Analytical Formalism to Produce Abundances in Atmospheres of Giant Exoplanets Under Chemical Equilibrium

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In this work, we follow the analytical formalism described in Heng et al. (2016). We simulated the abundance of molecules in a hot atmosphere dominated by hydrogen. To do this we consider a total of five reactions, three reactions treated by Heng et al. (2016) that relate methane (CH_4), water (H_2O), carbon monoxide (CO), dihydrogen (H_2), carbon dioxide (CO_2) and acetylene (C_2H_2), which corresponds to reactions (I)-(III).

Reaction I

$$\mathrm{CH_4 + H_2O \longleftrightarrow CO + 3\,H_2}$$

Dimentional constant equilibrium ($K'_{eq,1}$):

$$K'_{eq,1} = \frac{n_{\mathrm{CO}}\; n^3_{\mathrm{H_2}}}{n_{\mathrm{CH_4}}\; n_{\mathrm{H_2O}}}$$

Normalization using hydrogen abundance, where $\tilde{n}_x = n_x / n_{\mathrm{H_2}}$.

$$K'_{eq,1} = \frac{n_{\mathrm{CO}}\; n^3_{\mathrm{H_2}}}{n_{\mathrm{CH_4}}\; n_{\mathrm{H_2O}}} \cdot \left(\frac{1/n^2_{\mathrm{H_2}}}{1/n^2_{\mathrm{H_2}}}\right)$$

$$\Rightarrow K'_{eq,1} = \frac{\tilde{n}_{\mathrm{CO}}\; n^2_{\mathrm{H_2}}}{\tilde{n}_{\mathrm{CH_4}}\; \tilde{n}_{\mathrm{H_2O}}}$$

Normalized (K'_1)

Normalization multiplying by $\left(\frac{1}{1/n^2_{\mathrm{H_2}}}\right)$

$$K'_1 \equiv \frac{K'_{eq,1}}{n^2_{\mathrm{H_2}}}$$

$$\Rightarrow K'_1 = \frac{\tilde{n}_{\mathrm{CO}}}{\tilde{n}_{\mathrm{CH_4}}\; \tilde{n}_{\mathrm{H_2O}}} \tag{1}$$

Reaction II

$$\mathrm{CO_2 + H_2 \longleftrightarrow CO + H_2O}$$

Dimensional constant equilibrium $(K'_{eq,2})$

$$K'_{eq,2} = \frac{n_{\mathrm{CO}}\ n_{\mathrm{H_2O}}}{n_{\mathrm{CO_2}}\ n_{\mathrm{H_2}}}$$

$$K'_{eq,2} = \frac{n_{\mathrm{CO}}\ n_{\mathrm{H_2O}}}{n_{\mathrm{CO_2}}\ n_{\mathrm{H_2}}} \cdot \left(\frac{1/n^2_{\mathrm{H_2}}}{1/n^2_{\mathrm{H_2}}}\right)$$

$$\Rightarrow K'_{eq,2} = \frac{\tilde{n}_{\mathrm{CO}}\ \tilde{n}_{\mathrm{H_2O}}}{\tilde{n}_{\mathrm{CO_2}}}$$

Normalized (K'_2)

We don't need to normalize, hence $K'_2 \equiv K'_{eq,2}$

$$\Rightarrow K'_2 = \frac{\tilde{n}_{\mathrm{CO}}\ \tilde{n}_{\mathrm{H_2O}}}{\tilde{n}_{\mathrm{CO_2}}} \tag{2}$$

Reaction III

$$2\,\mathrm{CH_4} \longleftrightarrow \mathrm{C_2H_2} + 3\,\mathrm{H_2}$$

Dimensional constant equilibrium $(K'_{eq,3})$

$$K'_{eq,3} = \frac{n_{\mathrm{C_2H_2}}\ n^3_{\mathrm{H_2}}}{n^2_{\mathrm{CH_4}}}$$

$$K'_{eq,3} = \frac{n_{\mathrm{C_2H_2}}\ n^3_{\mathrm{H_2}}}{n^2_{\mathrm{CH_4}}} \cdot \left(\frac{1/n^2_{\mathrm{H_2}}}{1/n^2_{\mathrm{H_2}}}\right)$$

$$K'_{eq,3} = \frac{\tilde{n}_{\mathrm{C_2H_2}}\ n^2_{\mathrm{H_2}}}{\tilde{n}^2_{\mathrm{CH_4}}}$$

Normalized (K'_3)

Normalization multiplying by $\left(\frac{1}{1/n^2_{\mathrm{H_2}}}\right)$

$$K'_3 \equiv \frac{K'_{eq,3}}{n^2_{\mathrm{H_2}}}$$

$$\Rightarrow K'_3 = \frac{\tilde{n}_{\mathrm{C_2H_2}}}{\tilde{n}^2_{\mathrm{CH_4}}} \tag{3}$$

Stoichiometric book-keeping (counting the number of atoms of each species) yields

$$n_{\mathrm{C}} = n_{\mathrm{CH_4}} + n_{\mathrm{CO_2}} + n_{\mathrm{CO}} + 2n_{\mathrm{C_2H_2}} \tag{4}$$

$$n_{\mathrm{H}} = 4n_{\mathrm{CH_4}} + 2n_{\mathrm{H_2O}} + 2n_{\mathrm{H_2}} + 2n_{\mathrm{C_2H_2}} \tag{5}$$

$$n_{\mathrm{O}} = n_{\mathrm{H_2O}} + n_{\mathrm{CO}} + 2n_{\mathrm{CO_2}} \tag{6}$$

Then, we divide by $n_{\mathrm{H_2}}$

$$\frac{n_{\mathrm{C}}}{n_{H_2}} = \tilde{n}_{\mathrm{CH_4}} + \tilde{n}_{\mathrm{CO_2}} + \tilde{n}_{\mathrm{CO}} + 2\tilde{n}_{\mathrm{C_2H_2}} \tag{7}$$

$$\frac{n_{\mathrm{H}}}{n_{H_2}} = 4\tilde{n}_{\mathrm{CH_4}} + 2\tilde{n}_{\mathrm{H_2O}} + 2 + 2\tilde{n}_{\mathrm{C_2H_2}} \tag{8}$$

$$\frac{n_{\mathrm{O}}}{n_{H_2}} = \tilde{n}_{\mathrm{H_2O}} + \tilde{n}_{\mathrm{CO}} + 2\tilde{n}_{\mathrm{CO_2}} \tag{9}$$

Now, from equation (8) we obtain

$$\frac{1}{n_{H_2}} = \frac{1}{n_{\mathrm{H}}}[4\tilde{n}_{\mathrm{CH_4}} + 2\tilde{n}_{\mathrm{H_2O}} + 2 + 2\tilde{n}_{\mathrm{C_2H_2}}] \tag{10}$$

Which we use in equations (7) and (9)

$$\frac{n_{\mathrm{C}}}{n_H}[4\tilde{n}_{\mathrm{CH_4}} + 2\tilde{n}_{\mathrm{H_2O}} + 2 + 2\tilde{n}_{\mathrm{C_2H_2}}] = \tilde{n}_{\mathrm{CH_4}} + \tilde{n}_{\mathrm{CO_2}} + \tilde{n}_{\mathrm{CO}} + 2\tilde{n}_{\mathrm{C_2H_2}} \tag{11}$$

$$\frac{n_{\mathrm{O}}}{n_H}[4\tilde{n}_{\mathrm{CH_4}} + 2\tilde{n}_{\mathrm{H_2O}} + 2 + 2\tilde{n}_{\mathrm{C_2H_2}}] = \tilde{n}_{\mathrm{H_2O}} + \tilde{n}_{\mathrm{CO}} + 2\tilde{n}_{\mathrm{CO_2}} \tag{12}$$

By definition $\tilde{n}_{\mathrm{C}} = n_{\mathrm{C}}/n_{\mathrm{H}}$ and $\tilde{n}_{\mathrm{O}} = n_{\mathrm{O}}/n_{\mathrm{H}}$ so we obtain

$$\tilde{n}_{\mathrm{C}}[4\tilde{n}_{\mathrm{CH_4}} + 2\tilde{n}_{\mathrm{H_2O}} + 2 + 2\tilde{n}_{\mathrm{C_2H_2}}] = \tilde{n}_{\mathrm{CH_4}} + \tilde{n}_{\mathrm{CO_2}} + \tilde{n}_{\mathrm{CO}} + 2\tilde{n}_{\mathrm{C_2H_2}} \tag{13}$$

$$\tilde{n}_{\mathrm{O}}[4\tilde{n}_{\mathrm{CH_4}} + 2\tilde{n}_{\mathrm{H_2O}} + 2 + 2\tilde{n}_{\mathrm{C_2H_2}}] = \tilde{n}_{\mathrm{H_2O}} + \tilde{n}_{\mathrm{CO}} + 2\tilde{n}_{\mathrm{CO_2}} \tag{14}$$

From equation (10) we know also

$$\frac{\tilde{n}_{\mathrm{H}}}{\tilde{n}_{H_2}} = 4\tilde{n}_{\mathrm{CH_4}} + 2\tilde{n}_{\mathrm{H_2O}} + 2 + 2\tilde{n}_{\mathrm{C_2H_2}} \tag{15}$$

Now we can solve for the abundances of the five molecules using the equations 1, 2, 3, 13 and 14.

Using (1) and (2)

$$\frac{K_1'}{K_2'} = \frac{\tilde{n}_{CO}\ \tilde{n}_{CO_2}}{\tilde{n}_{CO}\ \tilde{n}_{CH_4}\ \tilde{n}^2_{H_2O}}$$

$$\Rightarrow \frac{K_1'}{K_2'} = \frac{\tilde{n}_{CO_2}}{\tilde{n}_{CH_4}\ \tilde{n}^2_{H_2O}} \tag{16}$$

Then

$$\tilde{n}_{CO_2} = \frac{K_1'\ \tilde{n}_{CH_4}\ \tilde{n}^2_{H_2O}}{K_2'} \tag{17}$$

We replace $\tilde{n}_{CO_2}$ on (13) and obtain

$$\tilde{n}_C[4\tilde{n}_{CH_4} + 2\tilde{n}_{H_2O} + 2 + 2\tilde{n}_{C_2H_2}] = \tilde{n}_{CH_4} + \left(\frac{K_1'\ \tilde{n}_{CH_4}\ \tilde{n}^2_{H_2O}}{K_2'}\right) + \tilde{n}_{CO} + 2\tilde{n}_{C_2H_2} \tag{18}$$

From (1) we know that

$$\tilde{n}_{CO} = K_1'\ \tilde{n}_{CH_4}\ \tilde{n}_{H_2O} \tag{19}$$

From (3) we know that

$$\tilde{n}_{C_2H_2} = K_3'\ \tilde{n}^2_{CH_4} \tag{20}$$

We replace (19) and (20) on (18), obtaining an equation in function of $\tilde{n}_{CH_4}$ and $\tilde{n}_{H_2O}$:

$$\tilde{n}_C\left[4\tilde{n}_{CH_4} + 2\tilde{n}_{H_2O} + 2 + 2\left(K_3'\ \tilde{n}^2_{CH_4}\right)\right] = \tilde{n}_{CH_4} + \left(\frac{K_1'\ \tilde{n}_{CH_4}\ \tilde{n}^2_{H_2O}}{K_2'}\right) + \left(K_1'\ \tilde{n}_{CH_4}\ \tilde{n}_{H_2O}\right) + 2\left(K_3'\ \tilde{n}^2_{CH_4}\right) \tag{21}$$

We replace (17), (19) and (20) on (14), obtaining an equation in function of $\tilde{n}_{CH_4}$ and $\tilde{n}_{H_2O}$:

$$\tilde{n}_O\left[4\tilde{n}_{CH_4} + 2\tilde{n}_{H_2O} + 2 + 2\left(K_3'\ \tilde{n}^2_{CH_4}\right)\right] = \tilde{n}_{H_2O} + \left(K_1'\ \tilde{n}_{CH_4}\ \tilde{n}_{H_2O}\right) + 2\left(\frac{K_1'\ \tilde{n}_{CH_4}\ \tilde{n}^2_{H_2O}}{K_2'}\right) \tag{22}$$

With which we can obtain an equation in function of $\tilde{n}_{CH_4}$ and $\tilde{n}_{H_2O}$:

$$\frac{K_1'\ \tilde{n}_{CH_4}\ \tilde{n}^2_{H_2O}}{K_2'} + 2K_3'\ \tilde{n}^2_{CH_4}\ (1 - \tilde{n}_C) - 2\tilde{n}_C\tilde{n}_{H_2O} + \tilde{n}_{CH_4} + K_1'\ \tilde{n}_{CH_4}\ \tilde{n}_{H_2O} - 4\tilde{n}_C\tilde{n}_{CH_4} - 2\tilde{n}_C = 0 \tag{23}$$

$$2\frac{K_1'\ \tilde{n}_{CH_4}\ \tilde{n}^2_{H_2O}}{K_2'} - 2K_3'\tilde{n}_O\ \tilde{n}^2_{CH_4} + \tilde{n}_{H_2O}(1 - 2\tilde{n}_O) + K_1'\ \tilde{n}_{CH_4}\ \tilde{n}_{H_2O} - 4\tilde{n}_O\tilde{n}_{CH_4} - 2\tilde{n}_O = 0 \tag{24}$$

Obtaining two coupled quadratic equations (equations 23 and 24).

In a similar way that Heng et al. did, we use an algebraic trick if we recast the equations (23) and (24) in terms of $\tilde{n}_{CO}$, rather than $\tilde{n}_{H_2O}$. We do this using the equation (1) and we obtain:

$$\tilde{n}_{H_2O} = \frac{\tilde{n}_{CO}}{\tilde{n}_{CH_4}\ K_1'} \tag{25}$$

Then, we used on (23) and (24):

$$\frac{\tilde{n}_{\mathrm{CO}}^2}{K_1' K_2' \tilde{n}_{\mathrm{CH}_4}} + 2K_3'\, \tilde{n}_{\mathrm{CH}_4}^2\, (1-\tilde{n}_{\mathrm{C}}) - 2\frac{\tilde{n}_{\mathrm{C}}\tilde{n}_{\mathrm{CO}}}{K_1'\tilde{n}_{\mathrm{CH}_4}} + \tilde{n}_{\mathrm{CH}_4} + \tilde{n}_{\mathrm{CO}} - 4\tilde{n}_{\mathrm{C}}\tilde{n}_{\mathrm{CH}_4} - 2\tilde{n}_{\mathrm{C}} = 0 \tag{26}$$

$$2\frac{\tilde{n}_{\mathrm{CO}}^2}{K_1'\, K_2'\, \tilde{n}_{\mathrm{CH}_4}} - 2K_3'\tilde{n}_{\mathrm{O}}\, \tilde{n}_{\mathrm{CH}_4}^2 + \frac{\tilde{n}_{\mathrm{CO}}}{\tilde{n}_{\mathrm{CH}_4}\, K_1'}(1-2\tilde{n}_{\mathrm{O}}) + \tilde{n}_{\mathrm{CO}} - 4\tilde{n}_{\mathrm{O}}\tilde{n}_{\mathrm{CH}_4} - 2\tilde{n}_{\mathrm{O}} = 0 \tag{27}$$

We multiply by $\tilde{n}_{\mathrm{CH}_4}$ and match the equations (26) and (27) to have no coupled terms and to be able to clear the equation and obtain $\tilde{n}_{\mathrm{CO}}$:

$$\begin{aligned}&\frac{\tilde{n}_{\mathrm{CO}}^2}{K_1'\, K_2'\, \tilde{n}_{\mathrm{CH}_4}} + \frac{\tilde{n}_{\mathrm{CO}}}{\tilde{n}_{\mathrm{CH}_4}\, K_1'}(1+2\tilde{n}_{\mathrm{C}}-2\tilde{n}_{\mathrm{O}}) - 2K_3'\, \tilde{n}_{\mathrm{CH}_4}^2(1-\tilde{n}_{\mathrm{C}}+\tilde{n}_{\mathrm{O}})\\ &- \tilde{n}_{\mathrm{CH}_4} - 4\tilde{n}_{\mathrm{O}}\tilde{n}_{\mathrm{CH}_4} - 2\tilde{n}_{\mathrm{O}} + 4\tilde{n}_{\mathrm{C}}\tilde{n}_{\mathrm{CH}_4} + 2\tilde{n}_{\mathrm{C}} = 0\end{aligned} \tag{28}$$

$$\frac{\tilde{n}_{\mathrm{CO}}^2}{K_1'\, K_2'} + \frac{\tilde{n}_{\mathrm{CO}}}{K_1'}(1+2\tilde{n}_{\mathrm{C}}-2\tilde{n}_{\mathrm{O}}) - 2K_3'\tilde{n}_{\mathrm{CH}_4}^3(1-\tilde{n}_{\mathrm{C}}+\tilde{n}_{\mathrm{O}}) - \tilde{n}_{\mathrm{CH}_4}^2 - 2\tilde{n}_{\mathrm{CH}_4}(2\tilde{n}_{\mathrm{O}}\tilde{n}_{\mathrm{CH}_4} + \tilde{n}_{\mathrm{O}} - 2\tilde{n}_{\mathrm{C}}\tilde{n}_{\mathrm{CH}_4} - \tilde{n}_{\mathrm{C}}) = 0 \tag{29}$$

$$\frac{\tilde{n}_{\mathrm{CO}}^2}{K_1'\, K_2'} + \frac{\tilde{n}_{\mathrm{CO}}}{K_1'}(1+2\tilde{n}_{\mathrm{C}}-2\tilde{n}_{\mathrm{O}}) - 2K_3'\tilde{n}_{\mathrm{CH}_4}^3(1-\tilde{n}_{\mathrm{C}}+\tilde{n}_{\mathrm{O}}) - \tilde{n}_{\mathrm{CH}_4}^2 - 2\tilde{n}_{\mathrm{CH}_4}(\tilde{n}_{\mathrm{O}}-\tilde{n}_{\mathrm{C}})(2\tilde{n}_{\mathrm{CH}_4}+1) = 0 \tag{30}$$

Heng et al.: “Notice how the mixing ratios of carbon monoxide and methane are no longer coupled to each other within the same equation—there are no “mixed” terms, unlike for each equation in (17) [this is eq. (26) and (27) in this document] between water and methane. This property has the virtue that we may cleanly take the approximation $\tilde{n}_{\mathrm{C}}, \tilde{n}_{\mathrm{O}} << 1$ and end up with a relatively simple expression for the mixing ratio of carbon monoxide,”

Using the quadratic formula:

$$\begin{aligned}\tilde{n}_{\mathrm{CO}} = &-\frac{\frac{1}{K_1'}(1+2\tilde{n}_{\mathrm{C}}-2\tilde{n}_{\mathrm{O}})}{\frac{2}{K_1'\, K_2'}}\\ &\pm \frac{\sqrt{\left(\frac{1}{K_1'}(1+2\tilde{n}_{\mathrm{C}}-2\tilde{n}_{\mathrm{O}})\right)^2 + 4\frac{1}{K_1'\, K_2'}[2K_3'\tilde{n}_{\mathrm{CH}_4}^3(1-\tilde{n}_{\mathrm{C}}+\tilde{n}_{\mathrm{O}}) + \tilde{n}_{\mathrm{CH}_4}^2 + 2\tilde{n}_{\mathrm{CH}_4}(\tilde{n}_{\mathrm{O}}-\tilde{n}_{\mathrm{C}})(2\tilde{n}_{\mathrm{CH}_4}+1)]}}{\frac{2}{K_1'\, K_2'}}\end{aligned} \tag{31}$$

$$\begin{aligned}\tilde{n}_{\mathrm{CO}} = &-\frac{K_2'}{2}(1+2\tilde{n}_{\mathrm{C}}-2\tilde{n}_{\mathrm{O}})\\ &\pm K_1'K_2'\sqrt{\frac{1}{4{K_1'}^2}(1+2\tilde{n}_{\mathrm{C}}-2\tilde{n}_{\mathrm{O}})^2 + \frac{1}{K_1'\, K_2'}[2K_3'\tilde{n}_{\mathrm{CH}_4}^3(1-\tilde{n}_{\mathrm{C}}+\tilde{n}_{\mathrm{O}}) + \tilde{n}_{\mathrm{CH}_4}^2 + 2\tilde{n}_{\mathrm{CH}_4}(\tilde{n}_{\mathrm{O}}-\tilde{n}_{\mathrm{C}})(2\tilde{n}_{\mathrm{CH}_4}+1)]}\end{aligned} \tag{32}$$

$$\begin{aligned}\tilde{n}_{\mathrm{CO}} = &-\frac{K_2'}{2}(1+2\tilde{n}_{\mathrm{C}}-2\tilde{n}_{\mathrm{O}})\\ &\pm \sqrt{\frac{{K_2'}^2}{4}(1+2\tilde{n}_{\mathrm{C}}-2\tilde{n}_{\mathrm{O}})^2 + K_1'\, K_2'[2K_3'\tilde{n}_{\mathrm{CH}_4}^3(1-\tilde{n}_{\mathrm{C}}+\tilde{n}_{\mathrm{O}}) + \tilde{n}_{\mathrm{CH}_4}^2 + 2\tilde{n}_{\mathrm{CH}_4}(\tilde{n}_{\mathrm{O}}-\tilde{n}_{\mathrm{C}})(2\tilde{n}_{\mathrm{CH}_4}+1)]}\end{aligned} \tag{33}$$

If $\tilde{n}_{\mathrm{C}}, \tilde{n}_{\mathrm{O}} \ll 1$ and considering that we assumed H_2-dominated atmospheres, which implies that the mixing ratios must be small, then $\tilde{n}_{\mathrm{CH}_4} \ll 1$, and we obtain:

$$\tilde{n}_{\mathrm{CO}} \approx -\frac{K'_2}{2} \pm \sqrt{\frac{{K'_2}^2}{4} + K'_1\ K'_2[2K'_3\tilde{n}^3_{\mathrm{CH_4}} + \tilde{n}^2_{\mathrm{CH_4}} + 2\tilde{n}_{\mathrm{CH_4}}(\tilde{n}_{\mathrm{O}} - \tilde{n}_{\mathrm{C}})]} \tag{34}$$

$$\tilde{n}_{\mathrm{CO}} \approx -\frac{K'_2}{2} \pm \sqrt{\frac{{K'_2}^2}{4}\left\{1 + 4\frac{K'_1}{K'_2}\tilde{n}_{\mathrm{CH_4}}[2K'_3\tilde{n}^2_{\mathrm{CH_4}} + \tilde{n}_{\mathrm{CH_4}} + 2(\tilde{n}_{\mathrm{O}} - \tilde{n}_{\mathrm{C}})]\right\}} \tag{35}$$

$$\tilde{n}_{\mathrm{CO}} \approx -\frac{K'_2}{2} \pm \frac{K'_2}{2}\sqrt{1 + 4\frac{K'_1}{K'_2}\tilde{n}_{\mathrm{CH_4}}[2K'_3\tilde{n}^2_{\mathrm{CH_4}} + \tilde{n}_{\mathrm{CH_4}} + 2(\tilde{n}_{\mathrm{O}} - \tilde{n}_{\mathrm{C}})]} \tag{36}$$

We named α:

$$\alpha = 4\frac{K'_1}{K'_2}\tilde{n}_{\mathrm{CH_4}}[2K'_3\tilde{n}^2_{\mathrm{CH_4}} + \tilde{n}_{\mathrm{CH_4}} + 2(\tilde{n}_{\mathrm{O}} - \tilde{n}_{\mathrm{C}})] \tag{37}$$

Then, assuming that $\alpha \ll 1$, we use Taylor and obtain:

$$\tilde{n}_{\mathrm{CO}} \approx -\frac{K'_2}{2} \pm \frac{K'_2}{2}\left\{1 + \frac{\alpha}{2}\right\} \tag{38}$$

$$\tilde{n}_{\mathrm{CO}} \approx -\frac{K'_2}{2} \pm \frac{K'_2}{2}\left\{1 + 2\frac{K'_1}{K'_2}\tilde{n}_{\mathrm{CH_4}}[2K'_3\tilde{n}^2_{\mathrm{CH_4}} + \tilde{n}_{\mathrm{CH_4}} + 2(\tilde{n}_{\mathrm{O}} - \tilde{n}_{\mathrm{C}})]\right\} \tag{39}$$

Then, we just consider the positive root, because abundances can't be negative:

$$\tilde{n}_{\mathrm{CO}} \approx K'_1\ \tilde{n}_{\mathrm{CH_4}}[2K'_3\tilde{n}^2_{\mathrm{CH_4}} + \tilde{n}_{\mathrm{CH_4}} + 2(\tilde{n}_{\mathrm{O}} - \tilde{n}_{\mathrm{C}})] \tag{40}$$

Which is similar to the one obtained by Heng et al.

Then, we relate this equation with eq. (19)

$$K'_1\ \tilde{n}_{\mathrm{CH_4}}\ \tilde{n}_{\mathrm{H_2O}} \approx K'_1\ \tilde{n}_{\mathrm{CH_4}}[2K'_3\tilde{n}^2_{\mathrm{CH_4}} + \tilde{n}_{\mathrm{CH_4}} + 2(\tilde{n}_{\mathrm{O}} - \tilde{n}_{\mathrm{C}})] \tag{41}$$

Obtaining the abundance of water in function on methane,

$$\tilde{n}_{\mathrm{H_2O}} \approx 2K'_3\tilde{n}^2_{\mathrm{CH_4}} + \tilde{n}_{\mathrm{CH_4}} + 2(\tilde{n}_{\mathrm{O}} - \tilde{n}_{\mathrm{C}}) \tag{42}$$

With which we can obtain the abundance of carbon dioxide in function on methane,

$$\tilde{n}_{\mathrm{CO_2}} \approx \frac{K'_1\ \tilde{n}_{\mathrm{CH_4}}\ [2K'_3\tilde{n}^2_{\mathrm{CH_4}} + \tilde{n}_{\mathrm{CH_4}} + 2(\tilde{n}_{\mathrm{O}} - \tilde{n}_{\mathrm{C}})]^2}{K'_2} \tag{43}$$

Using (40) in (30) and using again the fact that $\tilde{n}_{\mathrm{CH_4}} \ll 1$, noticing that

$$\begin{aligned}[2\ K'_3\tilde{n}^2_{\mathrm{CH_4}} + \tilde{n}_{\mathrm{CH_4}} + 2(\tilde{n}_{\mathrm{O}} - \tilde{n}_{\mathrm{C}})]^2 = {} & 4\ {K'_3}^2\ \tilde{n}^4_{\mathrm{CH_4}} + \tilde{n}^2_{\mathrm{CH_4}} + 4(\tilde{n}_{\mathrm{O}} - \tilde{n}_{\mathrm{C}})^2 + 4\ K'_3\tilde{n}^3_{\mathrm{CH_4}} \\ & + 8\ K'_3\tilde{n}^2_{\mathrm{CH_4}}(\tilde{n}_{\mathrm{O}} - \tilde{n}_{\mathrm{C}}) + 4\tilde{n}_{\mathrm{CH_4}}(\tilde{n}_{\mathrm{O}} - \tilde{n}_{\mathrm{C}})\end{aligned} \tag{44}$$

hence,

$$\begin{aligned}&\frac{{K'_1}^2\ \tilde{n}^2_{\mathrm{CH_4}}\ [4\ {K'_3}^2\ \tilde{n}^4_{\mathrm{CH_4}} + \tilde{n}^2_{\mathrm{CH_4}} + 4(\tilde{n}_{\mathrm{O}} - \tilde{n}_{\mathrm{C}})^2 + 4\ K'_3\tilde{n}^3_{\mathrm{CH_4}} + 8\ K'_3\tilde{n}^2_{\mathrm{CH_4}}(\tilde{n}_{\mathrm{O}} - \tilde{n}_{\mathrm{C}}) + 4\tilde{n}_{\mathrm{CH_4}}(\tilde{n}_{\mathrm{O}} - \tilde{n}_{\mathrm{C}})]}{K'_1\ K'_2} \\ &+ \frac{K'_1\tilde{n}_{\mathrm{CH_4}}[2K'_3\tilde{n}^2_{\mathrm{CH_4}} + \tilde{n}_{\mathrm{CH_4}} + 2(\tilde{n}_{\mathrm{O}} - \tilde{n}_{\mathrm{C}})]}{K'_1} - 2K'_3\tilde{n}^3_{\mathrm{CH_4}} - \tilde{n}^2_{\mathrm{CH_4}} - 2\tilde{n}_{\mathrm{CH_4}}(\tilde{n}_{\mathrm{O}} - \tilde{n}_{\mathrm{C}}) = 0\end{aligned} \tag{45}$$

Then we divide by $\tilde{n}_{\mathrm{CH_4}}$

$$\frac{K_1'\ \tilde{n}_{\mathrm{CH_4}}\ [4\ {K_3'}^2\ \tilde{n}_{\mathrm{CH_4}}^4 + \tilde{n}_{\mathrm{CH_4}}^2 + 4(\tilde{n}_{\mathrm{O}} - \tilde{n}_{\mathrm{C}})^2 + 4\ K_3'\tilde{n}_{\mathrm{CH_4}}^3 + 8\ K_3'\tilde{n}_{\mathrm{CH_4}}^2(\tilde{n}_{\mathrm{O}} - \tilde{n}_{\mathrm{C}}) + 4\tilde{n}_{\mathrm{CH_4}}(\tilde{n}_{\mathrm{O}} - \tilde{n}_{\mathrm{C}})]}{K_2'} \\ + [2K_3'\tilde{n}_{\mathrm{CH_4}}^2 + \tilde{n}_{\mathrm{CH_4}} + 2(\tilde{n}_{\mathrm{O}} - \tilde{n}_{\mathrm{C}})] - 2K_3'\tilde{n}_{\mathrm{CH_4}}^2 - \tilde{n}_{\mathrm{CH_4}} - 2(\tilde{n}_{\mathrm{O}} - \tilde{n}_{\mathrm{C}}) = 0 \tag{46}$$

$$\frac{4K_1'\ {K_3'}^2\ \tilde{n}_{\mathrm{CH_4}}^5 + K_1'\tilde{n}_{\mathrm{CH_4}}^3 + 4K_1'\tilde{n}_{\mathrm{CH_4}}(\tilde{n}_{\mathrm{O}} - \tilde{n}_{\mathrm{C}})^2 + 4K_1'\ K_3'\tilde{n}_{\mathrm{CH_4}}^4 + 8K_1'\ K_3'\tilde{n}_{\mathrm{CH_4}}^3(\tilde{n}_{\mathrm{O}} - \tilde{n}_{\mathrm{C}}) + 4K_1'\ \tilde{n}_{\mathrm{CH_4}}^2(\tilde{n}_{\mathrm{O}} - \tilde{n}_{\mathrm{C}})}{K_2'} \\ + [2K_3'\tilde{n}_{\mathrm{CH_4}}^2 + \tilde{n}_{\mathrm{CH_4}} + 2(\tilde{n}_{\mathrm{O}} - \tilde{n}_{\mathrm{C}})] - 2K_3'\tilde{n}_{\mathrm{CH_4}}^2 - \tilde{n}_{\mathrm{CH_4}} - 2(\tilde{n}_{\mathrm{O}} - \tilde{n}_{\mathrm{C}}) = 0 \tag{47}$$

$$\frac{4K_1'\ {K_3'}^2}{K_2'}\ \tilde{n}_{\mathrm{CH_4}}^5 + \frac{K_1'}{K_2'}\tilde{n}_{\mathrm{CH_4}}^3 + \frac{4K_1'(\tilde{n}_{\mathrm{O}} - \tilde{n}_{\mathrm{C}})^2}{K_2'}\tilde{n}_{\mathrm{CH_4}} + \frac{4K_1'\ K_3'}{K_2'}\tilde{n}_{\mathrm{CH_4}}^4 + \frac{8K_1'\ K_3'(\tilde{n}_{\mathrm{O}} - \tilde{n}_{\mathrm{C}})}{K_2'}\tilde{n}_{\mathrm{CH_4}}^3 \\ + \frac{4K_1'(\tilde{n}_{\mathrm{O}} - \tilde{n}_{\mathrm{C}})}{K_2'}\tilde{n}_{\mathrm{CH_4}}^2 + 2K_3'\tilde{n}_{\mathrm{CH_4}}^2 + \tilde{n}_{\mathrm{CH_4}} + 2(\tilde{n}_{\mathrm{O}} - \tilde{n}_{\mathrm{C}}) - 2K_3'\tilde{n}_{\mathrm{CH_4}}^2 - \tilde{n}_{\mathrm{CH_4}} - 2(\tilde{n}_{\mathrm{O}} - \tilde{n}_{\mathrm{C}}) = 0 \tag{48}$$

$$\frac{4K_1'\ {K_3'}^2}{K_2'}\ \tilde{n}_{\mathrm{CH_4}}^5 + \frac{4K_1'\ K_3'}{K_2'}\tilde{n}_{\mathrm{CH_4}}^4 + \frac{K_1'}{K_2'}\tilde{n}_{\mathrm{CH_4}}^3 + \frac{8K_1'\ K_3'(\tilde{n}_{\mathrm{O}} - \tilde{n}_{\mathrm{C}})}{K_2'}\tilde{n}_{\mathrm{CH_4}}^3 \\ + \frac{4K_1'(\tilde{n}_{\mathrm{O}} - \tilde{n}_{\mathrm{C}})}{K_2'}\tilde{n}_{\mathrm{CH_4}}^2 + \frac{4K_1'(\tilde{n}_{\mathrm{O}} - \tilde{n}_{\mathrm{C}})^2}{K_2'}\tilde{n}_{\mathrm{CH_4}} = 0 \tag{49}$$

$$\frac{4K_1'\ {K_3'}^2}{K_2'}\ \tilde{n}_{\mathrm{CH_4}}^5 + \frac{4K_1'\ K_3'}{K_2'}\tilde{n}_{\mathrm{CH_4}}^4 + \left[\frac{K_1'}{K_2'} + \frac{8K_1'\ K_3'(\tilde{n}_{\mathrm{O}} - \tilde{n}_{\mathrm{C}})}{K_2'}\right]\tilde{n}_{\mathrm{CH_4}}^3 \\ + \frac{4K_1'(\tilde{n}_{\mathrm{O}} - \tilde{n}_{\mathrm{C}})}{K_2'}\tilde{n}_{\mathrm{CH_4}}^2 + \left[\frac{4K_1'(\tilde{n}_{\mathrm{O}} - \tilde{n}_{\mathrm{C}})^2}{K_2'}\right]\tilde{n}_{\mathrm{CH_4}} = 0 \tag{50}$$

What corresponds to different coefficients to those that Heng et al. get (i.e. equation (22) in his paper).

New way...

We use eq. 4 and make the simplification that $2n_{\mathrm{H_2}} = n_{\mathrm{H}}$ (hydrogen-dominated atmospheres) like Heng & Tsai (2016) did.

$$\frac{n_{\mathrm{C}}}{n_{\mathrm{H_2}}} = \tilde{n}_{\mathrm{CH_4}} + \tilde{n}_{\mathrm{CO_2}} + \tilde{n}_{\mathrm{CO}} + 2\tilde{n}_{\mathrm{C_2H_2}} \tag{51}$$

$$2\frac{n_{\mathrm{C}}}{n_{\mathrm{H}}} = \tilde{n}_{\mathrm{CH_4}} + \tilde{n}_{\mathrm{CO_2}} + \tilde{n}_{\mathrm{CO}} + 2\tilde{n}_{\mathrm{C_2H_2}} \tag{52}$$

$$2\tilde{n}_{\mathrm{C}} = \tilde{n}_{\mathrm{CH_4}} + \tilde{n}_{\mathrm{CO_2}} + \tilde{n}_{\mathrm{CO}} + 2\tilde{n}_{\mathrm{C_2H_2}} \tag{53}$$

Now we replace $\tilde{n}_{\mathrm{CO}}$, $\tilde{n}_{\mathrm{CO_2}}$ and $\tilde{n}_{\mathrm{C_2H_2}}$ with eq. (40), (43) and (20) respectively

$$\tilde{n}_{\mathrm{CH_4}} + \frac{K_1'\ \tilde{n}_{\mathrm{CH_4}}\ [2K_3'\tilde{n}_{\mathrm{CH_4}}^2 + \tilde{n}_{\mathrm{CH_4}} + 2(\tilde{n}_{\mathrm{O}} - \tilde{n}_{\mathrm{C}})]^2}{K_2'} \\ + K_1'\ \tilde{n}_{\mathrm{CH_4}}[2K_3'\tilde{n}_{\mathrm{CH_4}}^2 + \tilde{n}_{\mathrm{CH_4}} + 2(\tilde{n}_{\mathrm{O}} - \tilde{n}_{\mathrm{C}})] + 2K_3'\ \tilde{n}_{\mathrm{CH_4}}^2 - 2\tilde{n}_{\mathrm{C}} = 0 \tag{54}$$

$$\tilde{n}_{\mathrm{CH_4}} + \frac{4K_1'\ {K_3'}^2}{K_2'}\ \tilde{n}_{\mathrm{CH_4}}^5 + \frac{K_1'}{K_2'}\tilde{n}_{\mathrm{CH_4}}^3 + \frac{4K_1'(\tilde{n}_{\mathrm{O}} - \tilde{n}_{\mathrm{C}})^2}{K_2'}\tilde{n}_{\mathrm{CH_4}} + \frac{4K_1'\ K_3'}{K_2'}\tilde{n}_{\mathrm{CH_4}}^4 + \frac{8K_1'\ K_3'(\tilde{n}_{\mathrm{O}} - \tilde{n}_{\mathrm{C}})}{K_2'}\tilde{n}_{\mathrm{CH_4}}^3 \\ + \frac{4K_1'(\tilde{n}_{\mathrm{O}} - \tilde{n}_{\mathrm{C}})}{K_2'}\tilde{n}_{\mathrm{CH_4}}^2 + 2K_1'K_3'\tilde{n}_{\mathrm{CH_4}}^3 + K_1'\tilde{n}_{\mathrm{CH_4}}^2 + 2K_1'\tilde{n}_{\mathrm{CH_4}}(\tilde{n}_{\mathrm{O}} - \tilde{n}_{\mathrm{C}}) + 2K_3'\ \tilde{n}_{\mathrm{CH_4}}^2 - 2\tilde{n}_{\mathrm{C}} = 0 \tag{55}$$

Then, we finally obtain

$$\frac{4K_1' \; {K_3'}^2}{K_2'} \, \tilde{n}_{\mathrm{CH_4}}^5 + \frac{4K_1' \; K_3'}{K_2'} \tilde{n}_{\mathrm{CH_4}}^4 + \left[\frac{K_1'}{K_2'} + \frac{8K_1' \; K_3'(\tilde{n}_{\mathrm{O}} - \tilde{n}_{\mathrm{C}})}{K_2'} + 2K_1' K_3' \right] \tilde{n}_{\mathrm{CH_4}}^3$$
$$+ \left[\frac{4K_1'(\tilde{n}_{\mathrm{O}} - \tilde{n}_{\mathrm{C}})}{K_2'} + 2K_3' + K_1' \right] \tilde{n}_{\mathrm{CH_4}}^2 + \left[\frac{4K_1'(\tilde{n}_{\mathrm{O}} - \tilde{n}_{\mathrm{C}})^2}{K_2'} + 1 + 2K_1'(\tilde{n}_{\mathrm{O}} - \tilde{n}_{\mathrm{C}}) \right] \tilde{n}_{\mathrm{CH_4}} - 2\tilde{n}_{\mathrm{C}} = 0 \quad (56)$$

What corresponds to close coefficients to those that Heng et al. get (i.e. equation (22) in his paper).

References

- Heng, Kevin, and James R. Lyons. 2016. "CARBON DIOXIDE IN EXOPLANETARY ATMOSPHERES: RARELY DOMINANT COMPARED TO CARBON MONOXIDE AND WATER IN HOT, HYDROGEN-DOMINATED ATMOSPHERES". The Astrophysical Journal 817 (2): 149. doi:10.3847/0004-637x/817/2/149.