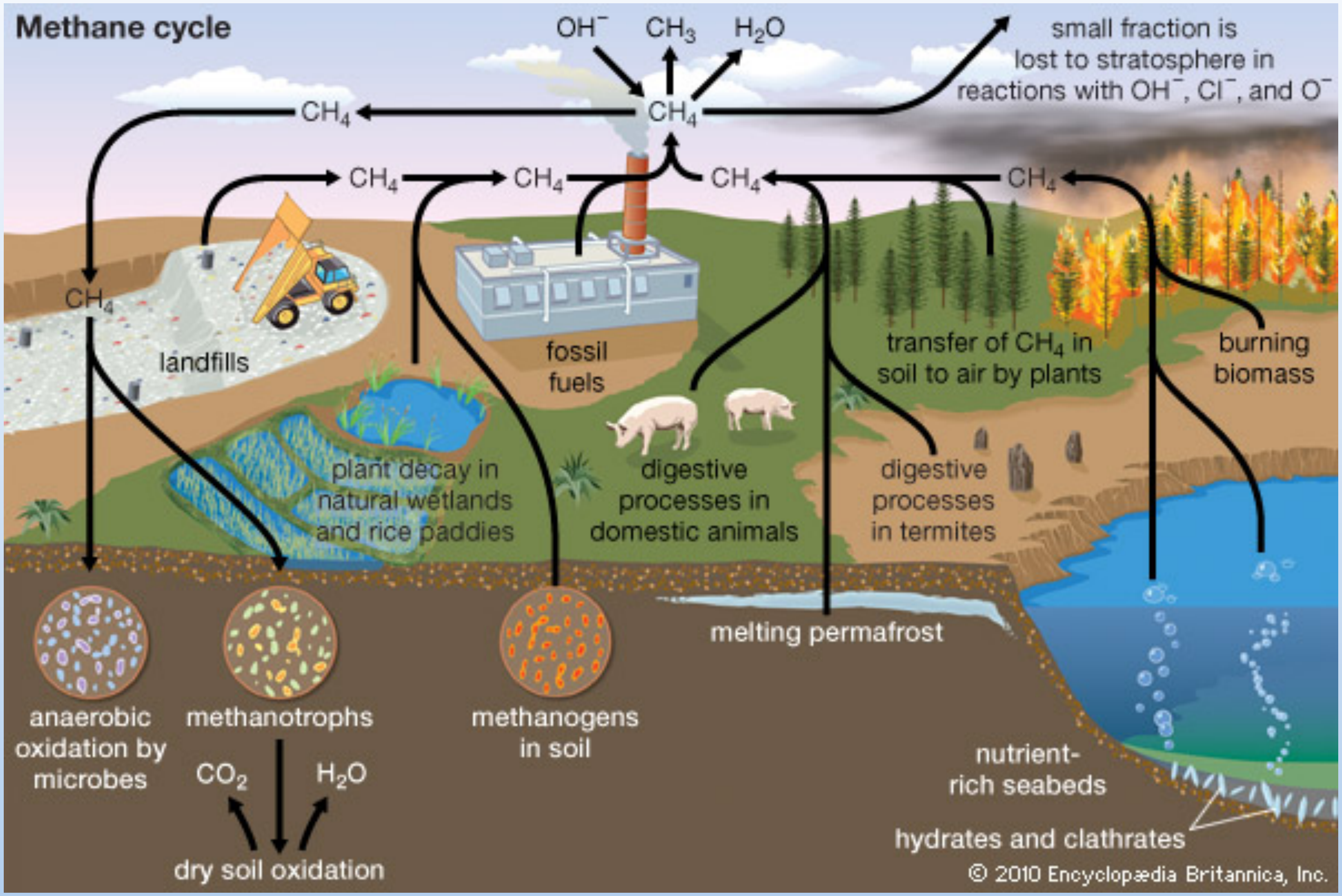
Atmospheric Chemistry

Lecture 6

Methane, water vapor and HO_x



$CH_4 \rightarrow H_2O \rightarrow HO_x$

Hydrogen oxides in the lower stratosphere

$$OH + O_3 \rightarrow HO_2 + O_2$$

$$HO_2 + O_3 \rightarrow OH + 2O_2$$

$$- - - - - - - - - - - --$$

$$net: \quad O_3 + O_3 \rightarrow O_2 + O_2 + O_2$$

Ozone cycle; no atomic oxygen necessary. Atomic oxygen, or lack thereof, limits ozone loss by other cycles in the lower stratosphere.

Chemical continuity equation for [OH]

$$\frac{d[OH]}{dt} = -k_{OH,O_3} \cdot [O_3] \cdot [OH] + k_{HO_2,O_3} \cdot [HO_2] \cdot [O_3]$$

In Steady-state where conversion reactions are faster than source/sink for HO_x

$$k_{OH,O_3} \cdot [O_3] \cdot [OH] = k_{HO_2,O_3} \cdot [HO_2] \cdot [O_3]$$

Solve for HO_2 to OH ratio

$$\frac{[HO_2]}{[OH]} = \frac{k_{OH,O_3}}{k_{HO_2,O_3}}$$ = ~ 30

Ratio depends only on reaction rates (therefore on temperature)

Hydrogen oxides in the upper stratosphere

$$OH + O \rightarrow H + O_2$$
$$H + O_2 + M \rightarrow HO_2 + M$$
$$HO_2 + O \rightarrow OH + O_2$$
$$- - - - - - - - - - - --$$
$$net: \quad O + O \rightarrow O_2$$

Atomic oxygen cycle. Important mostly in upper stratosphere and mesosphere where atomic oxygen is larger fraction of O_x. Leads to formation of hydrogen atoms. Mesosphere is generally place dominated by atom reactions. 3-body formation of complex molecules is slow.

Chemical continuity equation for [OH]

$$\frac{d[OH]}{dt} = -k_{OH,O} \cdot [O] \cdot [OH] + k_{HO_2,O} \cdot [O] \cdot [HO_2]$$

In Steady-state where conversion reactions are faster than source/sink for HO_x

$$k_{OH,O} \cdot [O] \cdot [OH] = k_{HO_2,O} \cdot [O] \cdot [HO_2]$$

Solve for HO_2 to OH ratio

$$\frac{[HO_2]}{[OH]} = \frac{k_{OH,O}}{k_{HO_2,O}} \quad = \sim 2$$

Ratio depends only on reaction rates (therefore on temperature)

Interference Reaction

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

$$OH + O_3 \rightarrow HO_2 + O_2$$
$$HO_2 + NO \rightarrow OH + NO_2$$
$$NO_2 + h\nu \rightarrow NO + O$$
$$O + O_2 + M \rightarrow O_3 + M$$
$$-------------$$
$$net : null$$

$$\frac{[HO_2]}{[OH]} = \frac{k_{OH,O_3} \cdot [O_3]}{k_{HO_2,O_3} \cdot [O_3] + k_{HO_2,NO} \cdot [NO]}$$

Increased NO_x leads to decrease in $[HO_2]/[OH]$

Production and Loss of HO_x

$$O(^1D) + H_2O \rightarrow OH + OH$$

$$OH + HO_2 \rightarrow H_2O + O_2$$

Water can be thought of as a source for HO_x or, alternatively as a reservoir for for HO_x.

$$\frac{d[HO_x]}{dt} = \frac{d[OH]}{dt} + \frac{d[HO_2]}{dt}$$

$$\frac{d[HO_x]}{dt} = 2k_{O^1D,H_2O} \cdot [O(^1D)] \cdot [H_2O] - 2k_{OH,HO_2} \cdot [OH] \cdot [HO_2]$$

Solving for [HO_x]

HO_x Continuity equation in Steady-State

$$2k_{O^1D,H_2O} \cdot [O(^1D)] \cdot [H_2O] = 2k_{OH,HO_2} \cdot [OH] \cdot [HO_2]$$

Recast in terms of ratios and [HO_x] = [OH] + [HO_2]

$$2k_{O^1D,H_2O} \cdot [O(^1D)] \cdot [H_2O] = 2k_{OH,HO_2} \cdot \frac{[OH]}{[HO_x]} \cdot \frac{[HO_2]}{[OH]} \cdot \frac{[OH]}{[HO_x]} \cdot [HO_x]^2$$

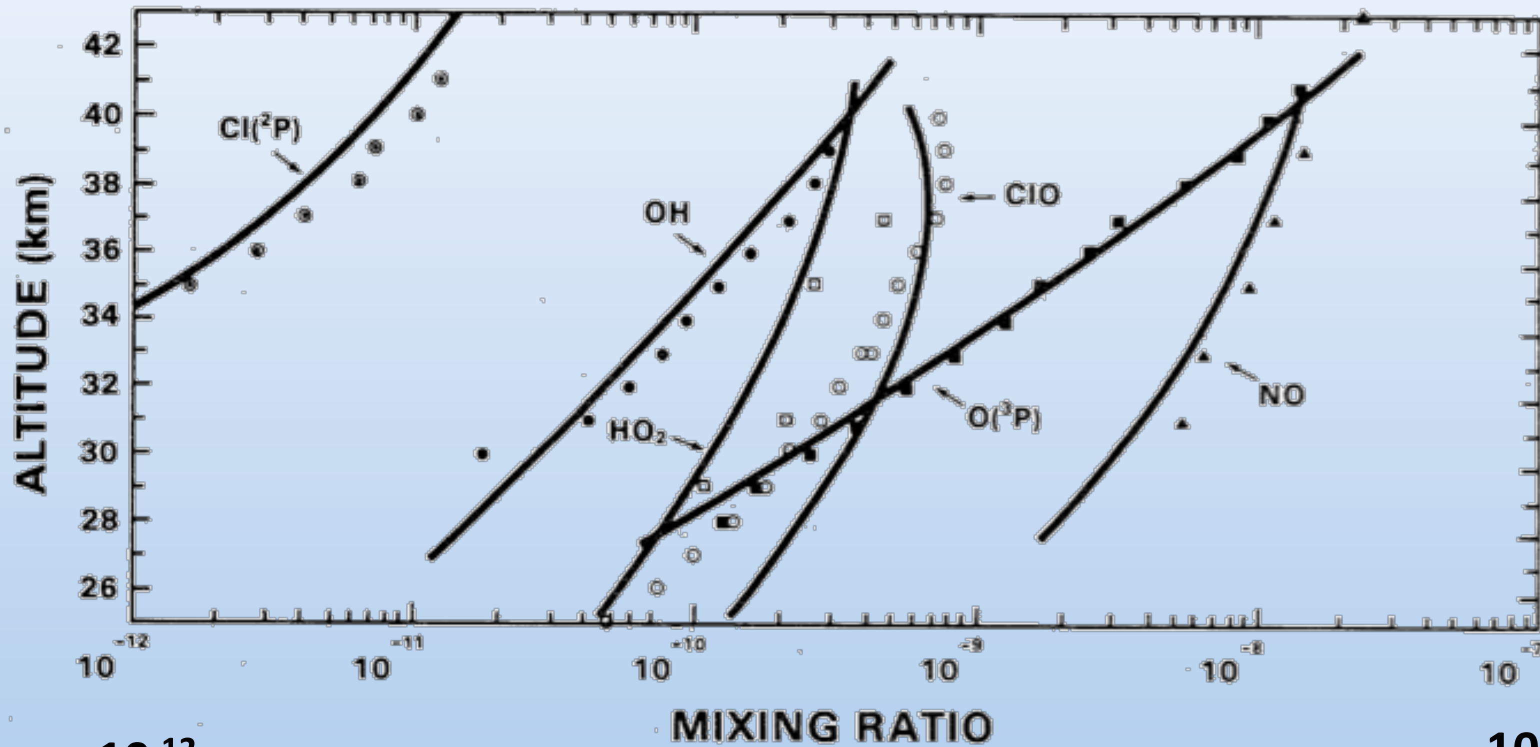
Calculate ratios

$$\frac{[OH]}{[HO_x]} = \frac{[OH]}{[OH]+[HO_2]} = \frac{1}{1+\frac{[HO_2]}{[OH]}} = \frac{1}{1+\beta}$$

Substitute

$$2k_{O^1D,H_2O} \cdot [O(^1D)] \cdot [H_2O] = 2k_{OH,HO_2} \cdot \frac{\beta}{(1+\beta)^2} \cdot [HO_x]^2$$

Some Radical Concentrations vs Altitude



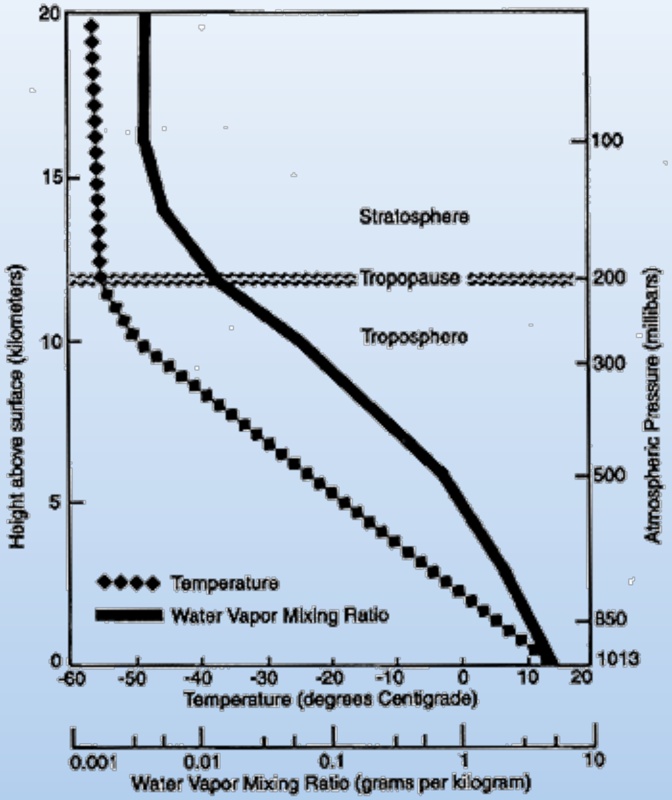
10^{-12} 10^{-7}

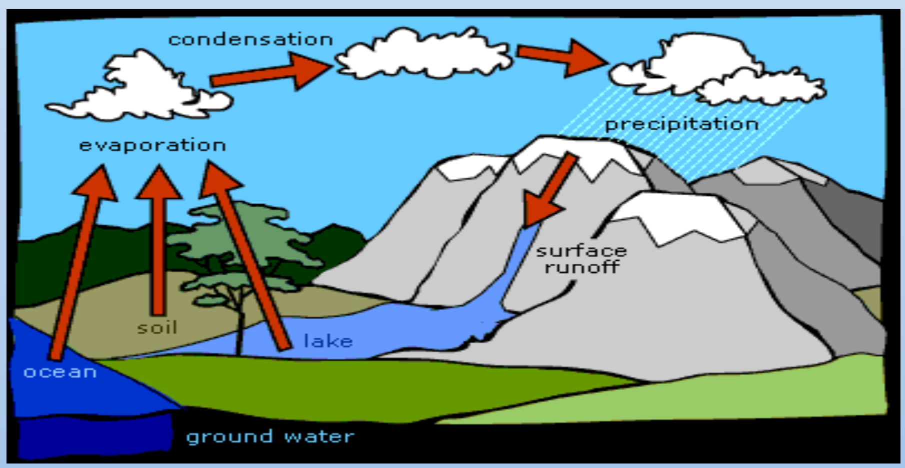
Ozone → few x 10^{-6}

Water vapor in the stratosphere

- Stratosphere is extremely dry (few parts per million)
- "Cold-trap" mechanism at tropopause
- Methane can act as source for extra water

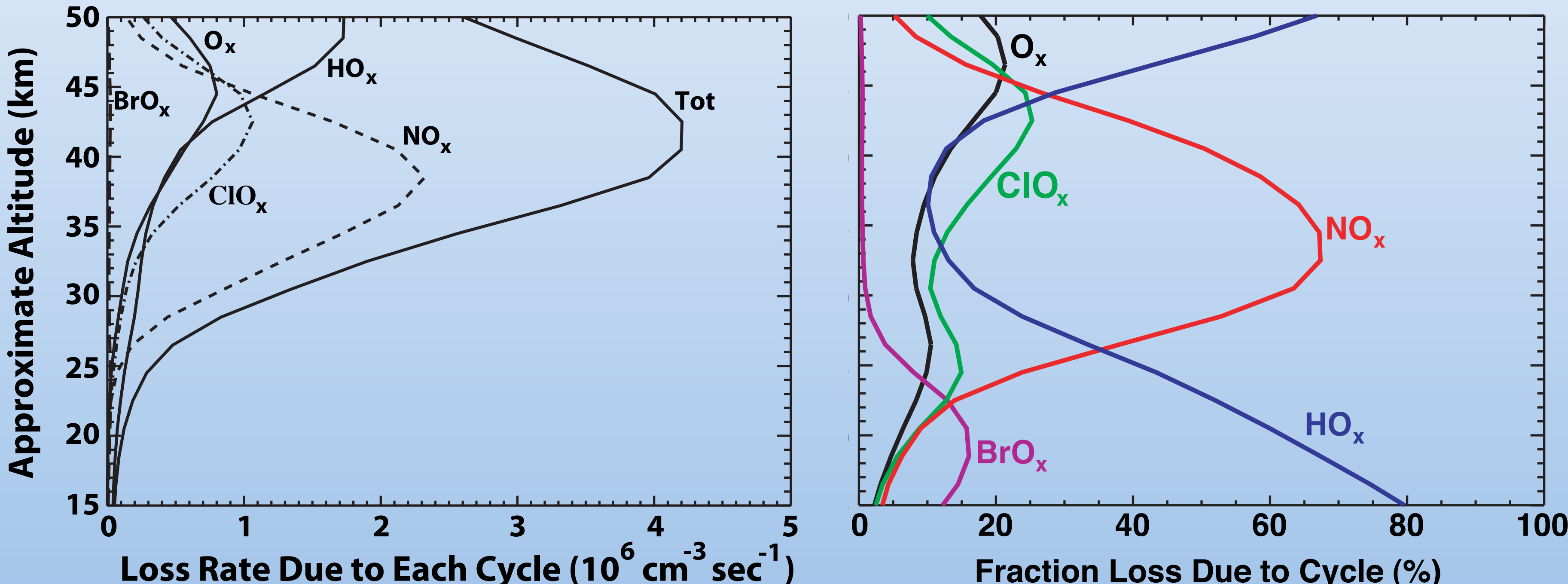
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$





Ozone Continuity Equation with NO_x and HO_x Terms

$$\frac{dO_x}{dt} = 2 \cdot J_{O_2} \cdot [O_2] - 2 \cdot k_{O,O_3} \cdot [O] \cdot [O_3] - 2 \cdot k_{O,NO_2} \cdot [O] \cdot [NO_2]$$
$$-2 \cdot k_{O,HO_2} \cdot [O] \cdot [HO_2] - 2 \cdot k_{O_3,HO_2} \cdot [O_3] \cdot [HO_2]$$



Reaction	A-Factor	E/R	k(298K)
$O + O_3 \rightarrow O_2 + O_2$	8.0×10^{-12}	2060	8.0×10^{-15}
$O + NO_2 \rightarrow NO + O_2$	6.5×10^{-12}	-120	9.7×10^{-12}
$O_3 + NO \rightarrow NO_2 + O_2$	2.0×10^{-12}	1400	1.8×10^{-14}
$O + HO_2 \rightarrow OH + O_2$	3.0×10^{-11}	-200	5.9×10^{-11}
$O + OH \rightarrow H + O_2$	2.2×10^{-11}	-120	3.3×10^{-11}
$O_3 + HO_2 \rightarrow OH + O_2 + O_2$	1.1×10^{-14}	500	2.0×10^{-15}
$O_3 + OH \rightarrow HO_2 + O_2$	1.6×10^{-12}	940	6.8×10^{-14}
$Cl + O_3 \rightarrow ClO + O_2$	2.9×10^{-11}	260	1.2×10^{-11}
$ClO + O \rightarrow Cl + O_2$	3.0×10^{-11}	-70	3.8×10^{-11}
$Br + O_3 \rightarrow BrO + O_2$	1.7×10^{-11}	800	1.2×10^{-12}
$BrO + ClO \rightarrow Br + Cl + O_2$	2.9×10^{-12}	-220	6.1×10^{-12}
$BrO + BrO \rightarrow Br + Br + O_2$	1.4×10^{-12}	-150	2.3×10^{-12}
$Cl + CH_4 \rightarrow HCl + CH_3$	1.1×10^{-11}	1400	1.0×10^{-13}
$OH + HCl \rightarrow H_2O + Cl$	2.6×10^{-12}	350	8.0×10^{-13}