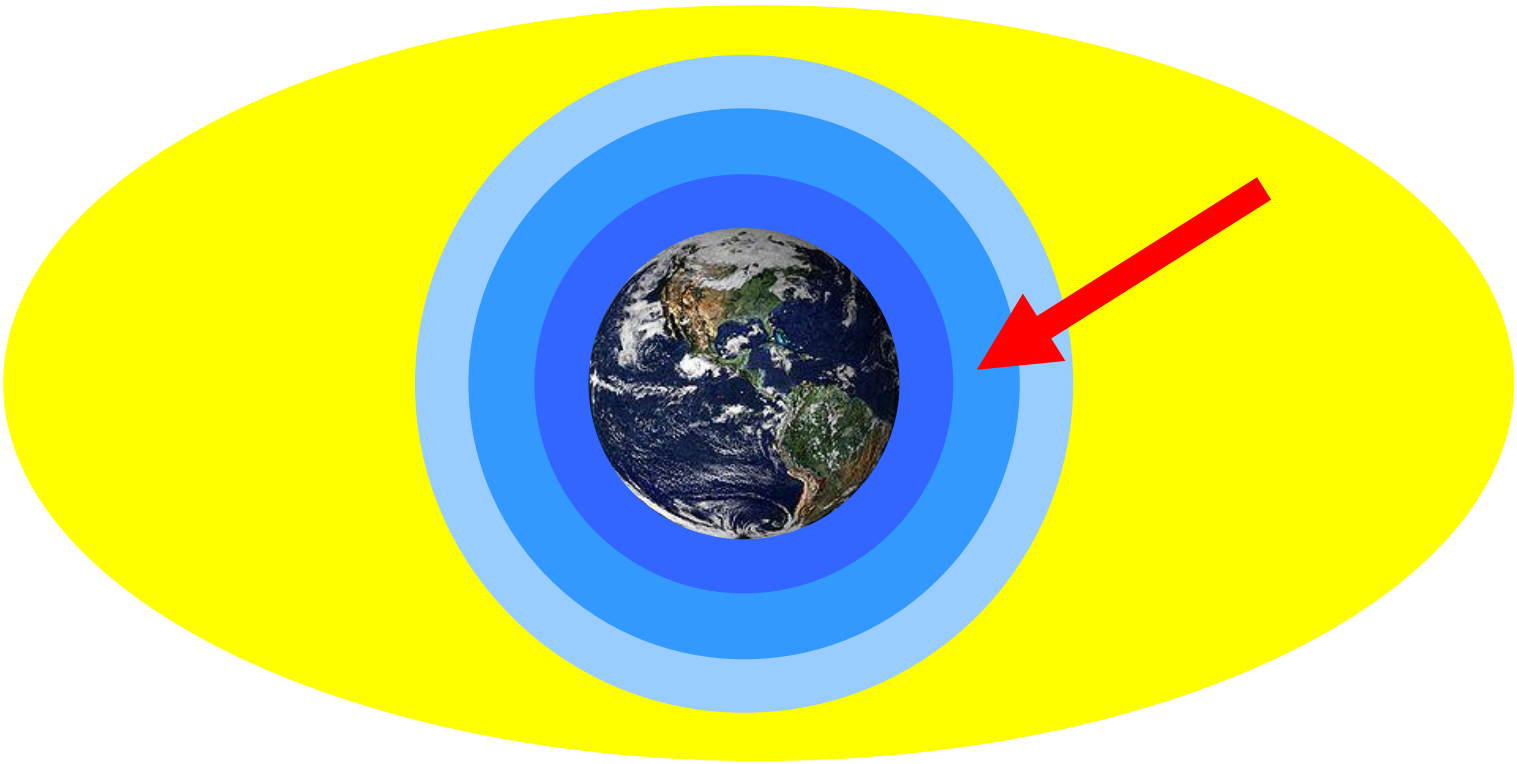
- Splitting into sub-pathways is not always unique!

Deletion of minor pathways

- Delete all pathways with <u>small</u> rates ($< f_{min}$)
  (f_{min} = prescribed parameter)

Otherwise: “Combinatorial explosion”:

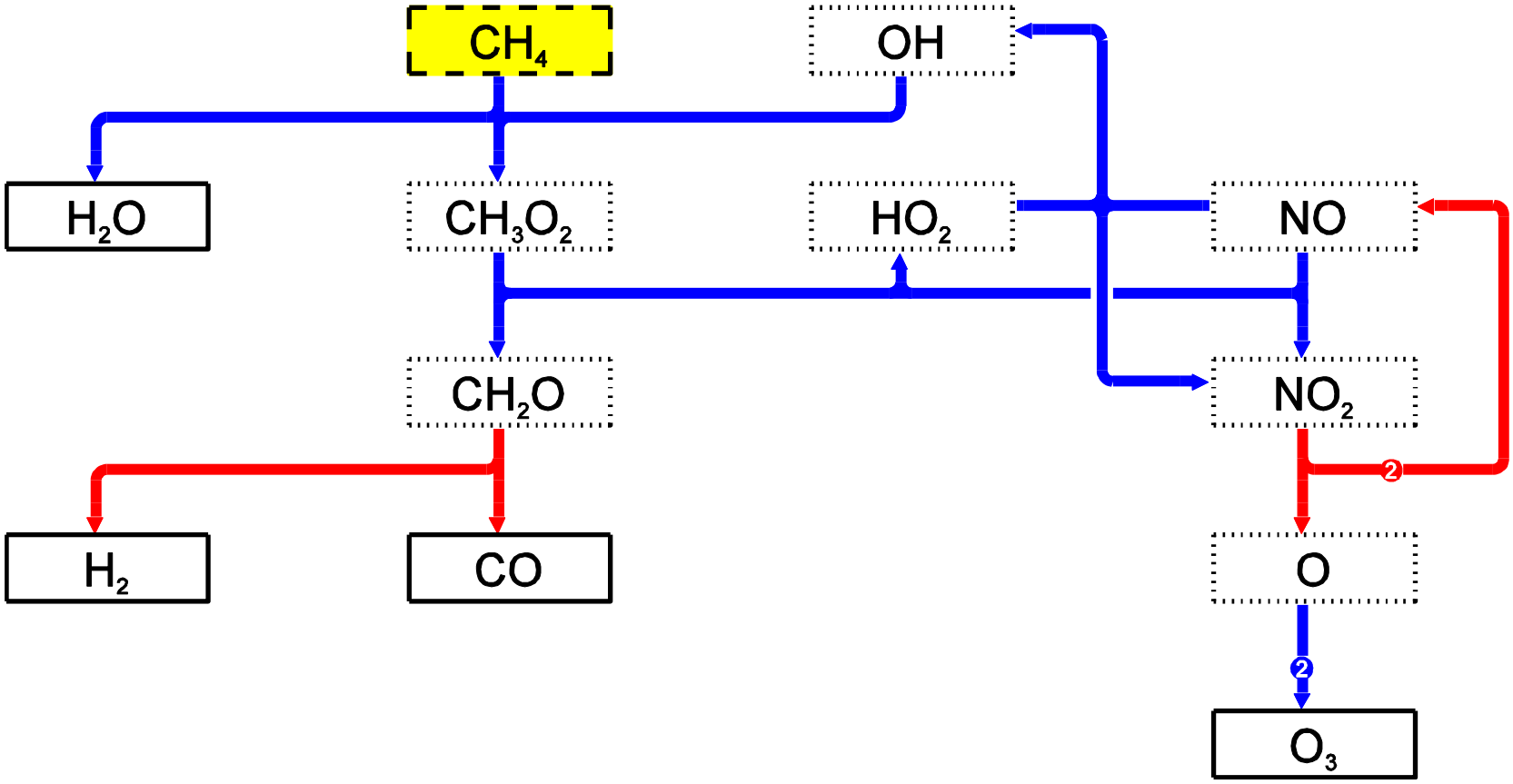




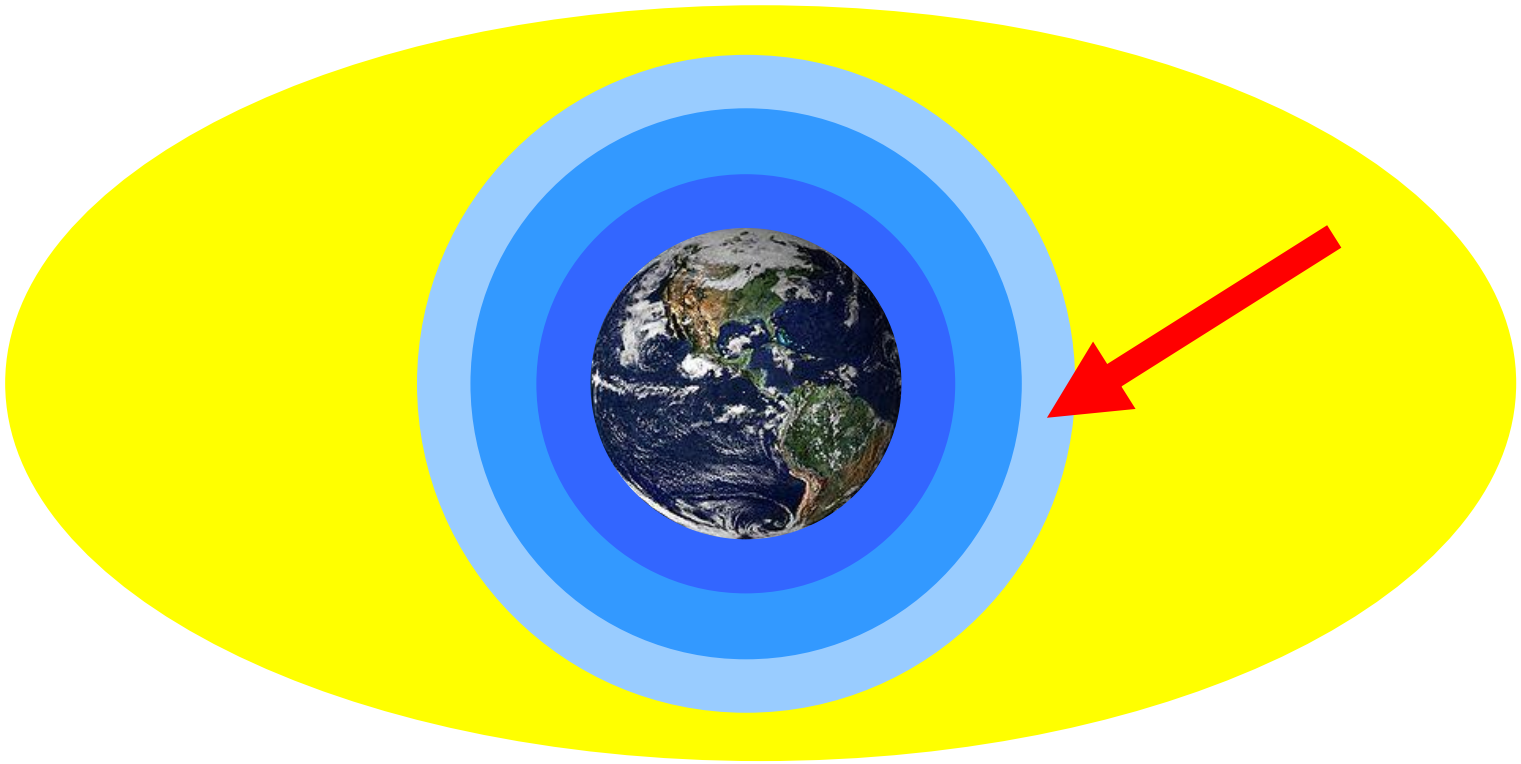
Stratospheric chemistry

Methane photo-oxidation

(67^0 N, 75 hPa, July)

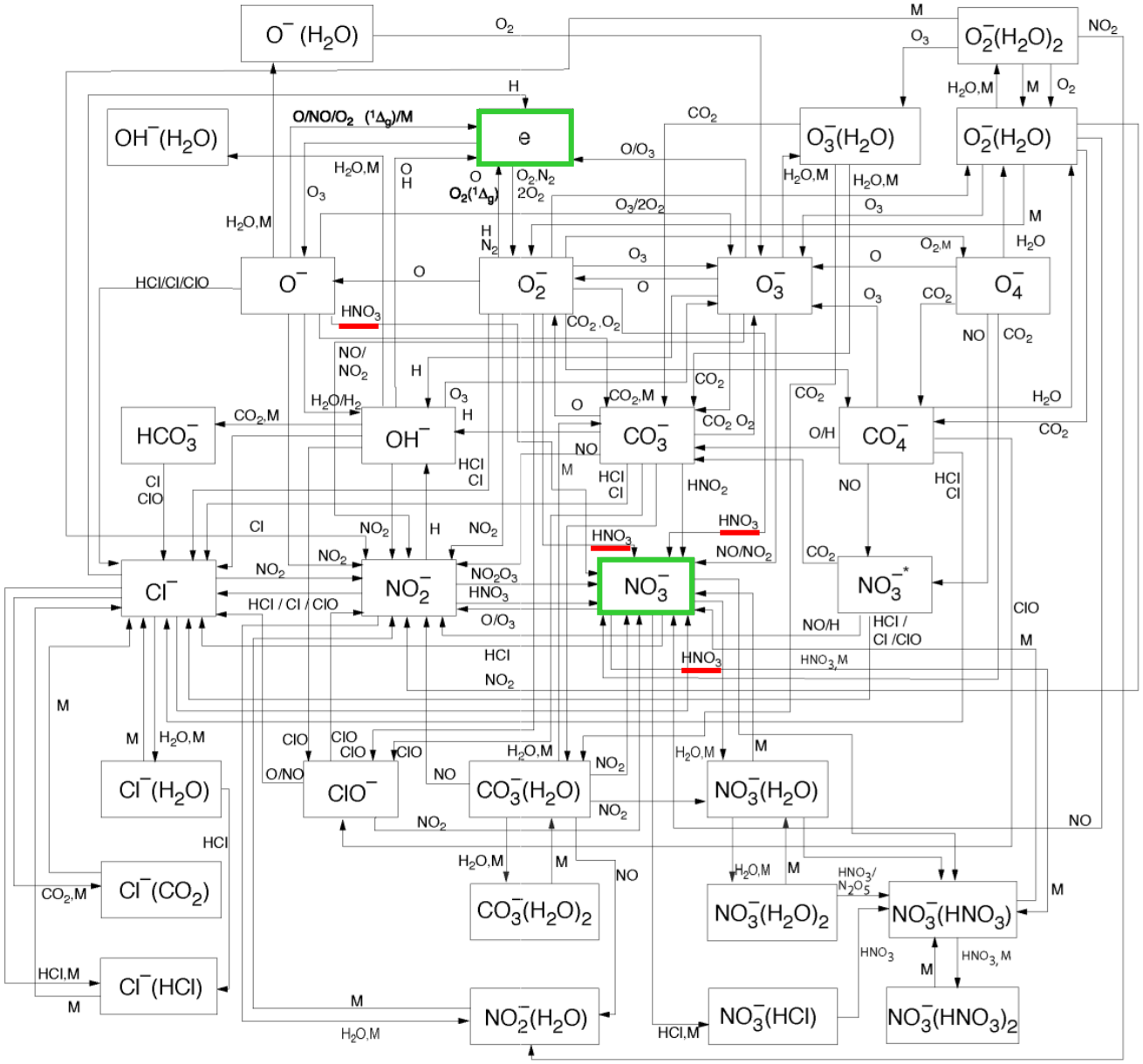


(Lehmann, J. Atmos. Chem., 2004)



Mesospheric chemistry

Chemistry of negative ions → HNO_3 production



e⁻

↓

…

↓

NO_3^-

↓

…

↓

HNO_3

P. Verronen (FMI)

HNO_3 formation

40 km:

$$O_2 + O_2 + e^- \rightarrow O_2^- + O_2$$

$$O_2^- + O_3 \rightarrow O_3^- + O_2$$

$$O_3^- + CO_2 \rightarrow CO_3^- + O_2$$

$$CO_3^- + NO_2 \rightarrow NO_3^- + CO_2$$

$$NO_3^- + H_2O + M \rightarrow NO_3^-(H_2O) + M$$

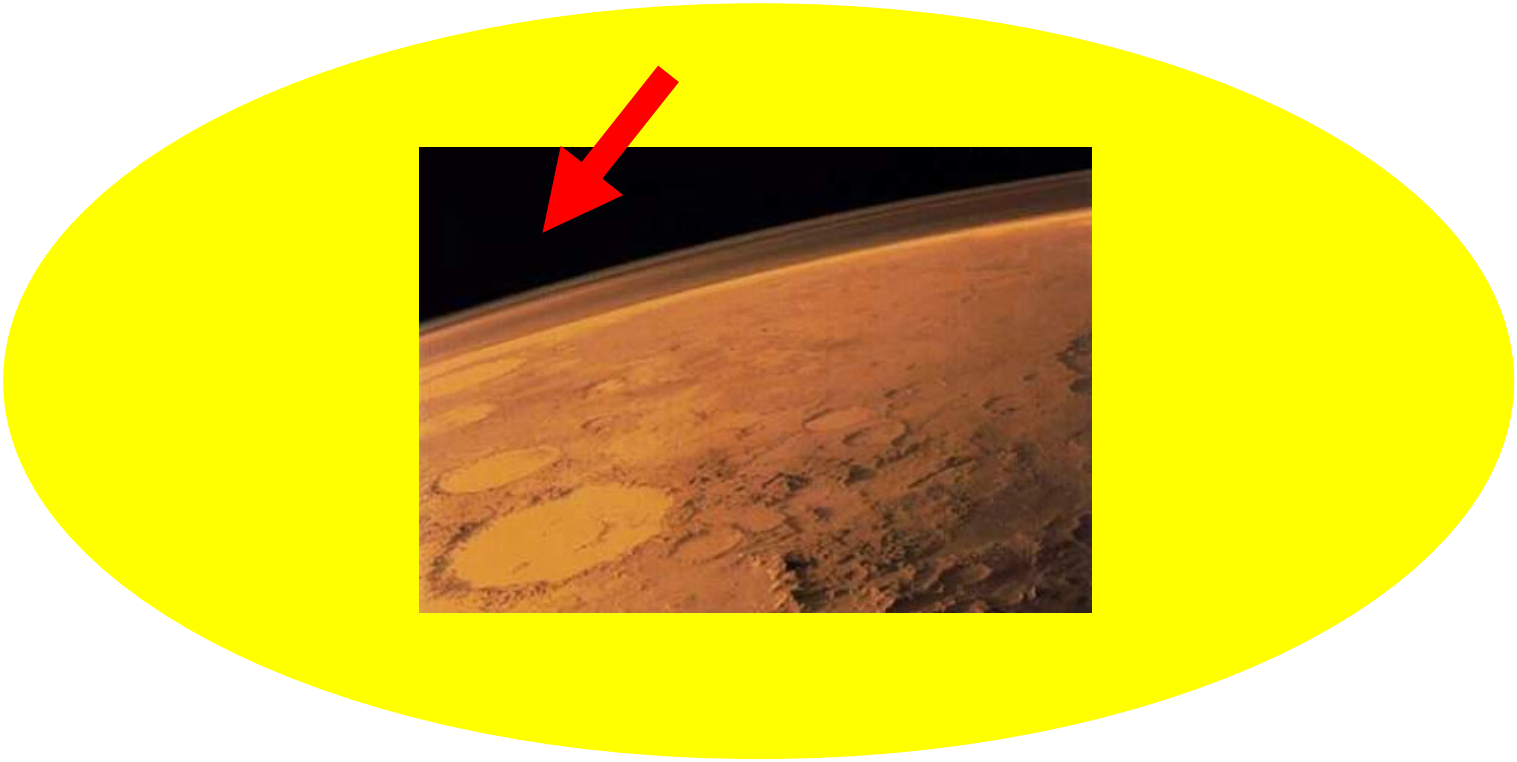
$$NO_3^-(H_2O) + HNO_3 \rightarrow NO_3^-(HNO_3) + H_2O$$

$$NO_3^-(HNO_3) + H^+(H_2O)_n \rightarrow HNO_3 + HNO_3 + M$$

$$e^- + NO_2 + O_3 + H^+(H_2O)_n \rightarrow HNO_3 + O_2 + M$$

6.6%

(cf. Verronen et al., J.G.R., 2011)



Atmospheric chemistry of Mars

CO_2 production

Near the surface of Mars:

$$2\ \{\ CO + OH \rightarrow CO_2 + H\ \}$$

$$2\ \{\ H + O_2 + M \rightarrow HO_2 + M\ \}$$

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$$

$$H_2O_2 + h\nu \rightarrow \mathbf{OH} + \mathbf{OH}$$

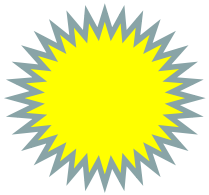
$$2\ CO + O_2 \rightarrow 2\ CO_2$$

13%

(Stock et al., Planet. Space Sci., 2012)

Atmospheric chemistry of
extra-solar planets

O_3 production in (Earth-like) planetary atmospheres



Near sun-like stars:

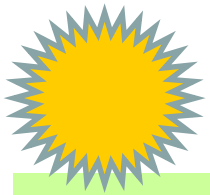
$$O_2 + h\nu \rightarrow O + O$$

$$2\{ O + O_2 + M \rightarrow O_3 + M \}$$

$$3\ O_2 \rightarrow 2\ O_3$$

"Chapman cycle"

(Earth's **stratosphere**)



Near cool dwarfs:

$$CO + OH \rightarrow CO_2 + H$$

$$H + O_2 + M \rightarrow HO_2 + M$$

$$NO + HO_2 \rightarrow NO_2 + OH$$

$$NO_2 + h\nu \rightarrow NO + O$$

$$O + O_2 + M \rightarrow O_3 + M$$

$$CO + 2\ O_2 \rightarrow CO_2 + O_3$$

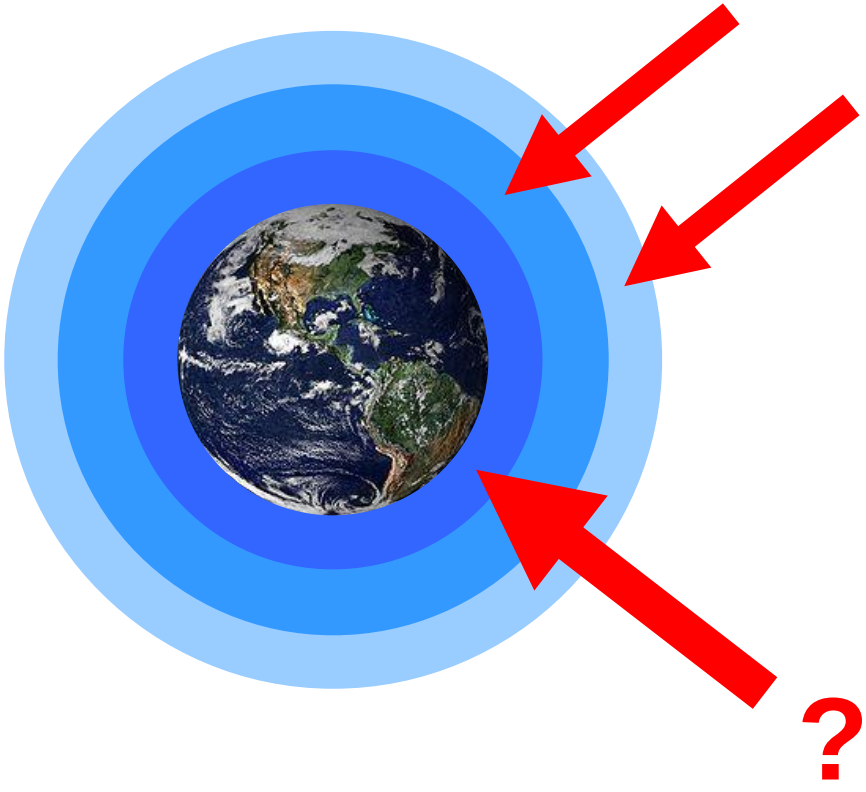
"Smog cycle"

(Earth's **troposphere**)

(Grenfell et al., Astrobiology, 2013)

Summary

Algorithm for the automatic determination of pathways in complex reaction systems:



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