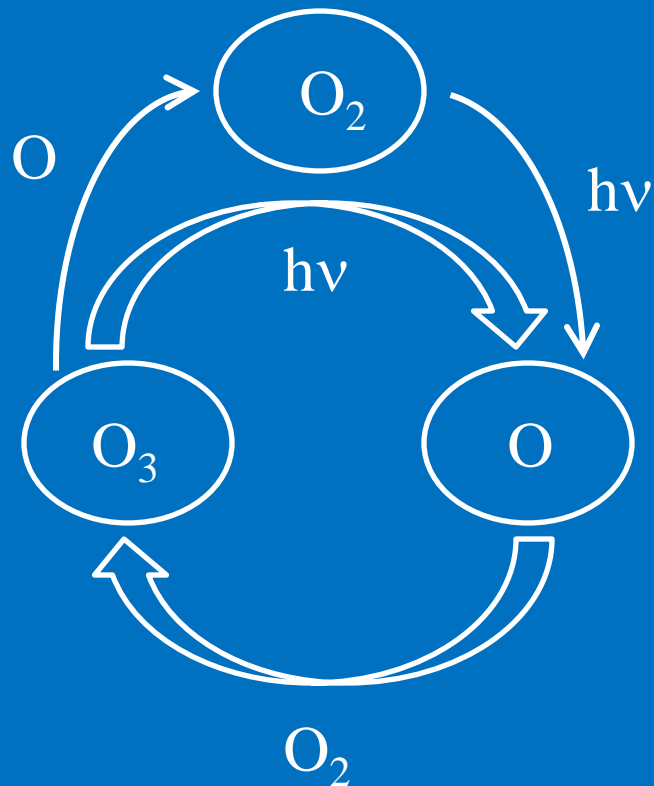# Reaction Cycles , Steady State, and Chapman Chemistry, Part 2

- Chapman Chemistry, Odd Oxygen
- Prediction vs. Observations
- Need for catalysts

rate1 = k_1 [O_2] [hν] = J_{O2} [O_2]

rate2 = k_2[O][O_2][M]

rate3 = J_{O3} [O_3]

rate4 = k_4[O][O_3]

Back to our equations in a bit more detail (also, see Problem 15)

$$\frac{d[O]}{dt} = 2J_1[O_2] - k_2[O][O_2][M] + J_3[O_3] - k_4[O][O_3]$$

$$\frac{d[O_3]}{dt} = k_2[O][O_2][M] - J_3[O_3] - k_4[O][O_3]$$

rate1 = k_1 [O_2] [hν] = J_{O2} [O_2]

rate2 = k_2[O][O_2][M]

rate3 = J_{O3} [O_3]

rate4 = k_4[O][O_3]

First, we added O and O_3 (odd oxygen)

$$\frac{d[O]}{dt} + \frac{d[O_3]}{dt} = 2J_{O2}[O_2] - 2k_4[O][O_3]$$

We get a similar result assuming that O_2 is in steady state – the math is harder
(Skip this slide if you don't care about the math!)

$$\frac{d[O_2]}{dt} = -J_{O2}[O_2] - k_2[O][O_2][M] + J_{O3}[O_3] + 2k_4[O][O_3]$$

$$= -2J_{O2}[O_2] + (J_{O2}[O_2] - k_2[O][O_2][M] + J_{O3}[O_3]) + 2k_4[O][O_3]$$

$$= -2J_{O2}[O_2] + \frac{d([O] - [O_3])}{dt} + 2k_4[O][O_3]$$

So, at steady state, both $d[O_2]/dt$ and the $d([O]-[O_3])dt$ terms will be zero. So that the following is true:

$$J_{O2}[O_2] = k_4[O][O_3]$$

$$\frac{d[O_2]}{dt} = -J_{O2}[O_2] - k_2[O][O_2][M] + J_{O3}[O_3] + 2k_4[O][O_3]$$

$$= -2J_{O2}[O_2] + (J_{O2}[O_2] - k_2[O][O_2][M] + J_{O3}[O_3]) + 2k_4[O][O_3]$$

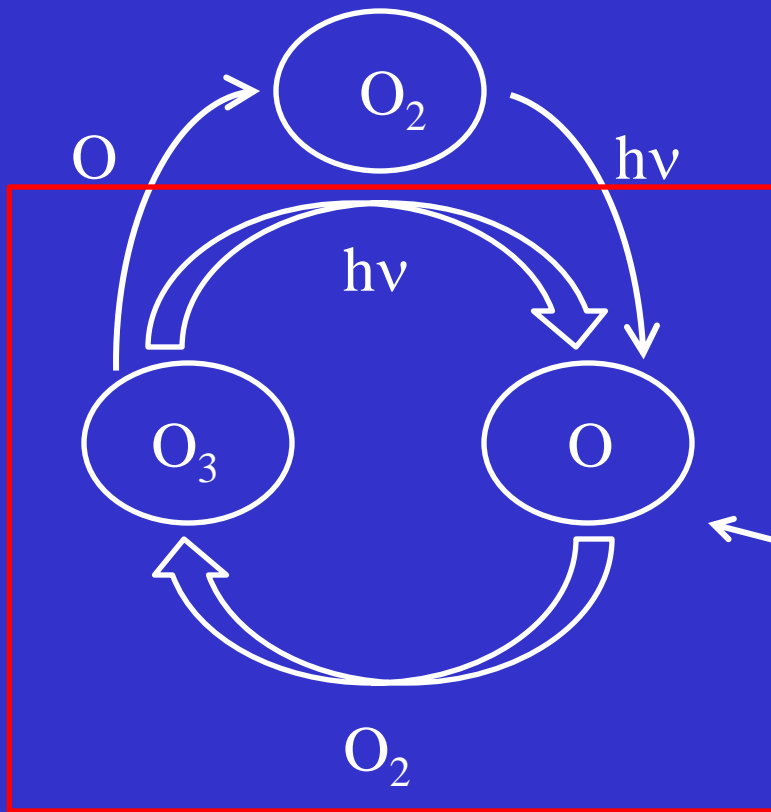$$= -2J_{O2}[O_2] + \frac{d([O] - [O_3])}{dt} + 2k_4[O][O_3]$$

This is just adding $J_{O2}[O_2] - J_{O2}[O_2] = 0$

You get a similar result assuming that O_2 is in steady state – the math is harder. Skip this slide if you don't care about the math!

$$\frac{d[O_2]}{dt} = -J_{O2}[O_2] - k_2[O][O_2][M] + J_{O3}[O_3] + 2k_4[O][O_3]$$

$$= -2J_{O2}[O_2] + (J_{O2}[O_2] - k_2[O][O_2][M] + J_{O3}[O_3]) + 2k_4[O][O_3]$$

$$= -2J_{O2}[O_2] + \boxed{\frac{d([O] - [O_3])}{2dt}} + 2k_4[O][O_3]$$

$$\boxed{\begin{aligned} \frac{d([O] - [O_3])}{2dt} &= \frac{1}{2}\left(2J_{O2}[O_2] - k_2[O][O_2][M] + J_{O3}[O_3] - k_4[O][O_3]\right) \\ &- \frac{1}{2}(k_2[O][O_2][M] - J_{O3}[O_3] - k_4[O][O_3]) \\ &= J_{O2}[O_2] - k_2[O][O_2][M] + J_{O3}[O_3] \end{aligned}}$$
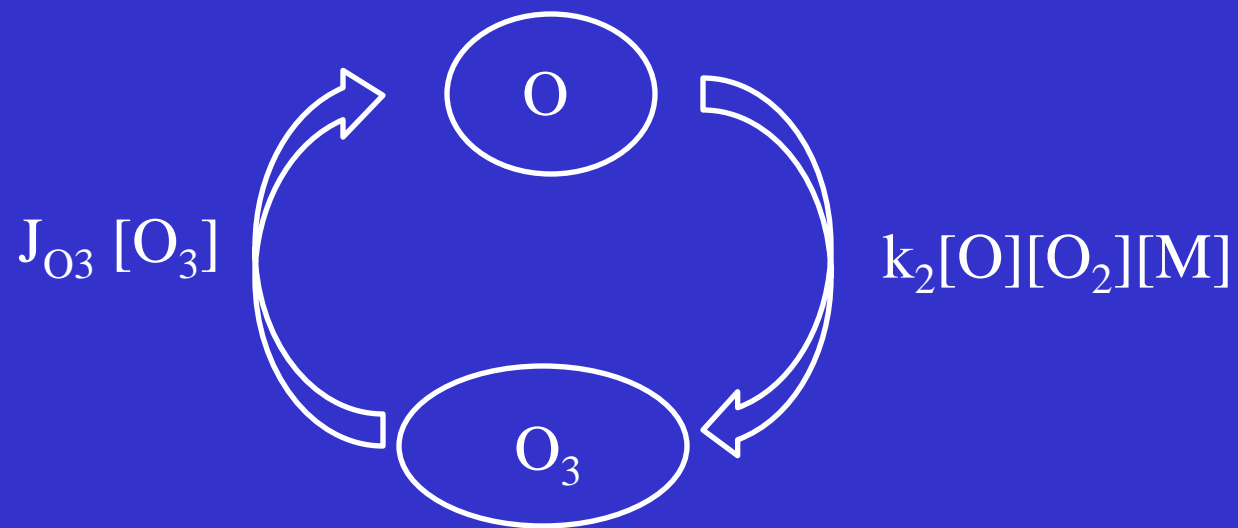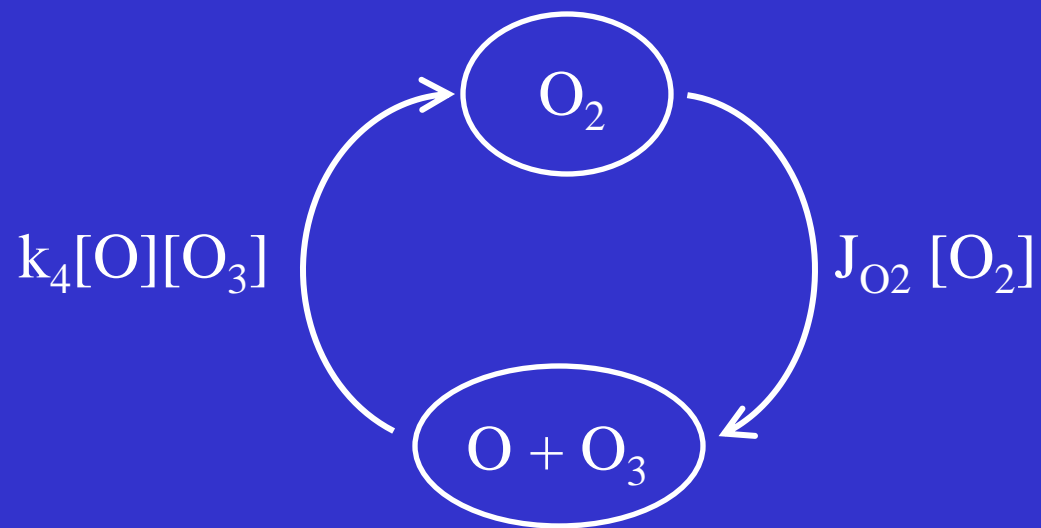
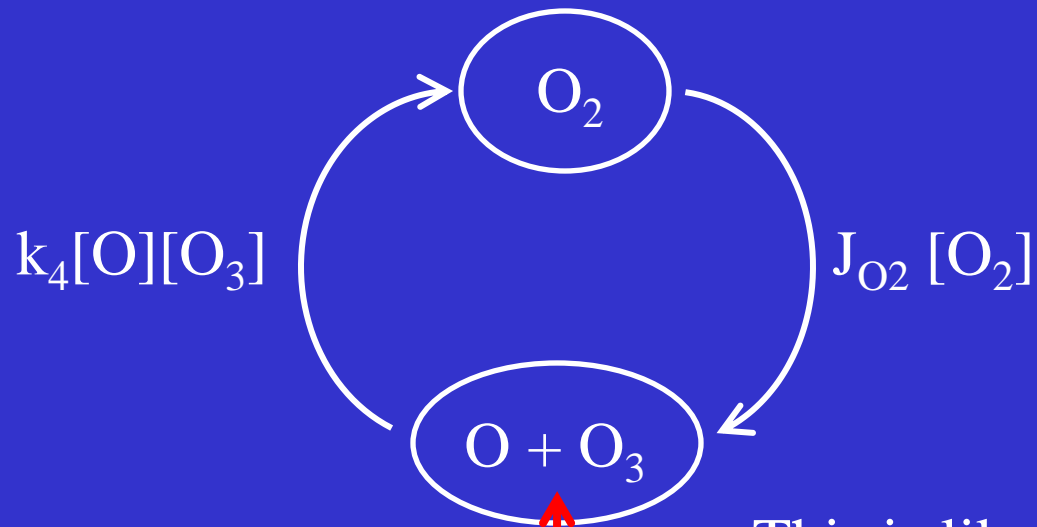rate1 = k_1 [O_2] [$h\nu$] = J_{O2} [O_2]
rate2 = k_2[O][O_2][M]
rate3 = J_{O3} [O_3]
rate4 = k_4[O][O_3]

We call O + O_3
"odd oxygen" or "Ox"

$$\frac{d[O_x]}{dt} = 2J_{O2}[O_2] - 2k_4[O][O_3]$$

Top cycle:

O_2 → $O + O_3$: $J_{O2} [O_2]$

$O + O_3$ → O_2 : $k_4[O][O_3]$

Bottom cycle:

O → O_3 : $k_2[O][O_2][M]$

O_3 → O : $J_{O3} [O_3]$

O_2

$k_4[O][O_3]$

$J_{O2} [O_2]$

$O + O_3$

This is like a cycle in a cycle!

$J_{O3} [O_3]$

O

$k_2[O][O_2][M]$

O_3
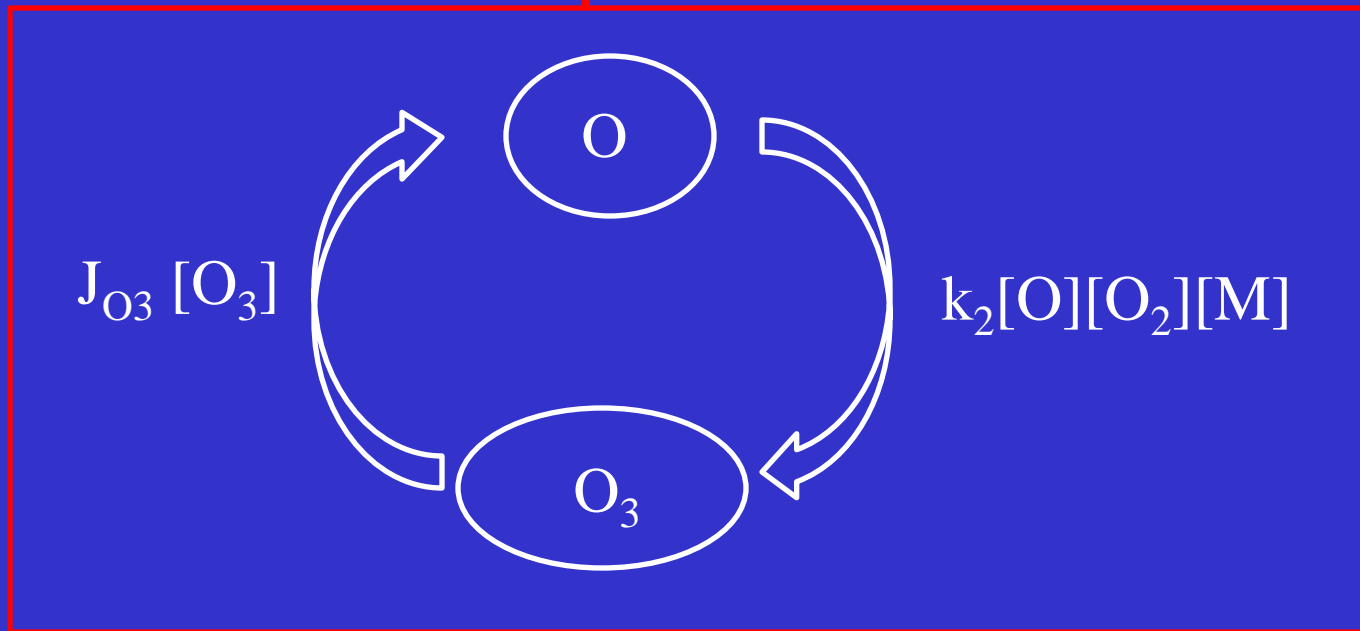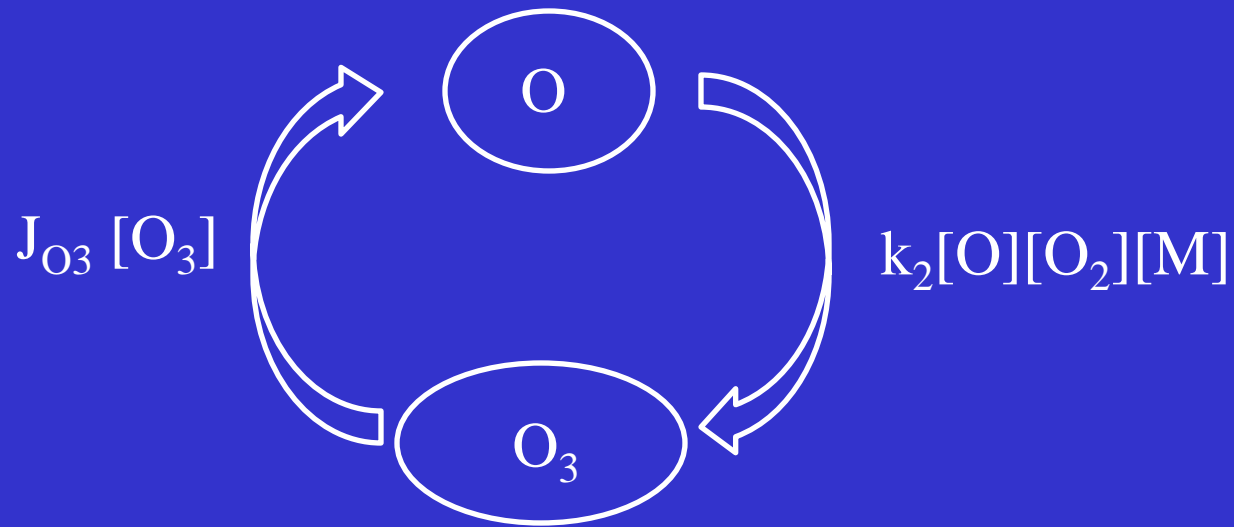
Let's assume that O and O_3 are in steady state.

$$k_2[O][O_2][M] = J_{O3} [O_3]$$

We already know that $J_{O2}[O_2] = k_4[O][O_3]$. Let's eliminate [O].

$$[O] = \frac{J_{O2}[O_2]}{k_4[O_3]}$$

$$[O_3]^2 = \frac{J_{O2} k_2 [O_2]^2 [M]}{J_{O3} k_4}$$

$$[O_3] = 0.21 \left(\frac{J_{O2}}{J_{O3}} \right)^{\frac{1}{2}} \left(\frac{k_2}{k_4} \right)^{\frac{1}{2}} [M]^{\frac{3}{2}}$$

Where we have used $[O_2] = 0.21 \ [M]$
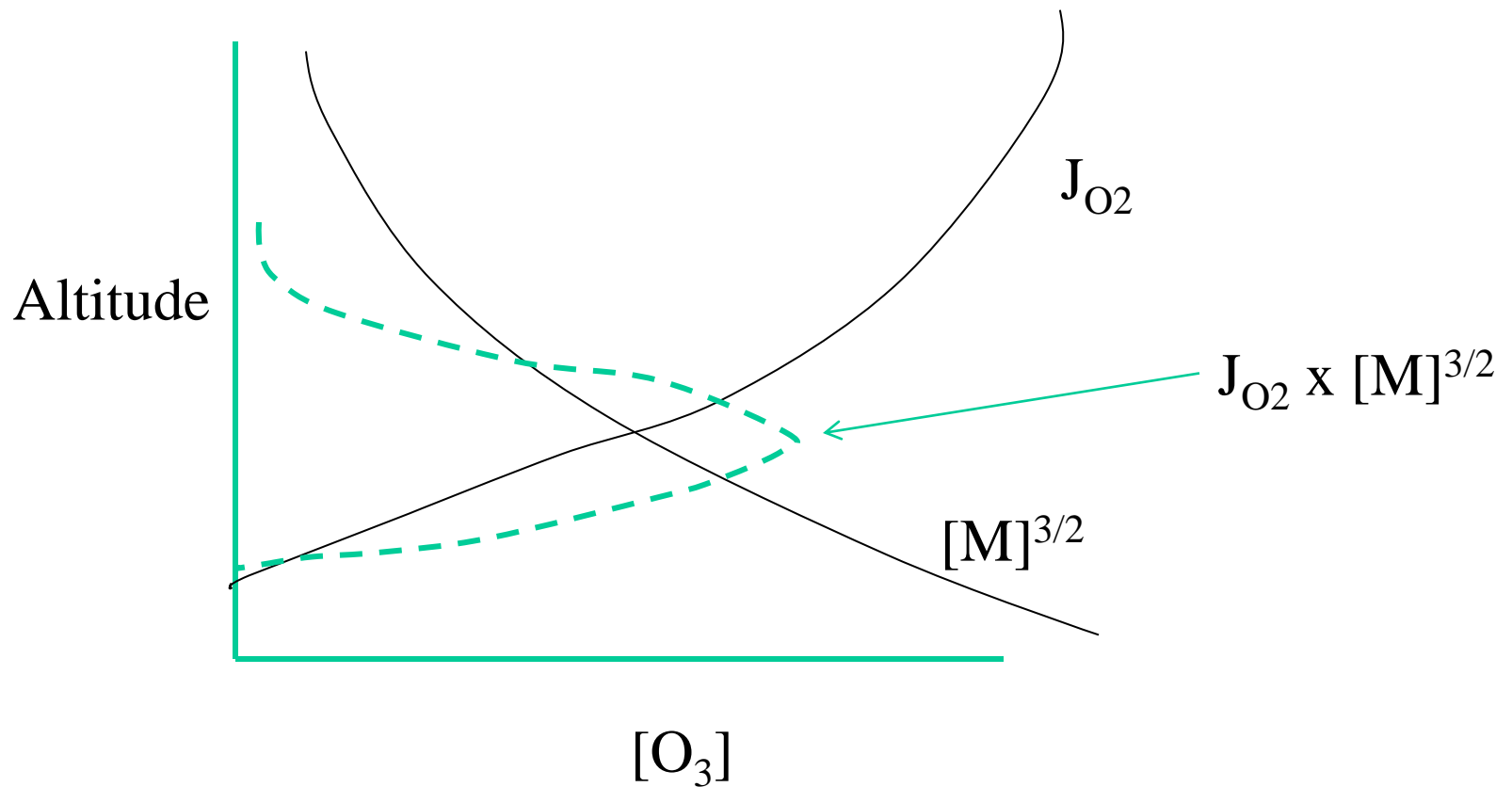
$$[O_3]^2 = \frac{J_{O2} k_2 [O_2]^2 [M]}{J_{O3} k_4}$$

Note – these are the reactions that make ozone from O_2

$$[O_3] = 0.21 \left(\frac{J_{O2}}{J_{O3}} \right)^{\frac{1}{2}} \left(\frac{k_2}{k_4} \right)^{\frac{1}{2}} [M]^{\frac{3}{2}}$$

These are the reactions that destroy ozone

Where we have used $[O_2] = 0.21 \, [M]$

We now see a formal mathematical equation that defines the layer of ozone.

<u>At 30 km:</u>
- $J_{O2} = 10^{-11}$ s^{-1}
- $J_{O3} = 5 \times 10^{-4}$ s^{-1}

<u>At 250 K</u>
- $k_2 = 9 \times 10^{-34}$ cm^6 $molecule^2$ s^{-1}
- $k_4 = 2 \times 10^{-15}$ cm^3 $molecule$ s^{-1}

So at 30 km, $[O_3] \sim (0.21) \times (9.5 \times 10^{-14})[M]^{3/2}$

Recall that we can get [M] from P and T (and P we can get from hydrostatic balance). At 30 km, $[M] \sim 4 \times 10^{17}$

$$So\ [O_3] \sim 5 \times 10^{12}$$

(so the mixing ratio of ozone is about 13 ppm)

We note that this is a bit on the high side – measurements show about half this
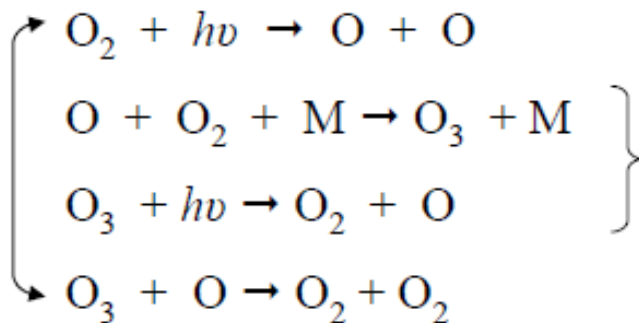
Chapman chemistry (in steady state)

$$O_2 + h\upsilon \rightarrow O + O$$

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

$$O_3 + h\upsilon \rightarrow O_2 + O$$

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

Slow and exactly balance

Fast and approx. balance

$$J_{O_2}[O_2] = k_4[O][O_3]$$

$$k_2[O][O_2][M] \sim J_{O_3}[O_3]$$

$$[O][O_3] = \frac{J_{O_2}}{k_4}[O_2]$$
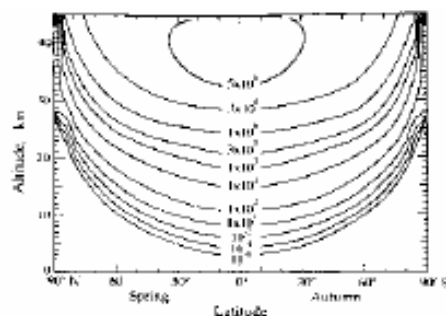
$$\frac{[O]}{[O_3]} \sim \frac{J_{O_3}}{k_2}\frac{1}{[O_2][M]}$$

$$[O_3] \sim 0.21\left(\frac{k_2}{k_4}\right)^{\frac{1}{2}}\left(\frac{J_{O_2}}{J_{O_3}}\right)^{\frac{1}{2}}[M]^{\frac{3}{2}}$$

FIGURE 4.5 Annually averaged rate of ozone formation (molecule cm⁻³s⁻¹ from the photolysis of O₂ (Johnson, 1975)

FIGURE 4.6 Comparison of computed concentrations of ozone with observations...
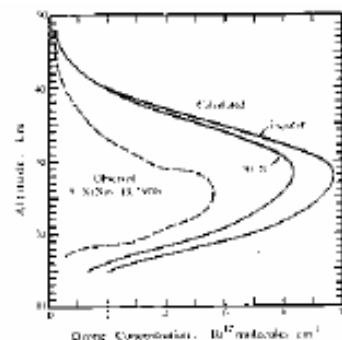
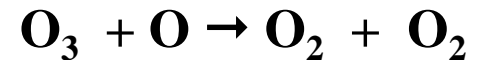How does this compare to observations? Chapman mechanism predicts more ozone than what is observed!
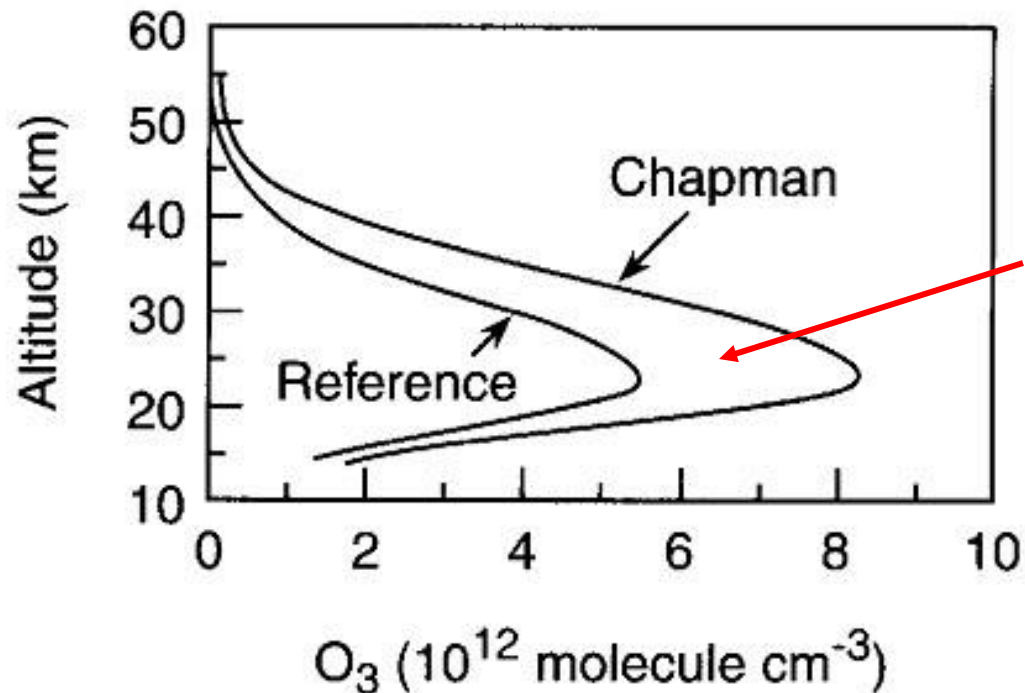
FIGURE 12.5 Model-calculated ozone vertical profiles for a Chapman or O_x model, with only O_2, O, and O_3 as reactive species and the reference atmosphere chosen to be typical of 1960 conditions (adapted from Kinnison et al., 1988).

What's missing?

Faster

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

We saw above that steady state ozone was determined by the ratio of production to loss, and that production (in the stratosphere, at least) is determined by a process that is dependent only on the abundance of O_2, which is relatively constant over time, and solar energy, which doesn't vary that significantly. So the only explanation for the overprediction of ozone by Chapman theory is that there must be additional losses. These will be due to catalysts.