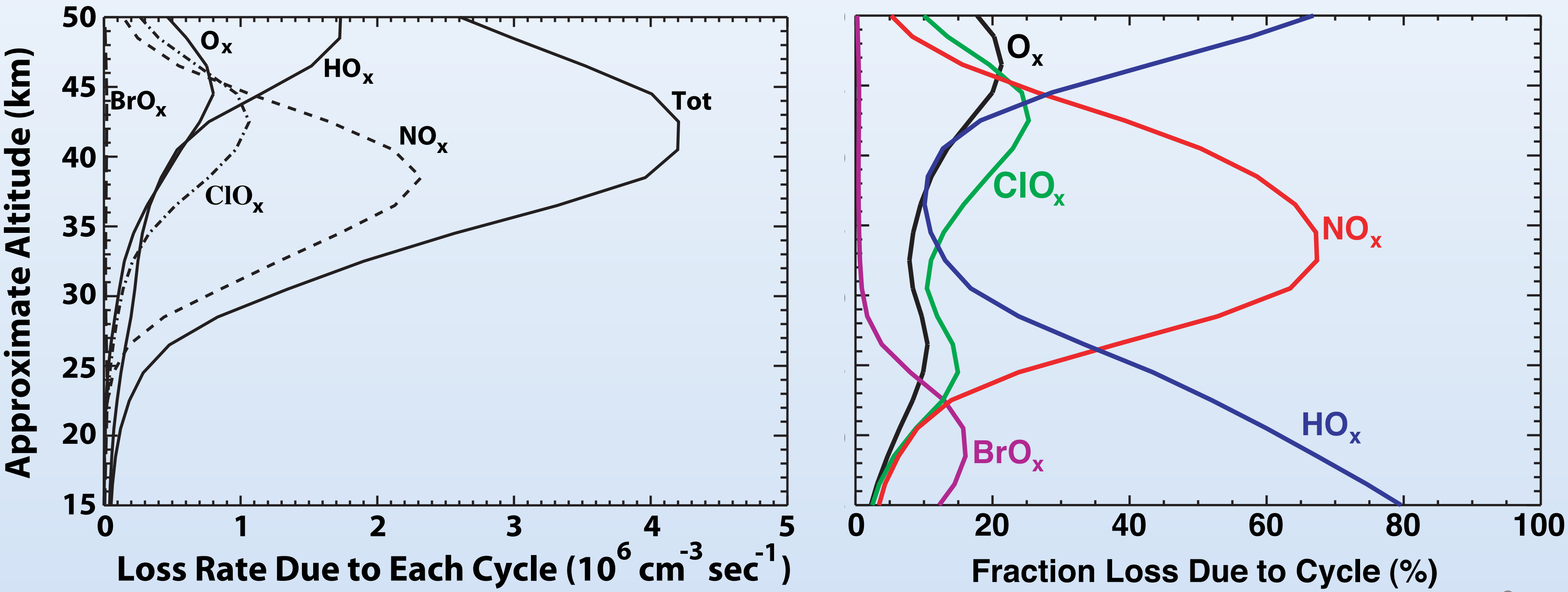
Atmospheric Chemistry

Lecture 7

Ozone Continuity Equation with NO_x and HO_x Terms

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



Recasting the [O_x] continuity equation

$$\frac{dO_x}{dt} = P_{O_x} - \kappa \cdot [O_3] - \alpha \cdot [ON] \cdot [O_3] - \beta \cdot [HO_x] \cdot [O_3]$$

where:

$$\alpha = 2 \cdot k_{O,NO_2} \cdot \frac{[O]}{[O_3]} \cdot \frac{[NO_2]}{[ON]}$$

$$\beta = 2 \cdot \left(k_{O_3,HO_2} + k_{O,HO_2} \cdot \frac{[O]}{[O_3]} \right) \cdot \frac{[HO_2]}{HO_x}$$

$$\kappa = 2 \cdot k_{O,O_3} \cdot \frac{[O]}{O_3} \cdot [O_3]$$

$$\frac{[O]}{[O_3]} = \frac{J_{O_3}}{k_{O,O2,M} \cdot [O_2] \cdot [M]}$$

“Odd” Nitrogen = ON

NO_x

N : nitrogen atom
NO : nitric oxide
NO_2 : nitrogen dioxide
NO_3 : nitrogen trioxide
N_2O_5 : dinitrogen pentoxide

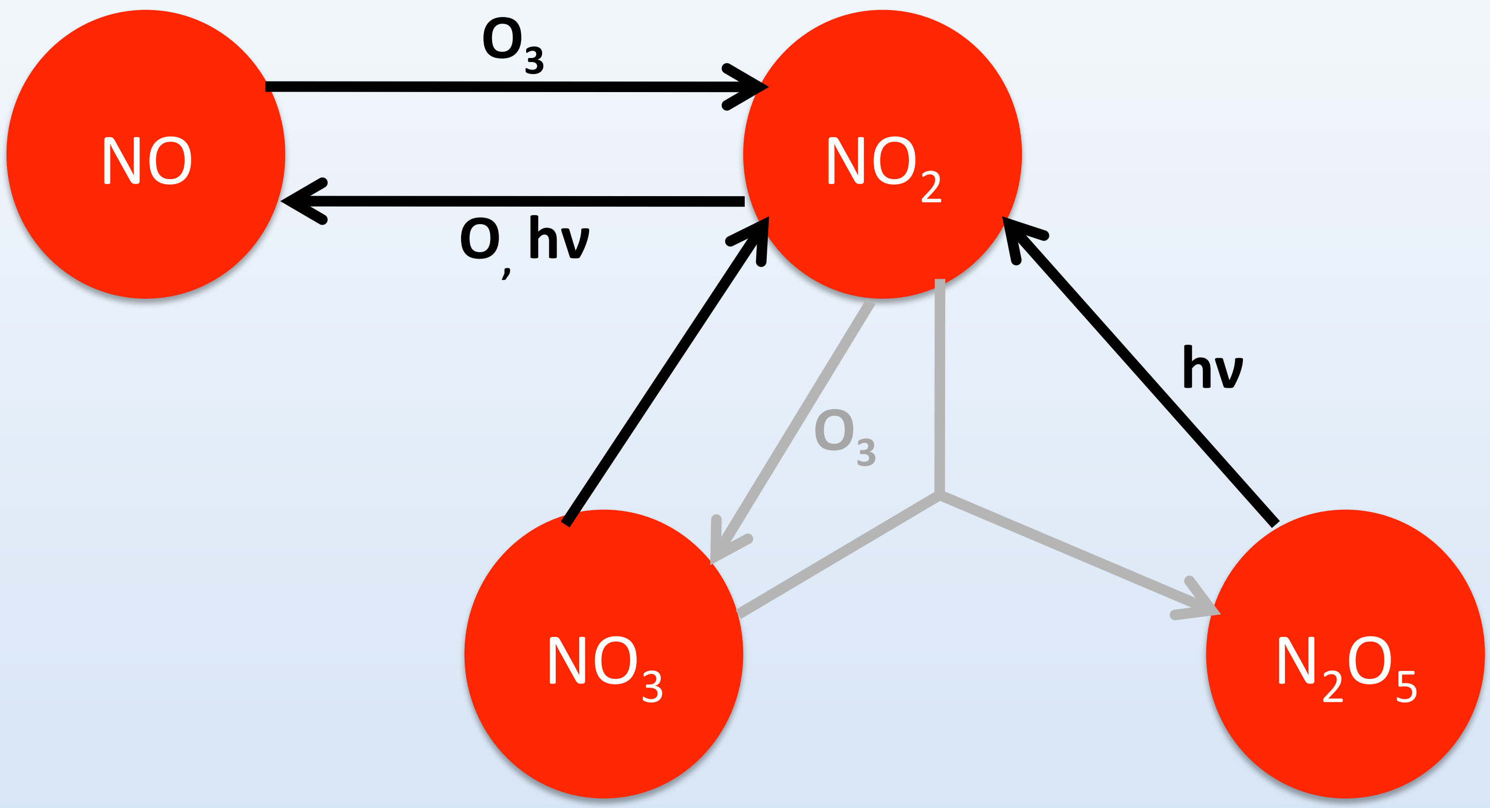
Even Nitrogen

N_2 : molecular nitrogen
N_2O : nitrous oxide

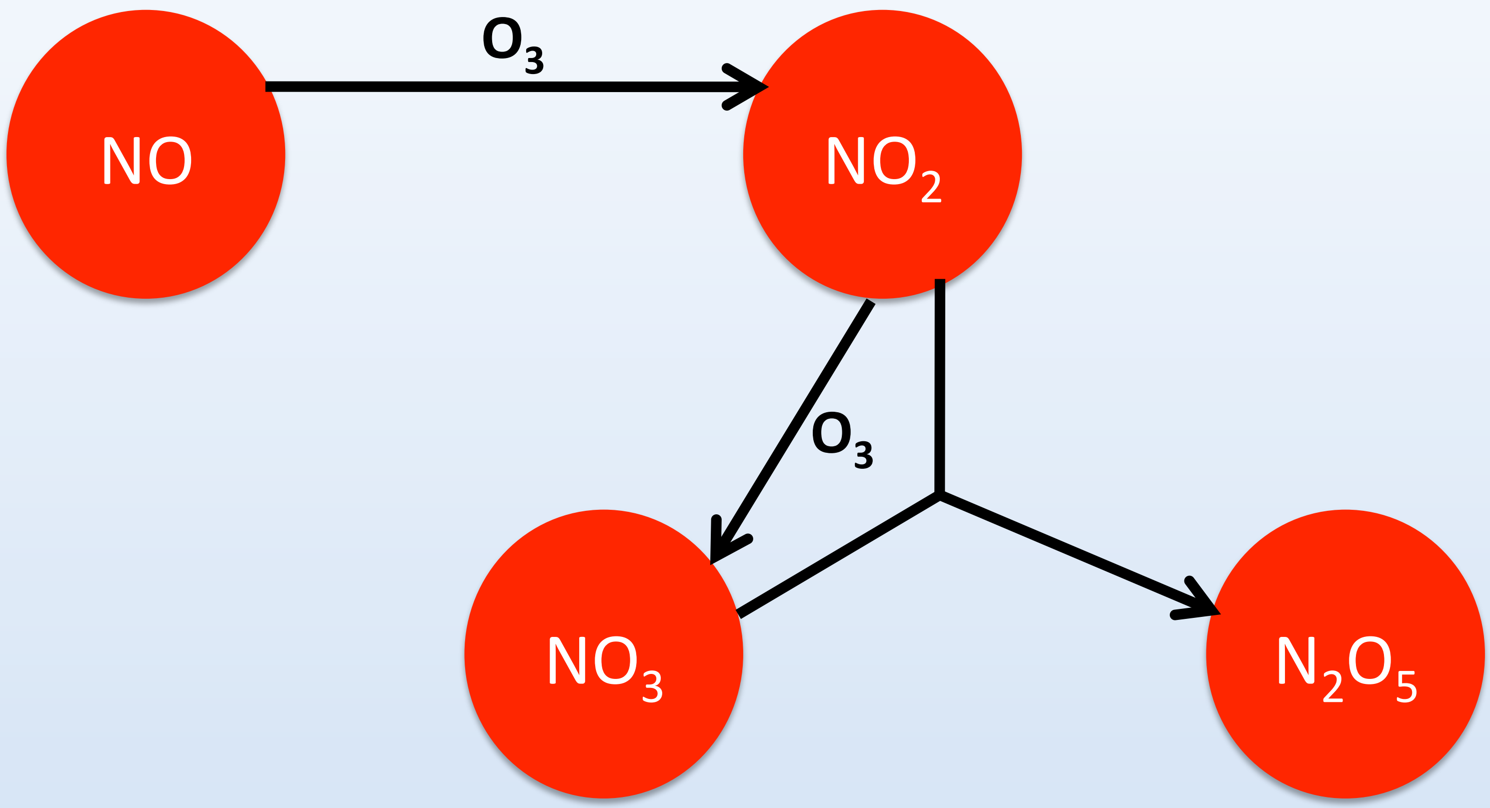
Reservoirs

HNO_3 : nitric acid
HO_2NO_2 : pernitric acid
$ClONO_2$: chlorine nitrate
$BrONO_2$: bromine nitrate

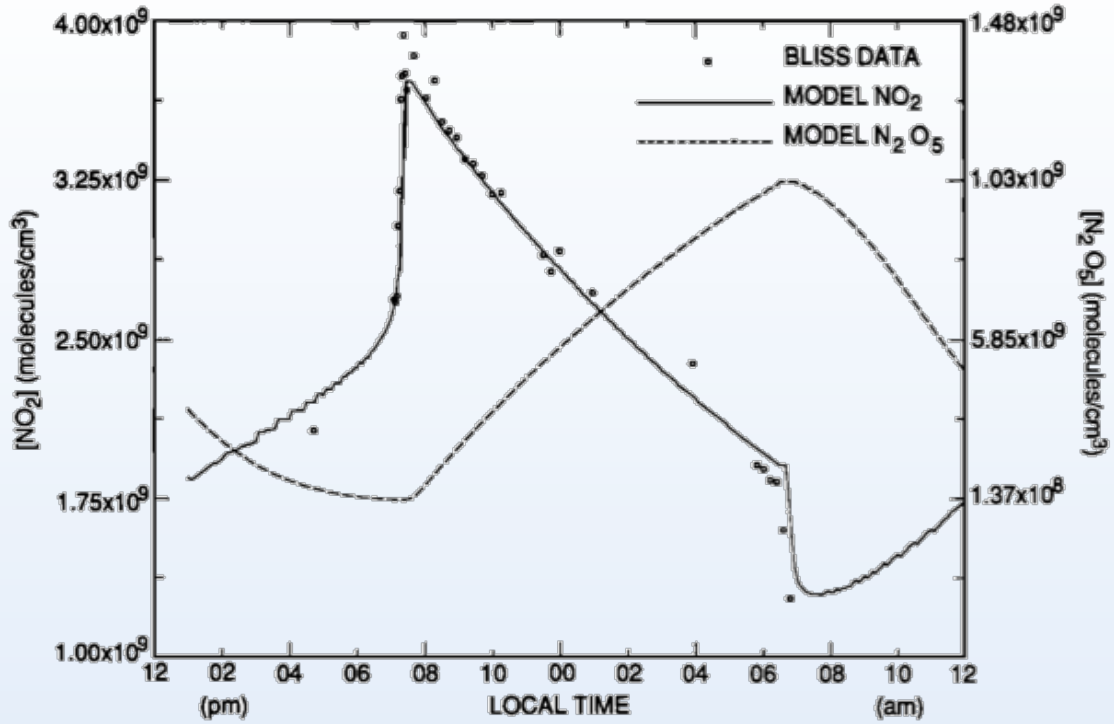
Daytime NO_x Chemistry



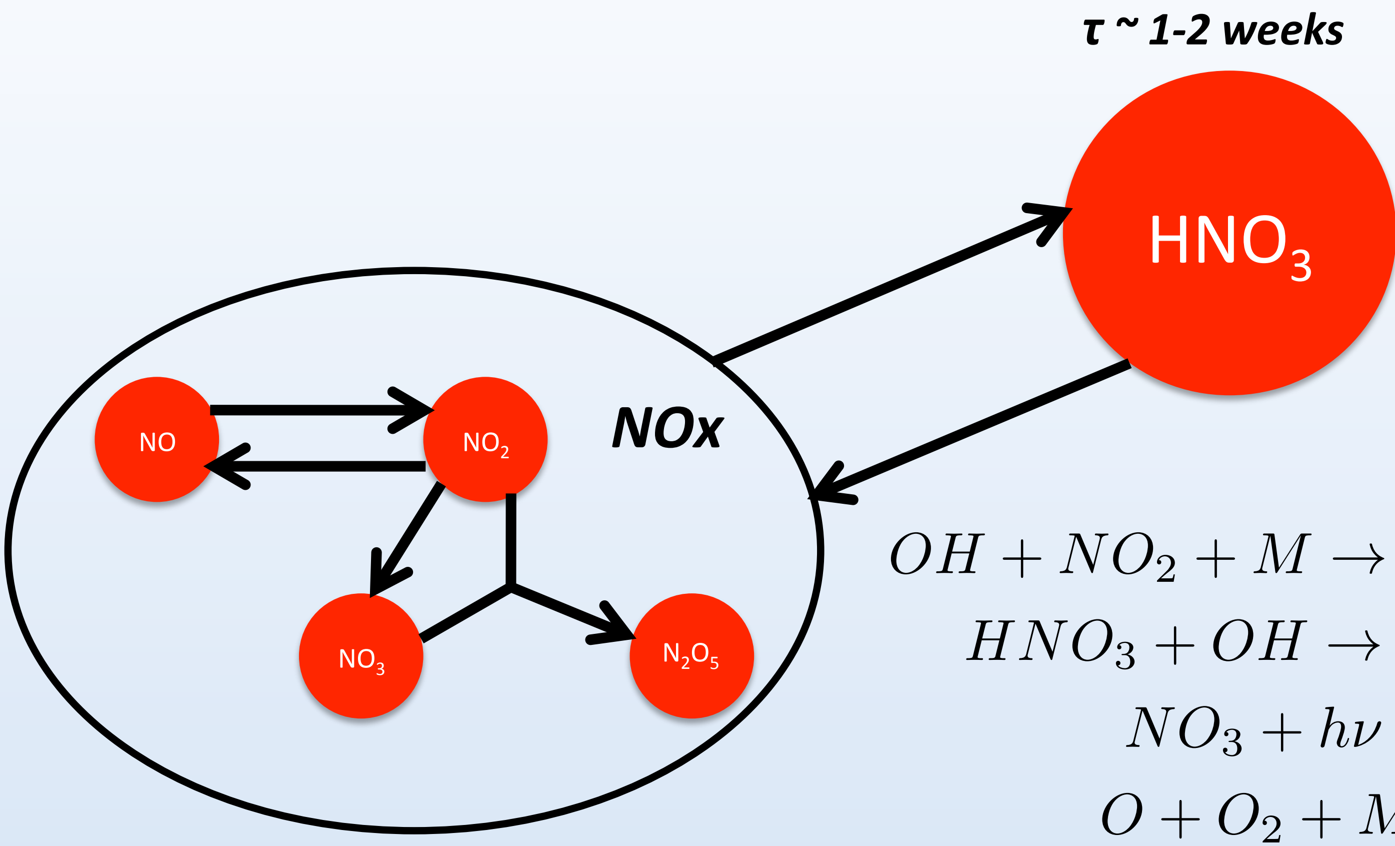
Nighttime NO_x Chemistry



Diurnal Variation of NO_2: Measurement from High-Altitude Balloon



Nitric Acid as a Reservoir for NO_x



$$OH + NO_2 + M \rightarrow HNO_3 + M$$
$$HNO_3 + OH \rightarrow H_2O + NO_3$$
$$NO_3 + h\nu \rightarrow NO_2 + O$$
$$O + O_2 + M \rightarrow O_3 + M$$

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$$net: OH + OH + O_2 \rightarrow H_2O + O_3$$

Steady-State Continuity Equation Including Loss Due to O_x, NO_x, and HO_x

$$P_{O_x} = \kappa \cdot [O_3] + \alpha \cdot [ON] \cdot [O_3] + \beta \cdot [HO_x] \cdot [O_3]$$

Solve for [O_3]

$$[O_3] = \frac{P_{O_x}}{\kappa + \alpha \cdot [ON] + \beta \cdot [HO_x]}$$

Take derivative of [O_3] with respect to [ON]

$$\frac{\partial [O_3]}{\partial [ON]} = \frac{-\alpha \cdot P_{O_x}}{(\kappa + \alpha \cdot [ON] + \beta \cdot [HO_x])^2}$$

Sensitivity of Ozone to Odd Nitrogen Change $S(O_3|ON)$

$$\frac{\partial[O_3]/[O_3]}{\partial[ON]/[ON]} = \frac{-\alpha \cdot [ON]}{\kappa + \alpha \cdot [ON] + \beta \cdot [HO_x]}$$

$$\frac{\partial[O_3]/[O_3]}{\partial[ON]/[ON]} = -\frac{l_{NO_x}}{l_{tot}}$$

For small perturbations, the fractional change in ozone for a given fractional change in odd nitrogen (or NO_x) is equal to the fraction of the baseline loss that is due to NO_x

Loss Rates due to Catalytic Cycles