Example of a (small) C-H-O chemical network (292 reactions)

This is not meant to be read in detail, but simply to give you a sense of the size of a chemical network.
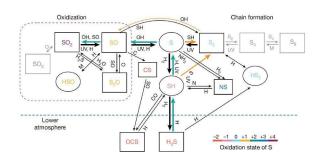
The production and loss terms are constructed from these rate coefficients.

Each reaction has a forward and reverse component. Typically, only one component is measured experimentally and one then uses theory to "reverse" the reaction.

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Tsai et al. (2017, ApJS, 228, 20)

Recent example: SO₂ production in WASP-39b (JWST data)

Some reactions involve photons!
(Photochemistry)

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Tsai et al. (2023, Nature, 617, 7961)

Why equations of chemical kinetics are "stiff"

Consider a simple system with simplistic production and loss rates (and cast in dimensionless units):

$$\frac{\partial n_{X_1}}{\partial t} = \mathcal{A}_1 n_{X_1} + \mathcal{A}_2 n_{Z_1} - n_{X_1},$$
$$\frac{\partial n_{Z_1}}{\partial t} = -\mathcal{A}_1 n_{X_1} - \mathcal{A}_2 n_{Z_1} - n_{Z_1}.$$

Problem 6.5.2 shows you how to solve this system of coupled equations:

$$n_{X_1} = 2\mathcal{A}_3 e^{-t} - \mathcal{A}_4 e^{-(\mathcal{A}_1+1)t},$$
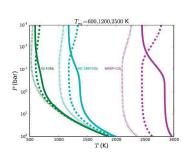$$n_{Z_1} = \mathcal{A}_4 e^{-(\mathcal{A}_1+1)t} - \mathcal{A}_3 e^{-t},$$

There are two chemical timescales in the problem: $t_{\text{chem}} = 1, (1 + A_1)^{-1}$

If $A_1 \gg 1$, then one of the chemical timescales is much shorter than the other. The shorter chemical timescale controls the numerical integration across time. Such a set of equations is said to be "stiff".
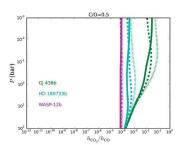
In realistic chemical networks, there are hundreds to thousands of chemical timescales that vary over many, many orders of magnitude.

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Can the abundance of CO₂ ever be greater than that of CO in a hydrogen-dominated atmosphere?

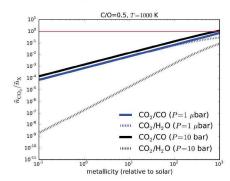Consider three objects with a variety of plausible temperature-pressure profiles

Using the same equilibrium-chemistry models we discussed, the ratio of CO₂ to CO abundances is well below unity

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Heng & Lyons (2016, ApJ, 817, 149)

Can the abundance of CO₂ ever be greater than that of CO in a hydrogen-dominated atmosphere?

The only way to make CO₂ more abundant than CO in a H₂-dominated atmosphere is to greatly increase the C/H and O/H elemental abundances to implausible values.

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Heng & Lyons (2016, ApJ, 817, 149)

Summary of Lecture 5

- Atmospheric chemistry teaches you how to be surprised, because it allows us to calculate the expected molecular abundances in chemical equilibrium given a set of temperatures, pressures and elemental abundances.

- The carbon-to-oxygen ratio (C/O) is a key parameter in controlling how carbon, oxygen and hydrogen are partitioned into molecules.

- Chemical equilibrium occurs when the chemical timescale is much shorter than all timescales associated with atmospheric dynamics (mixing).

- Systems in chemical equilibrium may be reduced to polynomial equations involving one of the chemical species.

- The quenching approximation is a simplified way of computing disequilibrium chemistry, but it does not always work.

- Chemical kinetics calculations typically employ chemical networks that involve hundreds, if not thousands, of chemical reactions.

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