Physics of planetary atmospheres

Lecture 6: Atmospheric (and ionospheric) chemistry

(Mainly based on Heng, chapters 6 and 7)

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Outline

Introduction into gas-phase chemistry and chemical modelling

First: environments characterized by low temperature and low pressure

Case example 1: simple ionospheric model of Mars

Second: Effect of higher pressure and temperature

Equilibrium constants K_{eq}, K_{eq}' and K'

Case example 2: The hydrogen atmosphere considered in Section 7.2 of book

Case example 3: Equilibrium C-H-O chemistry including in H_2 dominated atmosphere (Section 7.3-7.4 of book)

Introduction

It is hard to form one particle out of two (conservation of energy and momentum is required)

A collision complex tends to fall back into the reactants: $H + H \rightarrow H_2^* \rightarrow H + H$

Multibody reactions are possible under high enough pressure. May be visualized as a two-step process.

For example $H + H + M \rightarrow H_2 + M$ (M is any molecule)

1) $H + H \rightarrow H_2^*$, (* means excited)
2) $H_2^* + M \rightarrow H_2 + M^*$.

The third species comes in, colliding with the unstable H_2^*. Momentum and energy is shared with M.

Three-body reactions are typically neglected when modelling chemistry in low pressure environments such as planetary ionospheres, cometary comae, interstellar clouds…

Introduction

To break H_2 into H + H requires ~ **4.52 eV** (NIST chemistry webbook)

If we define the Heat of formation of H_2 as 0 eV, that is $\Delta H_f(H_2) = 0$ eV then we have

$\Delta H_f(H_2) + 4.52\ \text{eV} \approx \Delta H_f(H) + \Delta H_f(H) \rightarrow \Delta H_f(H) = 2.26\ \text{eV} = 218\ \text{kJ/mol}$.

To check whether a chemical reaction is energetically feasible at very low temperature one can compare the heat of formation of the reactants with those of the products, e.g.,

$$A + B \rightarrow C + D$$

If $\Delta H_f(C) + \Delta H_f(D) < \Delta H_f(A) + \Delta H_f(B)$ the forward reaction is (*or may be*) energetically possible, ***exoergic*** reaction

If $\Delta H_f(C) + \Delta H_f(D) > \Delta H_f(A) + \Delta H_f(B)$ the forward reaction is not energetically possible, ***endoergic*** reaction

Introduction into gas-phase chemical modelling
(we shall neglect transport throughout this lecture)

Change in number density of species *X* is given by

$dn_X/dt = P_X - L_X$

P_X production rate of *X*

L_X loss rate of *X*

At chemical equilibrium $P_X = L_X$

$$P_X = \sum_p Z_X(p) k_p \prod_{r(p)} n_r$$

Sum up the contribution from all processes *p* that leads to production of X

$$L_X = \sum_{p'} Y_X(p') k_{p'} \prod_{r(p')} n_r$$

Sum up the contribution from all processes *p'* that leads to loss of X

$Z_{X,p}$ ($Y_{X,p'}$) is the number of X species formed (lost) in the reaction *p* (*p'*) [dimensionless]
k_p (and $k_{p'}$) denotes the reaction rate coefficient for process *p* **(*p'*)** [unit depend on number of reactants]
r(p) denote the reactants in reaction *p,* and n_r is the number density of reactant *r* [m^{-3}]

Clarifying (?) example

$$P_X = \sum_p Z_X(p) k_p \prod_{r(p)} n_r$$

$$L_X = \sum_{p'} Y_X(p') k_{p'} \prod_{r(p')} n_r$$

Ozone formation in Earth's atmosphere exclusively via

p_1: $O + O_2 + M \rightarrow O_3 + M$

$Z_{O3}(p_1) = 1$, right? $P_{O_3} = k_{p_1} n_O n_{O_2} n_M$

Ozone loss mainly via photodissociation and reaction with O… (and pollutants neglected here)

p'_1: $O_3 + h\nu \rightarrow O_2 + O$ p'_2: $O_3 + O \rightarrow O_2 + O_2$

$$L_{O_3} = k_{p'_1} n_{O_3} + k_{p'_2} n_{O_3} n_O$$

Where to find rate coefficients?

Photodissociation and photoionization [s^{-1}]

e.g., Huebner & Mukherjee (2015), PSS, (http://phidrates.space.swri.edu)
Provide calculated frequencies at 1 AU for many atoms and molecules and for various radiation fields (including active and quite sun). For atmospheric modelling Beer-Lambert law need to be used (central inputs: impinging stellar spectra, atmospheric density profiles, cross-sections for photo-processes)

Two-body reactions [cm^3 s^{-1}]

UMIST database for astrochemistry (http://udfa.ajmarkwick.net)
Kinetic database for astrochemistry (http://kida.obs.u-bordeaux1.fr)

Provide rate coefficients particularly for binary reactions with references to original work.

Three-body reactions [cm^6 s^{-1}], *n*-body reactions [$cm^{2(n-1)}$ s^{-1}]

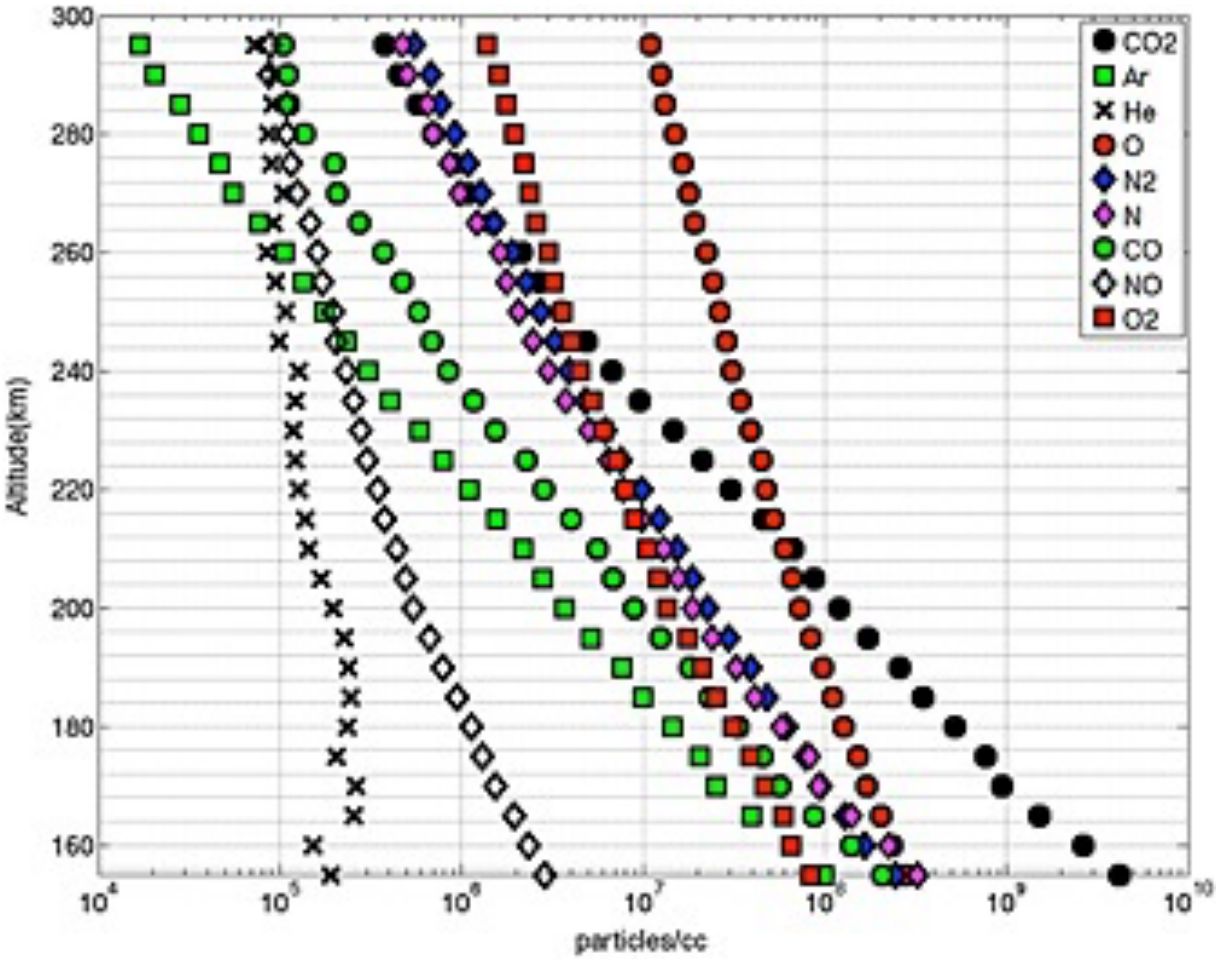
Not aware of any good database. Equilibrium chemistry can still be tackled as we shall see later.

Case example 1

Simple ionospheric model of Mars

Predict electron number density and dominant ions in the Martian ionosphere from information of abundances of neutrals near an altitude of ~200 km

Simple ionospheric model of Mars



MAVEN/NGIMS data from Martian dayside

Mars atmosphere is CO_2 dominated. Around ~200-250 km atomic oxygen becomes the dominant species.

We will use a *simple* chemical model to predict the dayside electron density near 200-210 km. We shall also use the model to predict which ion species that may be most abundant.

Simplifying assumption: concentration of CO_2 and O stable: $n(CO_2) \approx n(O) \approx 5\text{x}10^7$ cm^{-3}

Simple Mars ionospheric model (sorry for busy slide)

Photoionization of CO_2 and O leads primarily to “CO_2^+ + electron” and “O^+ + electron”, respectively.

$P(CO_2^+) \approx k_1 \times n(CO_2)$ $k_1 \approx 1.2\text{x}10^{-6}/1.524^2\ s^{-1}$ (see Huebner & Mukherjee, P&SS 2015)

$P(O^+) \approx k_2 \times n(O)$ $k_2 \approx 4.5\text{x}10^{-7}/1.524^2\ s^{-1}$

How is CO_2^+ lost? Check online reaction database (e.g., UMIST).
CO_2^+ is not reactive with CO_2. Reactive with O to produce O_2^+. CO_2^+ is also lost through electron recombination.

$L(CO_2^+)=n(CO_2^+) \times [k^{in}_1 \times n(O) + k^{DR}_1 \times n(e-)]$ $k^{in}_1= 1.64\text{x}10^{-10}\ cm^3s^{-1}$ $k^{DR}_1=3.80\text{x}10^{-7}\ (T_e/300)^{-0.5}\ cm^3s^{-1}$

How is O^+ lost? Check online reaction database (e.g., UMIST).
O^+ is not reactive with O. Reactive with CO_2 to produce O_2^+. Loss of O^+ through electron recombination negligible.

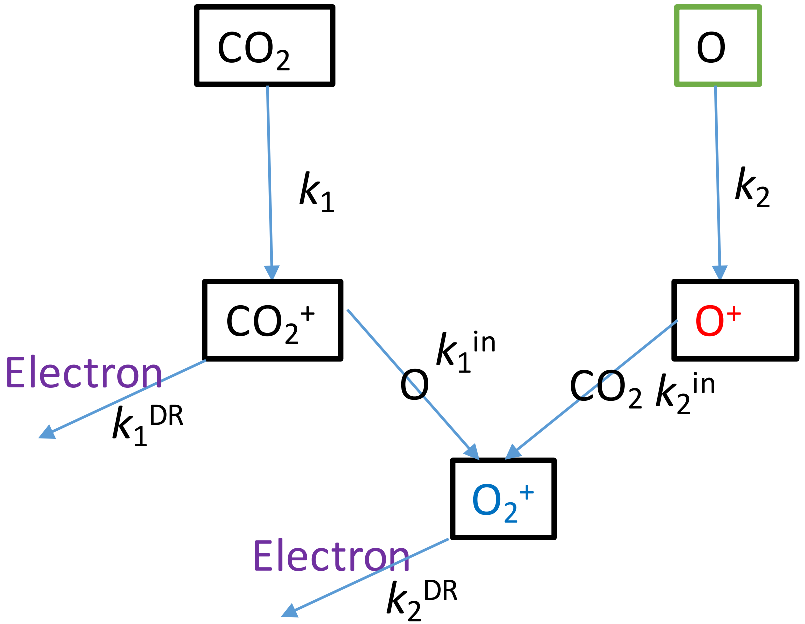
$L(O^+)=n(O^+) \times k^{in}_2 \times n(CO_2)$ $k^{in}_2= 9.40\text{x}10^{-10}\ cm^3s^{-1}$

We note that $P(O_2^+) = n(CO_2^+) \times k^{in}_1 \times n(O) + n(O^+) \times k^{in}_2 \times n(CO_2)$

O_2^+ is not reactive with CO_2 or O, so only lost trough electron recombination.

$L(O_2^+)=n(O_2^+) \times k^{DR}_2 \times n(e-)$ $k^{DR}_2=1.95\text{x}10^{-7}\ (T_e/300)^{-0.7}\ cm^3s^{-1}$

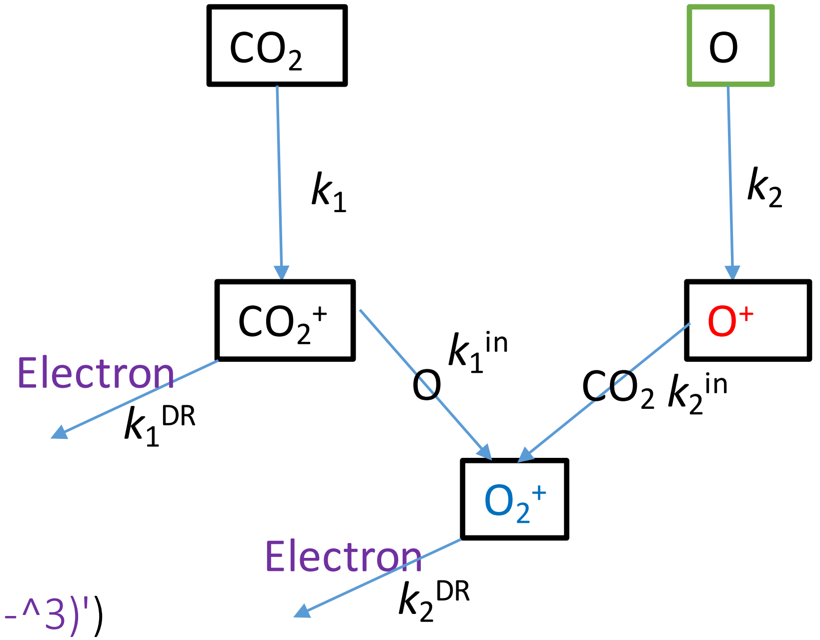
Last but not least: $n(e-)=n(CO_2^+) + n(O^+) + n(O_2^+)$


CO_2
O
k_1
k_2
CO_2^+
O^+
k_1^{in}
O
CO_2 k_2^{in}
Electron
k_1^{DR}
O_2^+
Electron
k_2^{DR}

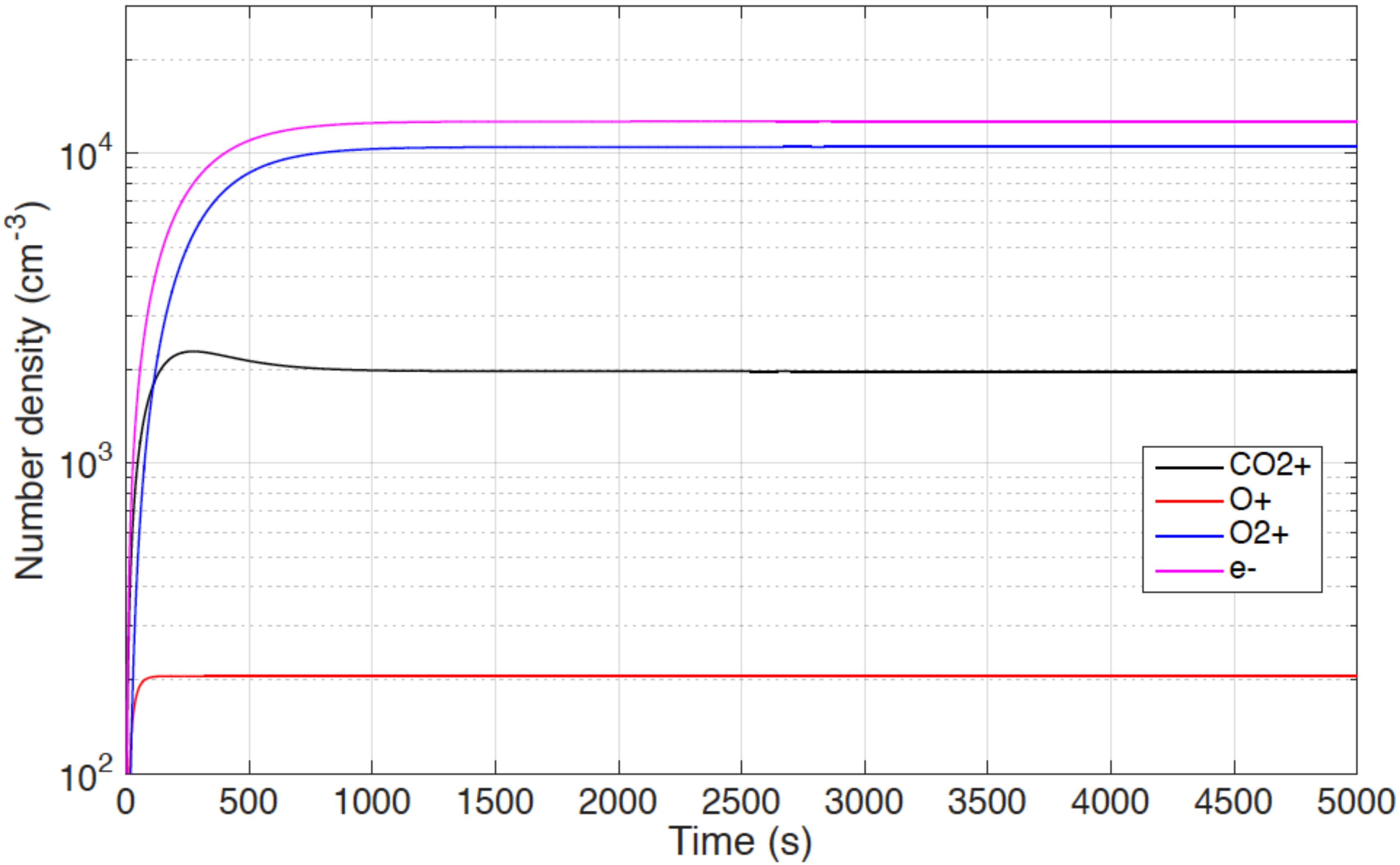
Simple Mars ionospheric model… Matlab code

```
clear all
close all

nCO2=5e+7; % cm-3
nO=5e+7; % cm-3
Te=300; % K
d_AU=1.524;  %AU

k1=1.2e-6*(1/d_AU)^2; % s-1
k2=4.5e-7*(1/d_AU)^2; %  s-1
kin1=1.64e-10; %cm3s-1
kin2=9.4e-10; %cm3s-1
kDR1=3.8e-7*(Te/300)^-0.5; % cm3s-1
kDR2=1.95e-7*(Te/300)^-0.7 % cm3s-1

dt= 0.1; % s
nCO2p(1)=0;
nOp(1)=0;
nO2p(1)=0;
ne(1)=0;
Time(1)=0;
```

```
for i=2:1:50000
nCO2p(i)= nCO2p(i-1)+…
+ nCO2*k1*dt- nCO2p(i-1)*(nO*kin1+ne(i-1)*kDR1)*dt;
nOp(i)= nOp(i-1)+nO*k2*dt-nOp(i-1)*nCO2*kin2*dt;
nO2p(i)=nO2p(i-1)+  nCO2p(i-1)*nO*kin1*dt +…
+ nOp(i-1)*nCO2*kin2*dt-nO2p(i-1)*ne(i-1)*kDR2*dt;
ne(i)= nCO2p(i)+ nOp(i)+ nO2p(i);
Time(i)=(i-1)*dt;
end

figure (1)
semilogy(Time,nCO2p,'k-')
hold on
semilogy(Time,nOp,'r-')
semilogy(Time,nO2p,'b-')
semilogy(Time,ne,'m-')
grid on
xlabel('Time (s)')
ylabel('Number density (cm^-^3)')
legend('CO2+','O+','O2+','e-')
```



Simple Mars ionospheric model… results



Steady state reached rather quickly… ten minutes

$n_e \approx 10^4$ cm^{-3}

O_2^+ dominant ~10^4 cm^{-3}

CO_2^+ ~10^3 cm^{-3}

O^+ few hundred cm^{-3}

Predictions near *z*=200 km

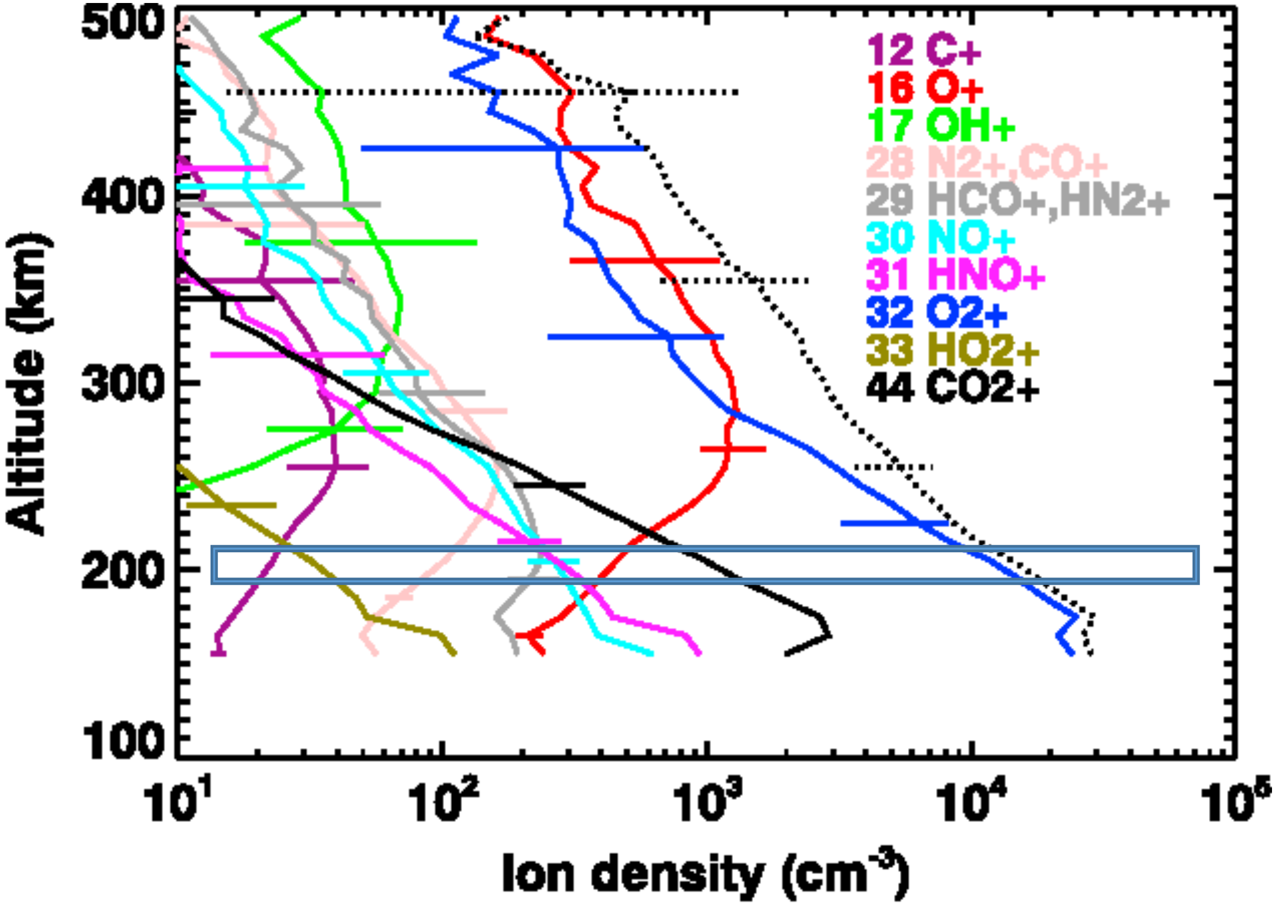
$n_e \approx 10^4$ cm^{-3}

O_2^+ dominant ~10^4 cm^{-3}

CO_2^+ ~10^3 cm^{-3}

O^+ few hundred cm^{-3}

MAVEN/NGIMS observations



So far we have looked at low *P* and low *T* environments. At high pressure multi-body reactions can be efficient. At high enough temperatures…

Molecules internally excited to higher degree.
More important: Maxwellian speed distribution. Collision energies can be higher than energy barriers.

While A + B → C + D may be the only possibility reaction direction at low temperature…
at high temperature A + B <--> C + D

Forward reaction → rate coefficient k_f
Reverse reaction ← rate coefficient k_r

Equilibrium rate coefficient (possibly dimensional). Balance $k_f n_A n_B$ with $k_r n_C n_D$

$K_{eq}' \equiv k_f/k_r = n_C n_D / n_A n_B$ (in this example K_{eq}' is dimensionless but that does not apply in general)

Ok, that was K_{eq}', what about K_{eq} and K' discussed in the book?

K_{eq}' , K' *and* K_{eq}

K_{eq}' may be **dimensional** and is defined as the ratio k_f/k_r. It is related to K_{eq} via

$K_{eq}' = K_{eq}(k_B T/P_0)^x = K_{eq} n_0^{-x}$ (see Eq. 6.17 in book)

where *x* is "the number of reactants minus the number of products" involved in the forward reaction.

K' is just a normalized equilibrium constant (up to us what to normalize against). For instance, in a later case example we relate it to K_{eq}' via $K' = K_{eq}'/n_{\mathrm{H2}}^2$.

K_{eq} is **dimensionless** and related to the **Gibbs free energy** via (Eq. 6.14 in book)

$$K_{eq} = \exp\left(-\frac{\Delta G^0_{reaction}}{RT}\right)$$

(R=8.314 J K^{-1} mol^{-1} is universal gas constant, T is temperature in K)

$$\Delta G^0_{reaction} = \sum_p \Delta G^0_f(p) - \sum_r \Delta G^0_f(r)$$

ΔG^0_f values at P_0=1 bar and different T are tabulated at e.g., https://janaf.nist.gov

The Gibbs free energy ($\Delta G^0 = \Delta H^0 - T\Delta S^0$) is the maximum amount of non-expansion work that can be extracted from a thermodynamically closed system (wikipedia). For an introduction into the Gibbs free energy associated with chemical reactions, see for instance http://chem1.com/acad/webtext/thermeq/TE4.html,

Clarifying (?) example

$K_{eq} = \exp(-\Delta G_{reac,0}/RT)$ $K_{eq}' = K_{eq}(k_B T/P_0)^x = K_{eq} n_0^{-x}$ $K' = K_{eq}'/n_{H2}^2$

Consider the net reaction

$CH_4 + H_2O \leftrightarrow CO + 3H_2$

Note that x=-2 (difference between the number of reactants and products in the forward direction)

We get $K' = K_{eq}'/n_{H2}^2 = K_{eq} n_0^2/n_{H2}^2 = K_{eq}(P_0/P)^2 = (P_0/P)^2 \exp(-\Delta G_{reac,0}/RT)$

(in agreement with 7.31 in book)

$$\Delta G^0_{reaction} = \sum_p \Delta G^0_f(p) - \sum_r \Delta G^0_f(r)$$

Find ΔG^0_f (vary with T) for the involved products (CO, H, H, H) and reactants (CH_4, H_2O) (https://janaf.nist.gov)

Case example 2

The hydrogen atmosphere considered in Section 7.2 of the book

For a given pressure, how will the relative abundances of atomic (H) and molecular (H_2) hydrogen vary with the temperature?

The hydrogen atmosphere considered in Section 7.2 of the book

Reaction direction at low temperature

$$2H + M <-> H_2 + M$$

→

$$dn_H/dt = -2k_f n_H^2 n_M + 2k_r n_{H2} n_M$$

@ equilibrium $K_{eq}{}' = k_f/k_r = n_{H2}/n_H^2$

$$dn_{H2}/dt = -k_r n_{H2} n_M + k_f n_H^2 n_M$$

Book keeping: n_{total} (total number density of hydrogen atoms, a constant)

$n_{total} = n_H + 2n_{H2} \rightarrow n_H + 2K_{eq}{}' n_H^2 - n_{total} = 0$ (quadratic equation)

$$n_H = \frac{-1 + \sqrt{1 + 8K_{eq}{}' n_{total}}}{4K_{eq}{}'}$$

Check limits…

$2H + M <\!\!-\!\!> H_2 + M$ @ equilibrium $K_{eq}' = k_f/k_r = n_{H2}/n_H^2$

→

Reaction direction at low temperature

$$n_H = \frac{-1 + \sqrt{1 + 8K_{eq}' n_{total}}}{4K_{eq}'}$$

$$\lim_{K_{eq}' \to \infty} \frac{-1 + \sqrt{1 + 8K_{eq}' n_{total}}}{4K_{eq}'} = 0$$

$$\lim_{K_{eq}' \to 0} \frac{-1 + \sqrt{1 + 8K_{eq}' n_{total}}}{4K_{eq}'} = \lim_{K_{eq}' \to 0} \frac{\frac{1}{2}\left(1 + 8K_{eq}' n_{total}\right)^{-1/2} 8n_{total}}{4} = n_{total}$$

Recall

$$n_{total} = n_H + 2n_{H2} \rightarrow 1 = \frac{n_H}{n_{total}} + 2\frac{n_{H2}}{n_{total}} = \widetilde{n_H} + 2\widetilde{n_{H2}}$$

$$n_H = \frac{-1 + \sqrt{1 + 8K_{eq}{}' n_{total}}}{4K_{eq}{}'}$$

$$\frac{n_H}{n_{total}} = \widetilde{n_H} = \frac{-1 + \sqrt{1 + 8K_{eq}{}' n_{total}}}{4K'_{eq} n_{total}} = \frac{-1 + \sqrt{1 + 8K'}}{4K'}$$

$$\widetilde{n_{H2}} = \frac{1 - \widetilde{n_H}}{2}$$

Generating top panel of Fig. 7.1 is straightforward. Generating the bottom panel is a bit more tricky.

K_{eq}' is defined as the ratio k_f/k_r. It is related to K_{eq} via

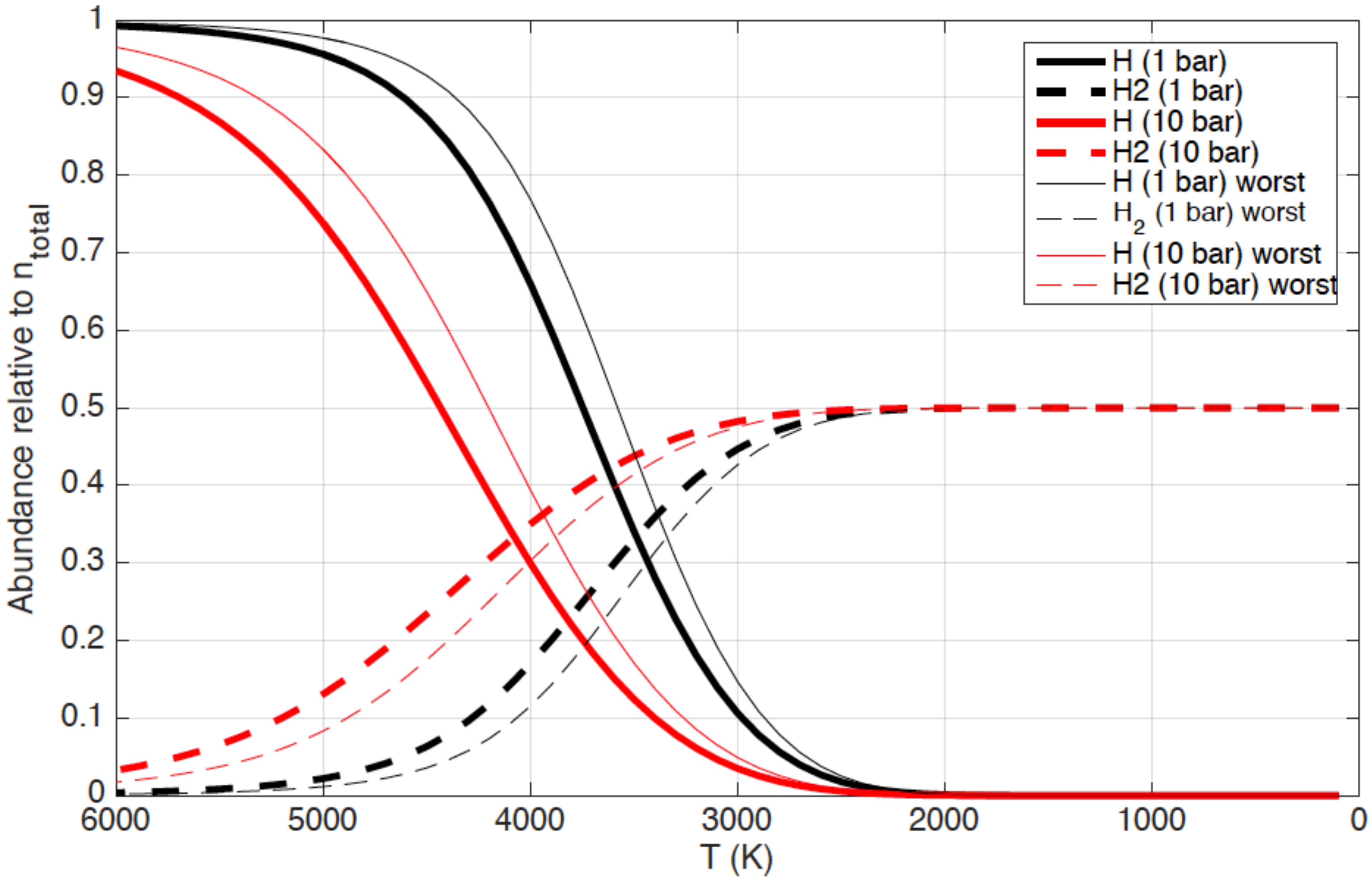
$K_{eq}' = K_{eq}(k_B T/P_0)^x = K_{eq} n_0^{-x}$ (see Eq. 6.17 in book)

where x is "the number of reactants minus the number of products" involved in the forward reaction.

2H + M <-> H_2 + M gives $x = 1$ and so $K' = K_{eq}' n_{total} = K_{eq} n_0^{-1} n_{total} \approx (P/P_0)\ \exp(-\Delta G_{reac,0}/RT)$

We asume; $n_0 \approx n_{total.}$. In worst case $n_0 = n_{total.}/2$

Results (appears as if the “$n_0 \approx n_{total}$ assumption” is used in the book, but possible error is quite small)



For a given pressure, how will the relative abundances of atomic (H) and molecular (H_2) hydrogen vary with the temperature?

When the temperature is below ~3000 K (expected to be the case in most exoplanet atmospheres) it is fair to assume that the hydrogen is nearly exclusively in molecular form.

Case example 3

C-H-O chemistry in H_2 dominated atmosphere
(considered in Sections 7.3 & 7.4 of the book)

Given a series of net reactions, elemental abundances of C and O, how will the molecular composition vary with the temperature?

C-H-O chemistry in H_2 dominated atmosphere (considered in Section 7.3 of the book)

	Reaction direction at low temperature	
$CH_4 + H_2O \leftrightarrow CO + 3H_2$	←	(1)
$2CH_4 \leftrightarrow C_2H_2 + 3H_2$	←	(2)
$CO_2 + H_2 \leftrightarrow CO + H_2O$	←	(3)

Given:

Relevant net reactions (1,2,3)

Pressure, Temperature

$n(H_2)=p/k_BT$

elemental abundance of O

C/O ratio

Gibbs free energies of formation

$$k_{1R}n_{CO}n_{H2}^3 + 2k_{2R}n_{C2H2}n_{H2}^3 = k_{1F}n_{CH4}n_{H2O} + 2k_{2F}n_{CH4}^2 \qquad CH_4$$

$$k_{1R}n_{CO}n_{H2}^3 + k_{3F}n_{CO2}n_{H2} = k_{1F}n_{CH4}n_{H2O} + k_{3R}n_{CO}n_{H2O} \qquad H_2O$$

$$k_{1F}n_{CH4}n_{H2O} + k_{3F}n_{CO2}n_{H2} = k_{1R}n_{CO}n_{H2}^3 + k_{3R}n_{CO}n_{H2O} \qquad CO$$

$$k_{2F}n_{CH4}^2 = k_{2R}n_{C2H2}n_{H2}^3 \qquad C_2H_2$$

$$k_{3R}n_{CO}n_{H2O} = k_{3F}n_{CO2}n_{H2} \qquad CO_2$$

$$K_{eq,1}{}' = \frac{N_{CO}n_{H2}^2}{N_{CH4}N_{H2O}}$$

$$K'_{eq,2} = \frac{N_{C2H2}n_{H2}^2}{N_{CH4}^2}$$

$$K'_{eq,3} = \frac{N_{CO}N_{H2O}}{N_{CO2}}$$

Here we denote n_X/n_{H2} by N_X

$$K_{eq,1}{}' = \frac{N_{CO} n_{H2}^2}{N_{CH4} N_{H2O}}$$

$$\frac{K_{eq,1}{}'}{n_{H2}^2} = \frac{N_{CO}}{N_{CH4} N_{H2O}} = K_1'$$

$$\frac{z}{yx} = a$$

$$K'_{eq,2} = \frac{N_{C2H2} n_{H2}^2}{N_{CH4}^2}$$

$$\frac{K_{eq,2}{}'}{n_{H2}^2} = \frac{N_{C2H2}}{N_{CH4}^2} = K_2'$$

$$\frac{t}{y^2} = b$$

$$K'_{eq,3} = \frac{N_{CO} N_{H2O}}{N_{CO2}}$$

$$K'_{eq,3} = \frac{N_{CO} N_{H2O}}{N_{CO2}} = K_3'$$

$$\frac{zx}{s} = c$$

$$N_{CH4} + N_{CO} + N_{CO2} + 2N_{C2H2} = \frac{n_C^*}{n_{H2}} \approx 2F_C$$

$$y + z + s + 2t = 2d$$

$$N_{H2O} + N_{CO} + 2N_{CO2} = \frac{n_O^*}{n_{H2}} \approx 2F_O$$

$$x + z + 2s = 2e$$

Recall: we denote n_X/n_{H2} by N_x

n_c^* is number density of carbon atoms, “how many carbon atoms are there in total in a given volume”

F_c and F_O are the elemental abundances of carbon (solar values ~3 x 10^{-4}, ~6 x 10^{-4}, respectively)

$$\frac{z}{yx} = a$$

$$\frac{t}{y^2} = b$$

$$\frac{zx}{s} = c$$

$$y + z + s + 2t = 2d$$

$$x + z + 2s = 2e$$

$$x = \frac{z}{ay}$$

$$z = -\frac{c}{4}(1 + ay) + \sqrt{\frac{c^2}{16}(1 + ay)^2 + acey}$$

$$\frac{d + \frac{1}{4}x - \frac{1}{2}y - \frac{1}{4}z - \frac{1}{2}e}{y^2} = b$$

ALGEBRA!

$$y + z + \frac{2e - x - z}{2} + 2t = 2d$$

$$\sum_{i=0}^{5} A_i y^i = 0$$

with

$$A_5 = 16b^2$$

$$A_4 = (16b - 2abc)$$

$$A_3 = (16b[e - 2d] - ac + 4)$$

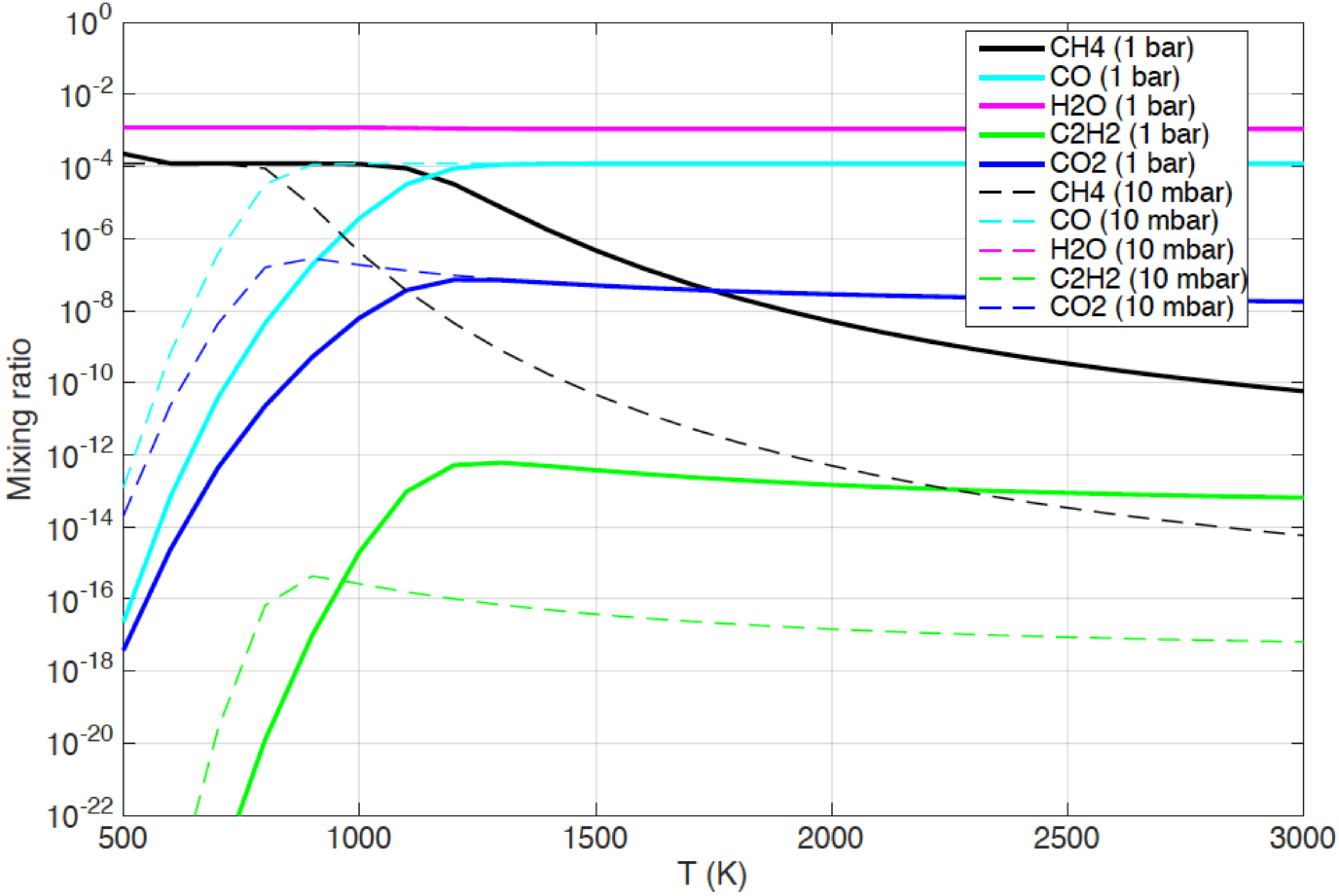
$$A_2 = \left(2\frac{bc}{a} + 2acd - 16d - 2ace + 8e\right)$$

$$A_1 = 16d^2 - 16de + \frac{c}{a} + 4e^2 + 2ce$$

$$A_0 = -2\frac{cd}{a}$$

Not identical (and not equivalent) with equation in book.
(I do not rule out mistakes from my side)

C/O = 0.1



Mixing ratio
10^{0}
10^{-2}
10^{-4}
10^{-6}
10^{-8}
10^{-10}
10^{-12}
10^{-14}
10^{-16}
10^{-18}
10^{-20}
10^{-22}
500
1000
1500
2000
2500
3000
T (K)
CH4 (1 bar)
CO (1 bar)
H2O (1 bar)
C2H2 (1 bar)
CO2 (1 bar)
CH4 (10 mbar)
CO (10 mbar)
H2O (10 mbar)
C2H2 (10 mbar)
CO2 (10 mbar)

Insights from modelling **of H_2 dominated atmospheres**

(see distributed print-outs of Fig. 7.2 and Fig. 7.3 of Heng)

- In a carbon-poor atmosphere atmosphere, water is expected to be the main carrier of oxygen.
- When C/O takes on the solar value or higher CO becomes the main carrier of oxygen at high temperatures.
- CH_4 is the main carrier of carbon at low temperature, with increasing temperature CO gradually takes over.
- When the elemental abundance of carbon is low, carbon dioxide is less abundant than carbon monoxide.
- Acetelyne (C_2H_2) is typically sub-dominant in carbon-poor atmospheres. May become dominant carrier of carbon if the atmosphere is carbon rich and hot.
- When the temperature is ”low” (~800 K) the trends exhibited by the mixing ratios versus the C/O ratio are relativily simple: constant mixing ratio of water while the carbon carrying molecules show simple scalings.
- At hotter temperatures the trends are more complex. When carbon-poor the atmospheres are methane-poor and water rich. When carbon rich, they are methane rich and water poor. Transition around C/O ≈ 1.

Some concluding remarks

- The atmospheric chemistry depends in part on the temperature… the temperature depends in part on the chemistry
- We have completely over-looked condensation (resulting in haze or cloud formation)
- We have not considered how transport may influence the picture (we have not compared time scales for chemical reactions with transport time scales)
- While we can predict relative abundances of different species at chemical equilibrium, we have not assessed how long time it takes to reach such a state (is it a matter of minutes? days? years? the age of the Universe?)
- It does not require a chemist to do chemical modelling.

Homework:

Problem 7.6.4 (on nitrogen chemistry) in Heng's book.