Ensure conservation of mass for each element (C, H, O):

$$n_{\mathrm{CH_4}} + n_{\mathrm{CO}} + 2n_{\mathrm{C_2H_2}} = n_{\mathrm{C}},$$
$$n_{\mathrm{H_2O}} + n_{\mathrm{CO}} = n_{\mathrm{O}},$$
$$4n_{\mathrm{CH_4}} + 2n_{\mathrm{H_2O}} + 2n_{\mathrm{C_2H_2}} + 2n_{\mathrm{H_2}} = n_{\mathrm{H}}$$

One is simply counting the number of atoms that constitute each molecule!

After some algebraic manipulation (see Chapter 7.3 of textbook), one ends up with a cubic equation involving methane:

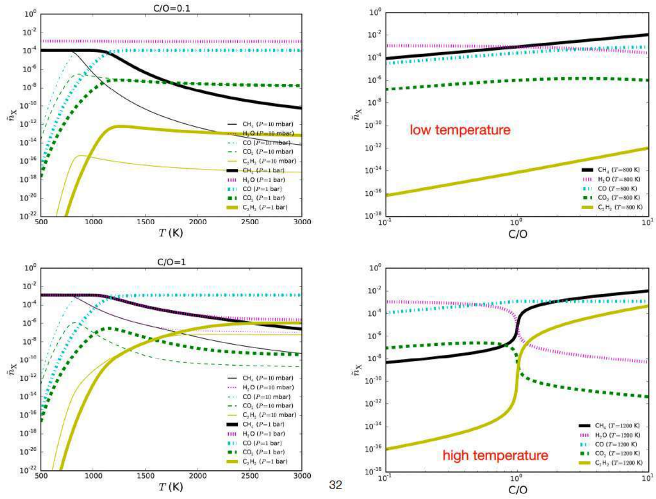
$$\mathcal{C}_3 \tilde{n}_{\mathrm{CH_4}}^3 + \mathcal{C}_2 \tilde{n}_{\mathrm{CH_4}}^2 + \mathcal{C}_1 \tilde{n}_{\mathrm{CH_4}} + \mathcal{C}_0 = 0$$

$$\begin{aligned}
\mathcal{C}_3 &= 2K'K_2'\left(\tilde{n}_{\mathrm{O}} - \tilde{n}_{\mathrm{C}} + 1\right),\\
\mathcal{C}_2 &= K'\left(4\tilde{n}_{\mathrm{O}} - 4\tilde{n}_{\mathrm{C}} + 1\right)\\
&\quad - K_2'\left[4\tilde{n}_{\mathrm{O}}\tilde{n}_{\mathrm{C}} + 2\left(1 - 2\tilde{n}_{\mathrm{O}}\right)\left(\tilde{n}_{\mathrm{C}} - 1\right)\right],\\
\mathcal{C}_1 &= 2K'\left(\tilde{n}_{\mathrm{O}} - \tilde{n}_{\mathrm{C}}\right) - 4\tilde{n}_{\mathrm{C}} - 2\tilde{n}_{\mathrm{O}} + 1,\\
\mathcal{C}_0 &= -2\tilde{n}_{\mathrm{C}}.
\end{aligned}$$

$$K' \equiv \frac{K'_{\mathrm{eq}}}{n_{\mathrm{H_2}}^2},\ K_2' \equiv \frac{K'_{\mathrm{eq},2}}{n_{\mathrm{H_2}}^2}.$$

If you add carbon dioxide (CO_2), you end up with a quintic equation for methane (Chapter 7.4 of textbook).

We can reproduce the published results of Madhusudhan (2012):



Well, how many molecules can you include and still solve the problem as a single polynomial equation?

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ANALYTICAL MODELS OF EXOPLANETARY ATMOSPHERES. III. GASEOUS C–H–O–N CHEMISTRY WITH NINE MOLECULES

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ABSTRACT

We present novel, analytical, equilibrium-chemistry formulae for the abundances of molecules in hot exoplanetary atmospheres that include the carbon, oxygen, and nitrogen networks. Our hydrogen-dominated solutions involve acetylene (C_2H_2), ammonia (NH_3), carbon dioxide (CO_2), carbon monoxide (CO), ethylene (C_2H_4), hydrogen cyanide (HCN), methane (CH_4), molecular nitrogen (N_2), and water (H_2O). By considering only the gas phase, we prove that the mixing ratio of carbon monoxide is governed by a decic equation (polynomial equation of order 10). We validate our solutions against numerical calculations of equilibrium chemistry that perform Gibbs free energy minimization and demonstrate that they are accurate at the ~1% level for temperatures from 500 to 3000 K. In hydrogen-dominated atmospheres, the ratio of abundances of HCN to CH_4 is nearly constant across a wide range of carbon-to-oxygen ratios, which makes it a robust diagnostic of the metallicity in the gas phase. Our validated formulae allow for the convenient benchmarking of chemical kinetics codes and provide an efficient way of enforcing chemical equilibrium in atmospheric retrieval calculations.

Key words: methods: analytical – planets and satellites: atmospheres

$$\begin{aligned}
\mathrm{CH_4} + \mathrm{H_2O} &\leftrightarrows \mathrm{CO} + 3\mathrm{H_2},\\
\mathrm{CO_2} + \mathrm{H_2} &\leftrightarrows \mathrm{CO} + \mathrm{H_2O},\\
2\mathrm{CH_4} &\leftrightarrows \mathrm{C_2H_2} + 3\mathrm{H_2},\\
\mathrm{C_2H_4} &\leftrightarrows \mathrm{C_2H_2} + \mathrm{H_2},\\
2\mathrm{NH_3} &\leftrightarrows \mathrm{N_2} + 3\mathrm{H_2},\\
\mathrm{NH_3} + \mathrm{CH_4} &\leftrightarrows \mathrm{HCN} + 3\mathrm{H_2}.
\end{aligned}$$

chemical reactions

$$\begin{aligned}
&\tilde{n}_{\mathrm{CH_4}} + \tilde{n}_{\mathrm{CO}} + \tilde{n}_{\mathrm{CO_2}} + \tilde{n}_{\mathrm{HCN}}\\
&\quad + 2\tilde{n}_{\mathrm{C_2H_2}} + 2\tilde{n}_{\mathrm{C_2H_4}} = 2\tilde{n}_{\mathrm{C}},\\
&\tilde{n}_{\mathrm{H_2O}} + \tilde{n}_{\mathrm{CO}} + 2\tilde{n}_{\mathrm{CO_2}} = 2\tilde{n}_{\mathrm{O}},\\
&2\tilde{n}_{\mathrm{N_2}} + \tilde{n}_{\mathrm{NH_3}} + \tilde{n}_{\mathrm{HCN}} = 2\tilde{n}_{\mathrm{N}}.
\end{aligned}$$

mass conservation

$$\begin{aligned}
K &= \frac{\tilde{n}_{\mathrm{CO}}}{\tilde{n}_{\mathrm{CH_4}}\tilde{n}_{\mathrm{H_2O}}} = \left(\frac{P_0}{P}\right)^2 \exp\left(-\frac{\Delta\tilde{G}_{0,1}}{\mathcal{R}_{\mathrm{univ}}T}\right),\\
K_2 &= \frac{\tilde{n}_{\mathrm{CO}}\tilde{n}_{\mathrm{H_2O}}}{\tilde{n}_{\mathrm{CO_2}}} = \exp\left(-\frac{\Delta\tilde{G}_{0,2}}{\mathcal{R}_{\mathrm{univ}}T}\right),\\
K_3 &= \frac{\tilde{n}_{\mathrm{C_2H_2}}}{\tilde{n}_{\mathrm{CH_4}}^2} = \left(\frac{P_0}{P}\right)^2 \exp\left(-\frac{\Delta\tilde{G}_{0,3}}{\mathcal{R}_{\mathrm{univ}}T}\right),\\
K_4 &= \frac{\tilde{n}_{\mathrm{C_2H_2}}}{\tilde{n}_{\mathrm{C_2H_4}}} = \frac{P_0}{P} \exp\left(-\frac{\Delta\tilde{G}_{0,4}}{\mathcal{R}_{\mathrm{univ}}T}\right),\\
K_5 &= \frac{\tilde{n}_{\mathrm{N_2}}}{\tilde{n}_{\mathrm{NH_3}}^2} = \left(\frac{P_0}{P}\right)^2 \exp\left(-\frac{\Delta\tilde{G}_{0,5}}{\mathcal{R}_{\mathrm{univ}}T}\right),\\
K_6 &= \frac{\tilde{n}_{\mathrm{HCN}}}{\tilde{n}_{\mathrm{NH_3}}\tilde{n}_{\mathrm{CH_4}}} = \left(\frac{P_0}{P}\right)^2 \exp\left(-\frac{\Delta\tilde{G}_{0,6}}{\mathcal{R}_{\mathrm{univ}}T}\right),
\end{aligned}$$

equilibrium constants (dimensionless)

Heng & Tsai (2016, ApJ, 829, 104)

$$\sum_{i=0}^{10} A_i\, \tilde{n_{\mathrm{CO}}}^i = 0$$

After some mind-bending algebra, one ends up with a **decic equation** (polynomial equation of order 10) involving carbon monoxide.

$$\begin{aligned}
D_2 &\equiv -KD_4^2 D_5 \tilde{n}_{\mathrm{CO}} + K^2 D_4 D_5^2 (2\tilde{n}_{\mathrm{C}} - \tilde{n}_{\mathrm{CO}})\\
&\quad - 2K_3 D_3 D_4^3 \tilde{n}_{\mathrm{CO}}^2 - \frac{K^2 D_5^3 \tilde{n}_{\mathrm{CO}}}{K_2},\\
D_3 &\equiv 1 + \frac{1}{K_4},\\
D_4 &\equiv 1 + \frac{2\tilde{n}_{\mathrm{CO}}}{K_2},\\
D_5 &\equiv 2\tilde{n}_{\mathrm{O}} - \tilde{n}_{\mathrm{CO}}.
\end{aligned}$$

$$\begin{aligned}
F_0 &= 8K^2\tilde{n}_{\mathrm{O}}^2\tilde{n}_{\mathrm{C}},\\
F_1 &= 2K\tilde{n}_{\mathrm{O}}\left\{-1 + 2K\left[2\tilde{n}_{\mathrm{C}}\left(\frac{2\tilde{n}_{\mathrm{O}}}{K_2} - 1\right) - \tilde{n}_{\mathrm{O}}\right] - \frac{4K\tilde{n}_{\mathrm{O}}^2}{K_2}\right\},\\
F_2 &= K\left(1 - \frac{8\tilde{n}_{\mathrm{O}}}{K_2}\right) - 2K_3D_3\\
&\quad + 2K^2\left[\tilde{n}_{\mathrm{C}}\left(1 - \frac{8\tilde{n}_{\mathrm{O}}}{K_2}\right) + 2\tilde{n}_{\mathrm{O}}\left(1 + \frac{\tilde{n}_{\mathrm{O}}}{K_2}\right)\right],\\
F_3 &= \frac{4K}{K_2}\left(1 - \frac{2\tilde{n}_{\mathrm{O}}}{K_2}\right) - \frac{12K_3D_3}{K_2}\\
&\quad + K^2\left[\frac{2(2\tilde{n}_{\mathrm{C}} + \tilde{n}_{\mathrm{O}})}{K_2} - 1\right],\\
F_4 &= \frac{K}{K_2}\left(\frac{4}{K_2} - K\right) - \frac{24K_3D_3}{K_2^2},\\
F_5 &= -\frac{16K_3D_3}{K_2^3}.
\end{aligned}$$

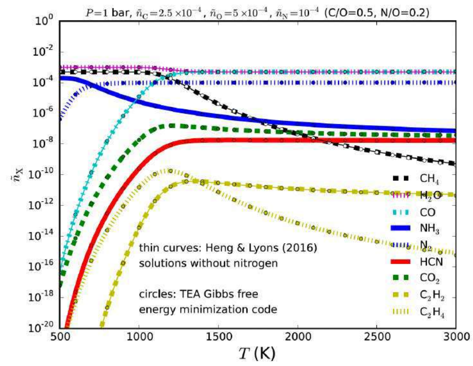
where the coefficients are $J_0 = F_0^2$, $J_1 = 2F_0F_1$, $J_2 = F_1^2 + 2F_0F_2$, $J_3 = 2F_0F_3 + 2F_1F_2$, $J_4 = 2F_0F_4 + 2F_1F_3 + F_2^2$, $J_5 = 2F_0F_5 + 2F_1F_4 + 2F_2F_3$, $J_6 = 2F_1F_5 + 2F_2F_4 + F_3^2$, $J_7 = 2F_2F_5 + 2F_3F_4$, $J_8 = 2F_3F_5 + F_4^2$, $J_9 = 2F_4F_5$, and $J_{10} = F_5^2$.

$$\begin{aligned}
A_0 &= 2K_5J_0,\\
A_1 &= 2K_5J_1 + 2KK_6\tilde{n}_{\mathrm{O}}F_0,\\
A_2 &= 2K_5J_2 + KK_6[2\tilde{n}_{\mathrm{O}}F_1 + F_0(8C_2\tilde{n}_{\mathrm{O}} - 1)]\\
&\quad + K_6^2F_0 - 8K^2K_6^2\tilde{n}_{\mathrm{O}}^2\tilde{n}_{\mathrm{N}},\\
A_3 &= 2K_5J_3 + KK_6[2\tilde{n}_{\mathrm{O}}F_2 + F_1(8C_2\tilde{n}_{\mathrm{O}} - 1)\\
&\quad + 4F_0C_2(2C_2\tilde{n}_{\mathrm{O}} - 1)] + K_6^2(F_1 + 6F_0C_2)\\
&\quad + 8K^2K_6^2\tilde{n}_{\mathrm{O}}\tilde{n}_{\mathrm{N}}(1 - 8C_2\tilde{n}_{\mathrm{O}}),\\
A_4 &= 2K_5J_4 + KK_6[2\tilde{n}_{\mathrm{O}}F_3 + F_2(8C_2\tilde{n}_{\mathrm{O}} - 1)\\
&\quad + 4F_1C_2(2C_2\tilde{n}_{\mathrm{O}} - 1) - 4F_0C_2^2]\\
&\quad + K_6^2(F_2 + 6F_1C_2 + 12F_0C_2^2)\\
&\quad - 2K^2K_6^2\tilde{n}_{\mathrm{N}}(1 - 32C_2\tilde{n}_{\mathrm{O}} + 96C_2^2\tilde{n}_{\mathrm{O}}^2),\\
A_5 &= 2K_5J_5 + KK_6[2\tilde{n}_{\mathrm{O}}F_4 + F_3(8C_2\tilde{n}_{\mathrm{O}} - 1)\\
&\quad + 4F_2C_2(2C_2\tilde{n}_{\mathrm{O}} - 1) - 4F_1C_2^2]\\
&\quad + K_6^2(F_3 + 6F_2C_2 + 12F_1C_2^2 + 8F_0C_2^3)\\
&\quad - 16K^2K_6^2\tilde{n}_{\mathrm{N}}C_2(1 - 12C_2\tilde{n}_{\mathrm{O}} + 16C_2^2\tilde{n}_{\mathrm{O}}^2),\\
A_6 &= 2K_5J_6 + KK_6[2\tilde{n}_{\mathrm{O}}F_5 + F_4(8C_2\tilde{n}_{\mathrm{O}} - 1)\\
&\quad + 4F_3C_2(2C_2\tilde{n}_{\mathrm{O}} - 1) - 4F_2C_2^2]\\
&\quad + K_6^2(F_4 + 6F_3C_2 + 12F_2C_2^2 + 8F_1C_2^3)\\
&\quad - 16K^2K_6^2\tilde{n}_{\mathrm{N}}C_2^2(3 - 16C_2\tilde{n}_{\mathrm{O}} + 8C_2^2\tilde{n}_{\mathrm{O}}^2),\\
A_7 &= 2K_5J_7 + KK_6[F_5(8C_2\tilde{n}_{\mathrm{O}} - 1)\\
&\quad + 4F_4C_2(2C_2\tilde{n}_{\mathrm{O}} - 1) - 4F_3C_2^2]\\
&\quad + K_6^2F_5 + 2K_6^2C_2(3F_4 + 6F_3C_2 + 4F_2C_2^2)\\
&\quad - 64K^2K_6^2\tilde{n}_{\mathrm{N}}C_2^3(1 - 2C_2\tilde{n}_{\mathrm{O}}),\\
A_8 &= 2K_5J_8 + 4KK_6C_2[F_5(2C_2\tilde{n}_{\mathrm{O}} - 1) - F_4C_2]\\
&\quad + 2K_6^2C_2(3F_5 + 6F_4C_2 + 4F_3C_2^2) - 32K^2K_6^2\tilde{n}_{\mathrm{N}}C_2^4,\\
A_9 &= 2K_5J_9 - 4KK_6F_5C_2^2 + 4K_6^2C_2^2(3F_5 + 2F_4C_2),\\
A_{10} &= 2K_5J_{10} + 8K_6^2F_5C_2^3.
\end{aligned}$$

Surprisingly, this was a novel mathematical solution!

Heng & Tsai (2016, ApJ, 829, 104)

So does this fancy algebra produce accurate solutions?



When compared to full numerical solutions involving a Gibbs free energy minimisation computer code, the differences are smaller than the widths of the curves (at least, on a logarithmic plot).

Heng & Tsai (2016, ApJ, 829, 104)