Modelling the [O_3]: A Kinetic Approach

Considering the Chapman reactions for the production and loss of ozone, we will attempt to derive an expression for the concentration of ozone in the stratosphere. Applying this expression at various altitudes, will allow us to predict the O_3 profile with altitude. Comparing these predicted results with the observed O_3 profile, allows us to evaluate the model and deduce if the set of Chapman reactions is adequate to predict the concentration behaviour of ozone.

(1)	$O_2 + h\nu \rightarrow O + O$	k_1, slow
(2)	$O + O_2 + M \rightarrow O_3 + M$	k_2, fast
(3)	$O_3 + h\nu \rightarrow O_2 + O$	k_3, fast
(4)	$O + O_3 \rightarrow O_2 + O_2$	k_4, slow

In several places in this derivation, we will use a simplifying approximation known as the *steady state assumption (SSA)*. The steady state assumption can be applied to a chemical species if it's production and loss rates remain roughly constant <u>over it's lifetime</u>. When the SSA applies, the rate of production = rate loss.

Let's start by examining if steady state kinetics is applicable for atomic O, the shortest lived O_x species in the Chapmann reactions. Consider the reactions leading to the loss of O, reactions (2) and (4) above.

$$\tau_O^{\text{chem loss}} = \frac{stock}{flux} = \frac{[O]}{k_2\,[O]\,[O_2]\,[M] + k_4\,[O]\,[O_3]} = \frac{1}{k_2\,[O_2]\,[M] + k_4\,[O_3]} \approx \frac{1}{k_2\,[O_2]\,[M]}$$

where $k_2\,[O_2]\,[M] >> k_4\,[O_3]$, since $k_2 > k_4$ and $[O_2]\,[M] >> [O_3]$

So to estimate the lifetime of atomic O, we need k_2, $[O_2]$ and [M].

k_2 has been estimated to be 1×10^{-33} cm^6 $molecules^{-2}$ s^{-1} in the stratosphere
[M] = n_{air} (i.e., the number density at specified P and T) ~ 10^{17} molecules cm^{-3} in the stratosphere

$[O_2] = \chi_{O2}\, n_{air} \sim 0.21 \times 10^{17}$ molecules cm^{-3}

Therefore, $\tau_O^{\text{chem loss}} = \dfrac{1}{k_2\,\chi_{O2}\,n_{air}^2} \sim$ seconds

Note: the lifetime of atomic O will vary depending on changes of P, T and light intensity, however these changes will not vary over the short lifetime of O (i.e, seconds).

Therefore, the steady state approximation can be applied to atomic O and the rate of production of O = rate of loss of O. Considering the fast reactions (2) and (3) only, we can say;

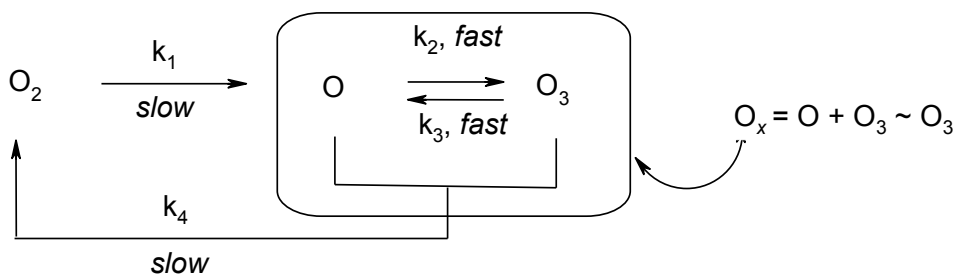
k_2 [O] [O_2] [M] = k_3 [O_3]

and rearranging yields, $$\frac{[O]}{[O_3]} = \frac{k_3}{k_2\ [O_2]\ [M]} = \frac{k_3}{k_2\ \chi_{O2}\ n_{air}^2}$$

substituting the approximate values for k_2, k_3 and n_{air}, the ratio of [O]/[O_3] << 1 (i.e., the [O_3] is much greater than the [O])

and therefore, [O_x] = [O] + [O_3] ≈ [O_3]

The consequence of this result is two-fold. Firstly, the [O_3] is controlled by the slow production/loss reactions (1) and (4), rather than the faster reactions (2) and (3). Secondly, the effective lifetime of O_3 against chemical loss is defined by the lifetime of O_x.



$$\tau_{Ox} = \frac{[O_x]}{2\,k_4\,[O][O_3]} \approx \frac{1}{2\,k_4\,[O]}$$

Note: the factor of 2 arises because reaction (4) consumes 2 moles of O_x (one O and one O_3).

τ_{Ox} ≈ days to years (depending on the [O], which varies in the stratosphere with altitude).

When [O] is relatively high (upper stratosphere), τ_{Ox} is low and steady state conditions apply to O_x species (i.e., rate of production of O_x = rate of loss O_x)

So, 2 k_1 [O_2] = 2 k_4 [O] [O_3]

$$[O_3] = \frac{2\,k_1\ [O_2]}{2\,k_4\ [O]} = \frac{k_1\ \chi_{O2}\ n_{air}}{k_4\ [O]}$$

Using the steady state concentration of atomic O derived earlier; $[O] = \dfrac{[O_3]\,k_3}{k_2\,\chi_{O2}\,n_{air}^2}$

And substituting into the expression for $[O_3]$, yields;

$$[O_3] = \frac{k_1\,\chi_{O2}\,n_{air}}{k_4\,\dfrac{[O_3]\,k_3}{k_2\,\chi_{O2}\,n_{air}^2}} = \frac{k_1\,k_2\,\chi_{O2}^2 n_{air}^3}{k_3 k_4\,[O_3]}$$

rearranging and solving for $[O_3]$ yields;

$$[O_3] = \sqrt{\frac{k_1\,k_2\,\chi_{O2}^2 n_{air}^3}{k_3 k_4}} = \left(\frac{k_1\,k_2}{k_3\,k_4}\right)^{1/2} \chi_{O2}\,n_{air}^{3/2}$$

Recall: k_1 and k_3 are photochemical rate constants whose magnitude depends on photon flux (J), absorption cross-section (σ) and the reaction quantum yield (ϕ). The textbook uses f in place of k to distinguish photochemical rate constants.

$$f = \int_{\lambda 1}^{\lambda 2} J_\lambda\,\sigma_\lambda \Phi_\lambda\,d\lambda$$

where J varies with time of day and σ and ϕ are constant for a given molecule.

Hence, with a knowledge of the rate constants (which can be experimentally determined), we are able to calculate the concentration of ozone at various altitudes through the atmosphere. Concentration profiles predicted with this model, overestimate by a factor of ~2 times the $[O_3]$ in the stratosphere. This suggests that the Chapman reactions are insufficient to account for all the possible ozone loss reactions. When the additional reactions involving HO_x and NO_x are included, the model does a much better job of predicting the actual $[O_3]$.

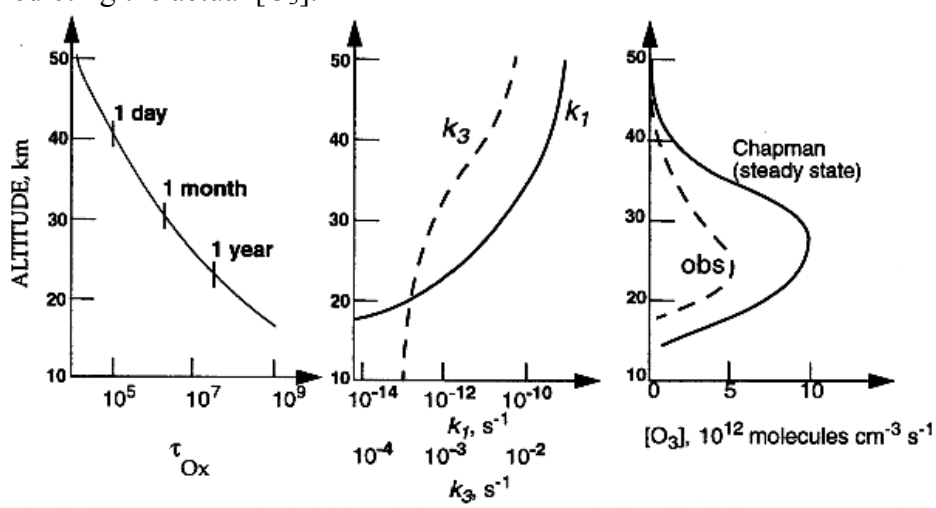


Fig. 10-5 Chapman mechanism at low latitudes. Left panel: Lifetime of O_x. Center panel: O_2 and O_3 photolysis rate constants. Right panel: calculated and observed vertical profiles of O_3 concentrations.

From: *Introduction to Atmospheric Chemistry*, D. J. Jacobs, Princeton Univ. Press, NJ, 1998.

Example Question: Applying the *steady state approximation* to **O** and $\mathbf{O_3}$ in the Chapman reactions, it can be shown that; $k_2[\mathbf{O_2}][\mathbf{O}][\mathrm{M}] \cong f_3[\mathbf{O_3}]$ and $f_1[\mathbf{O_2}] \cong k_4[\mathbf{O}][\mathbf{O_3}]$
Given the information below about the temperature dependence of the rate constants, predict the ozone concentration at 60 km altitude. The rate constants k_2 and k_4 vary with temperature as follows;

$$k_2 = 6.0 \text{ x } 10^{-34}\left(\frac{\mathrm{T}}{300}\right)^{-2.3} \text{cm}^6 \text{ molec}^{-2} \text{ s}^{-1} \quad k_4 = 8.0 \text{ x } 10^{-12} e^{\left\{\frac{-2060}{\mathrm{T}}\right\}} \text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$$

The photochemical rate constants f_1 and f_3 do not vary appreciably with temperature and are given by 1 x 10^{-11} s^{-1} and 1 x 10^{-3} s^{-1}, respectively.