



# Planetary Atmospheres - Thermo and Photochemistry

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# Outline



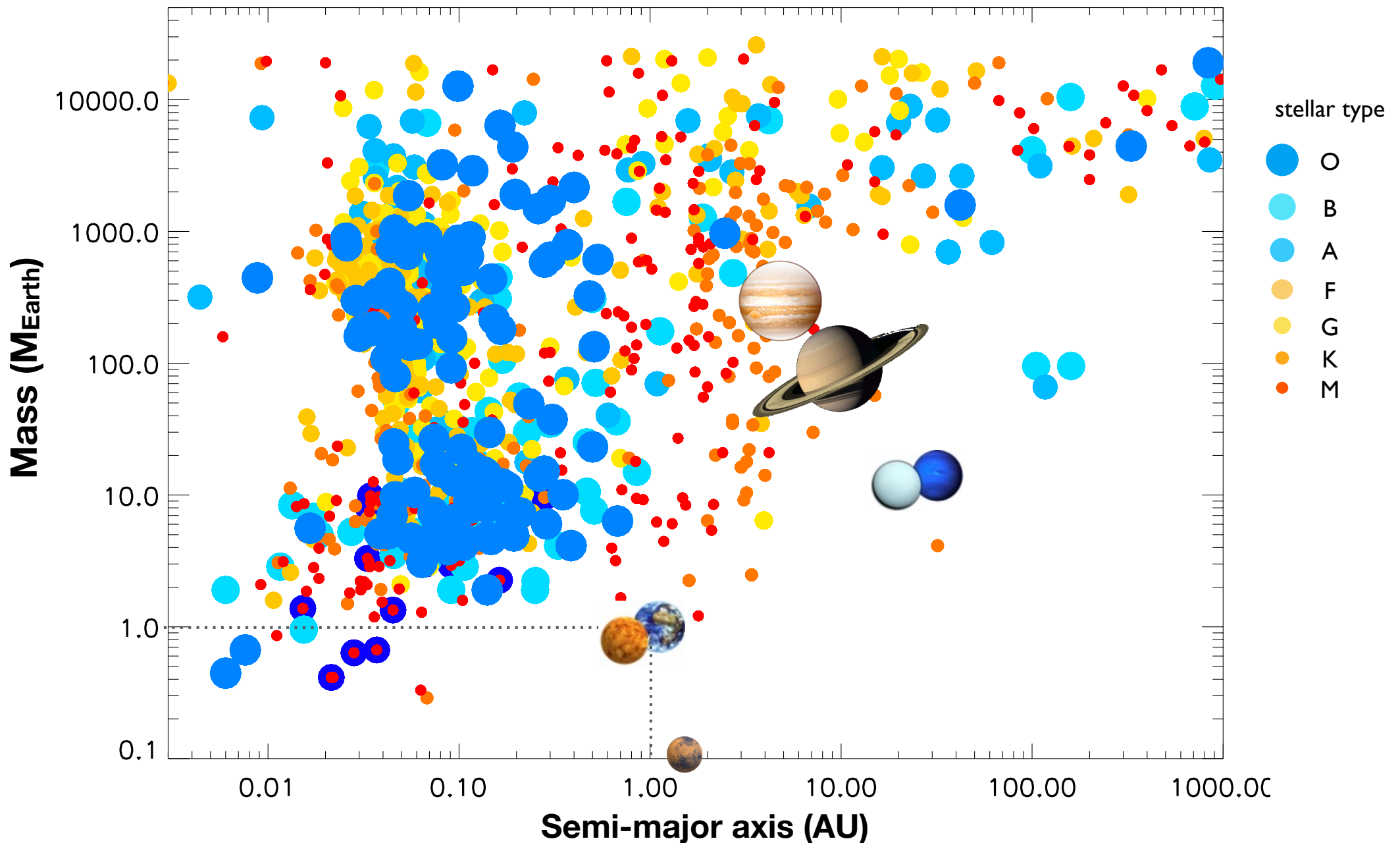
- Introduction - Structure of exoplanet atmospheres
- Thermodynamics - Thermochemical equilibrium
- Chemical kinetics
- Photochemistry
- Tools: 1D kinetic models - ingredients + key results

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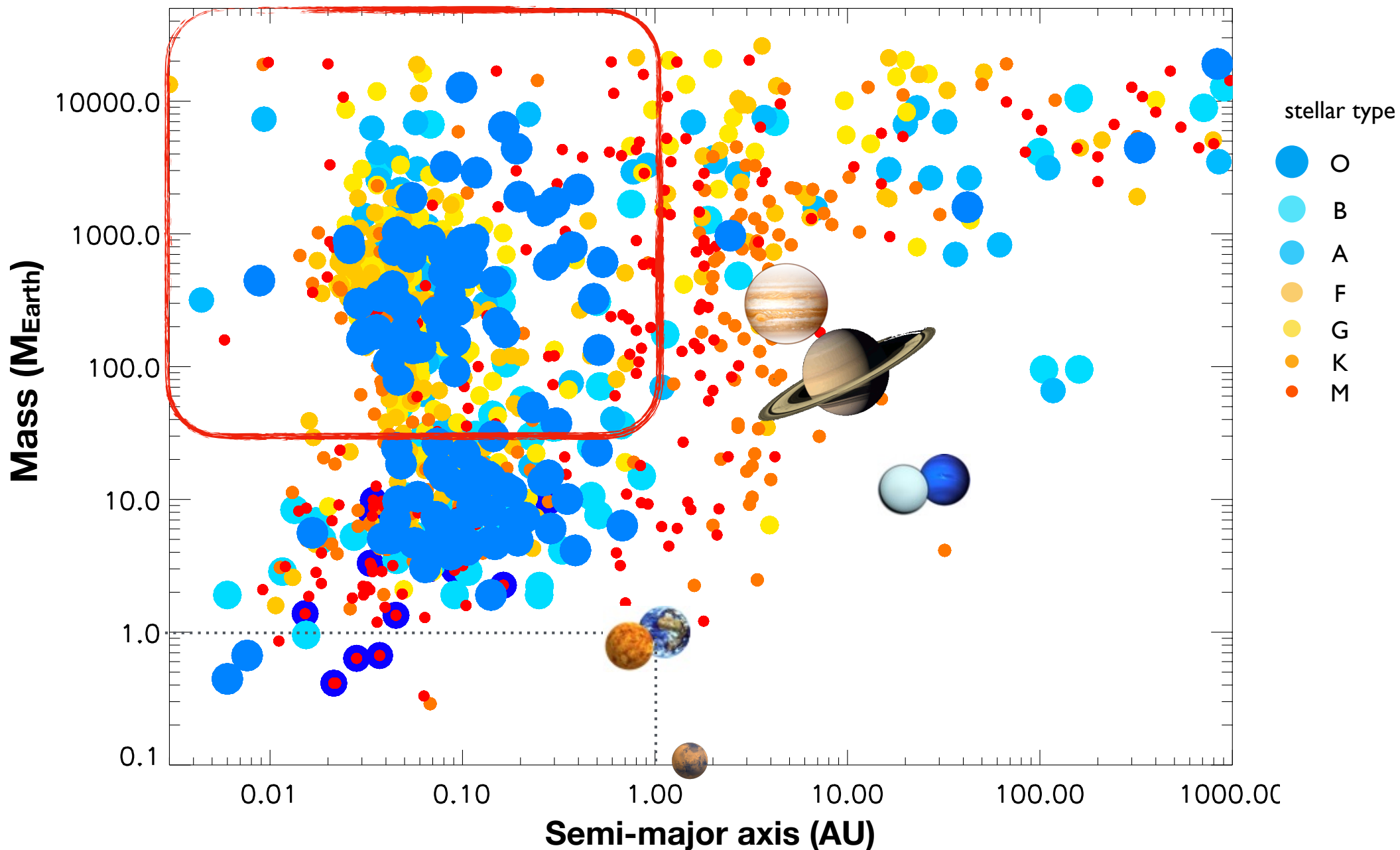
# Diversity of planetary worlds



source: [exoplanet.eu](http://exoplanet.eu) (september, 28st 2021)

**4843 exoplanets + 8 solar system planets**

# Diversity of planetary worlds



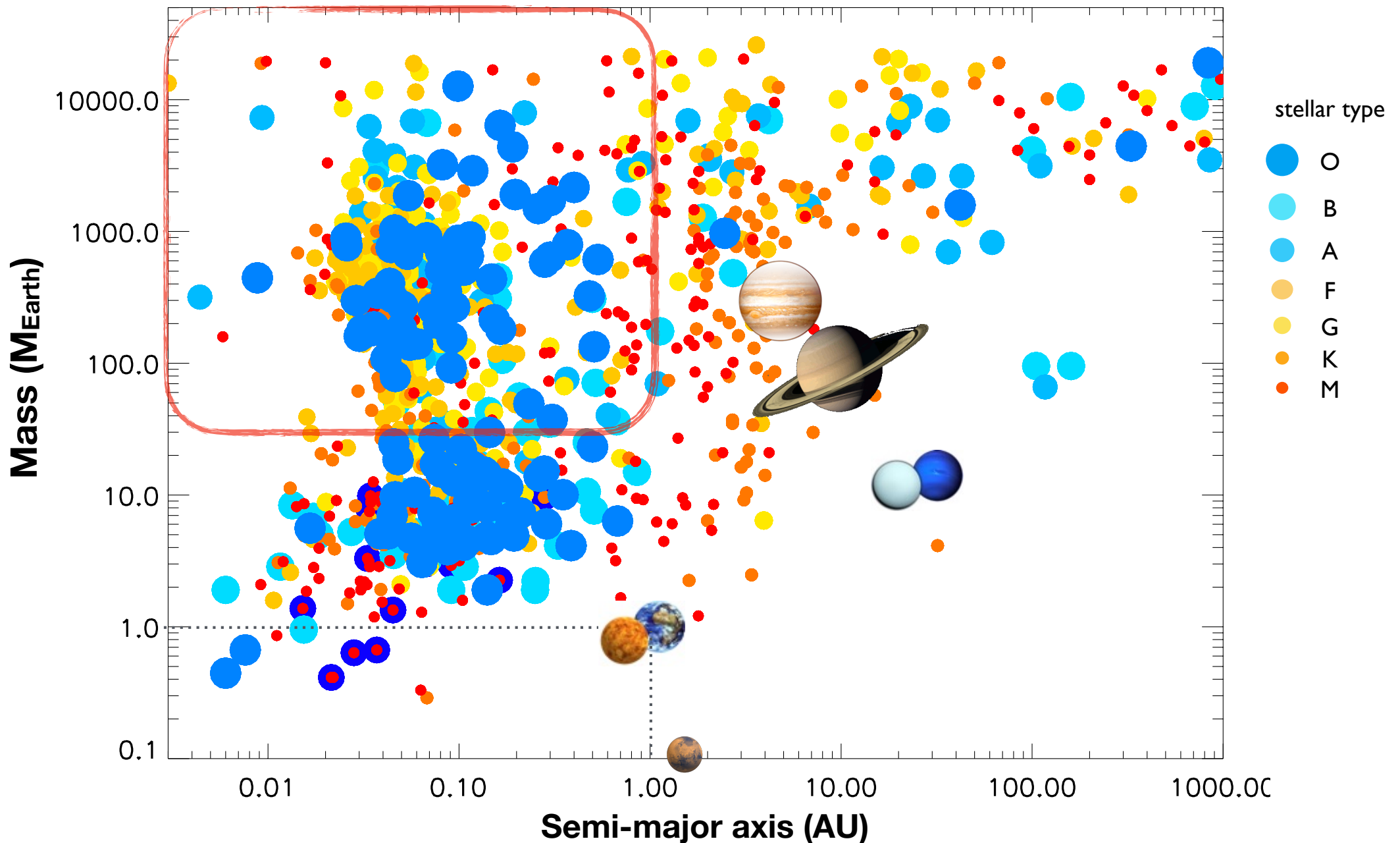
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4843 exoplanets + 8 solar system planets

# Some scientific questions

- What is the history of these planets ?
- How did they form ?
- ➡ What is the chemical composition of their atmosphere ?
- ➡ What are the elemental ratios ?
- ➡ Are they the same than their host star ? or are they enriched ?
- ➡ **Determine one or several scenarios of planetary formation, common with the Solar System (if possible)**

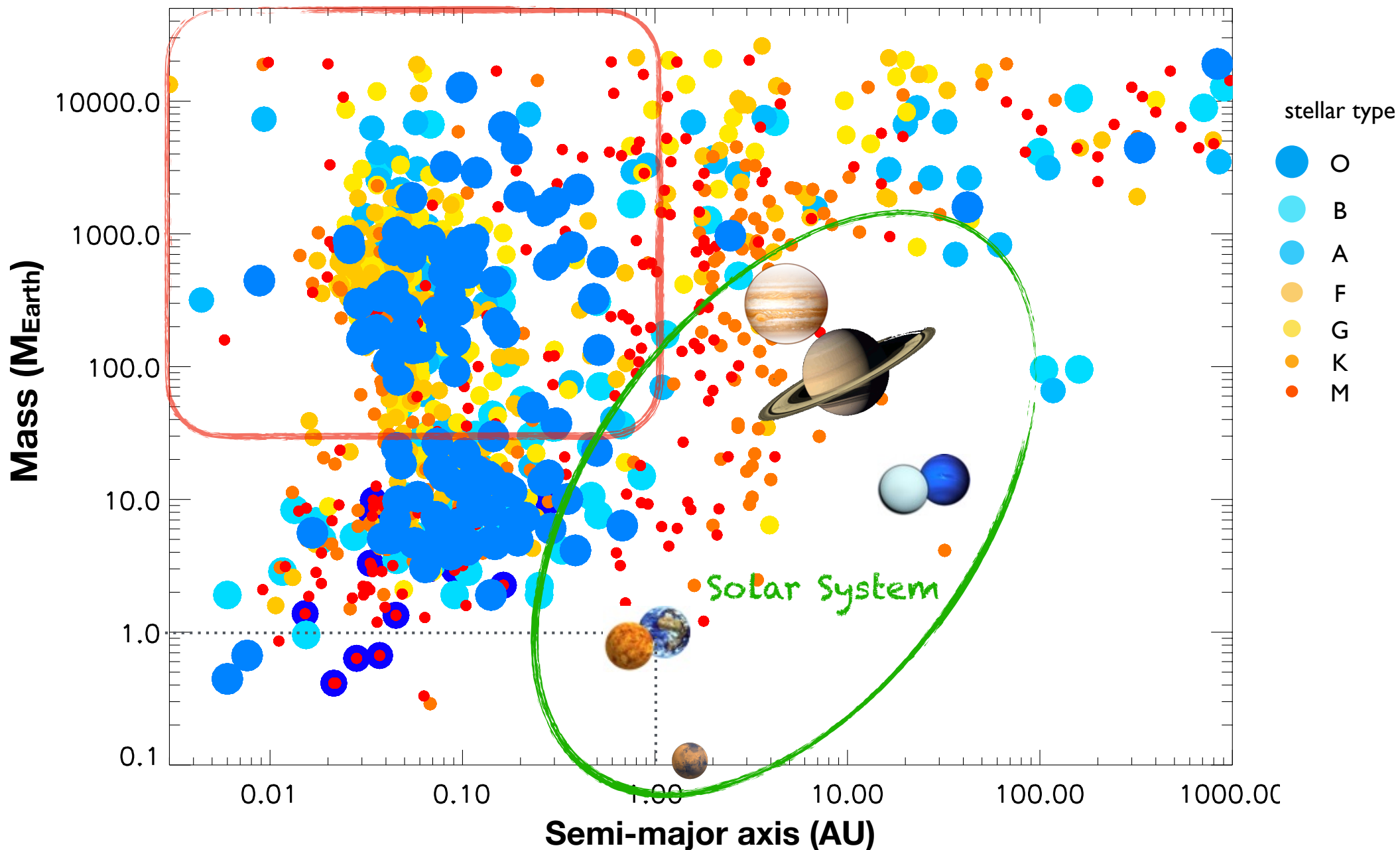
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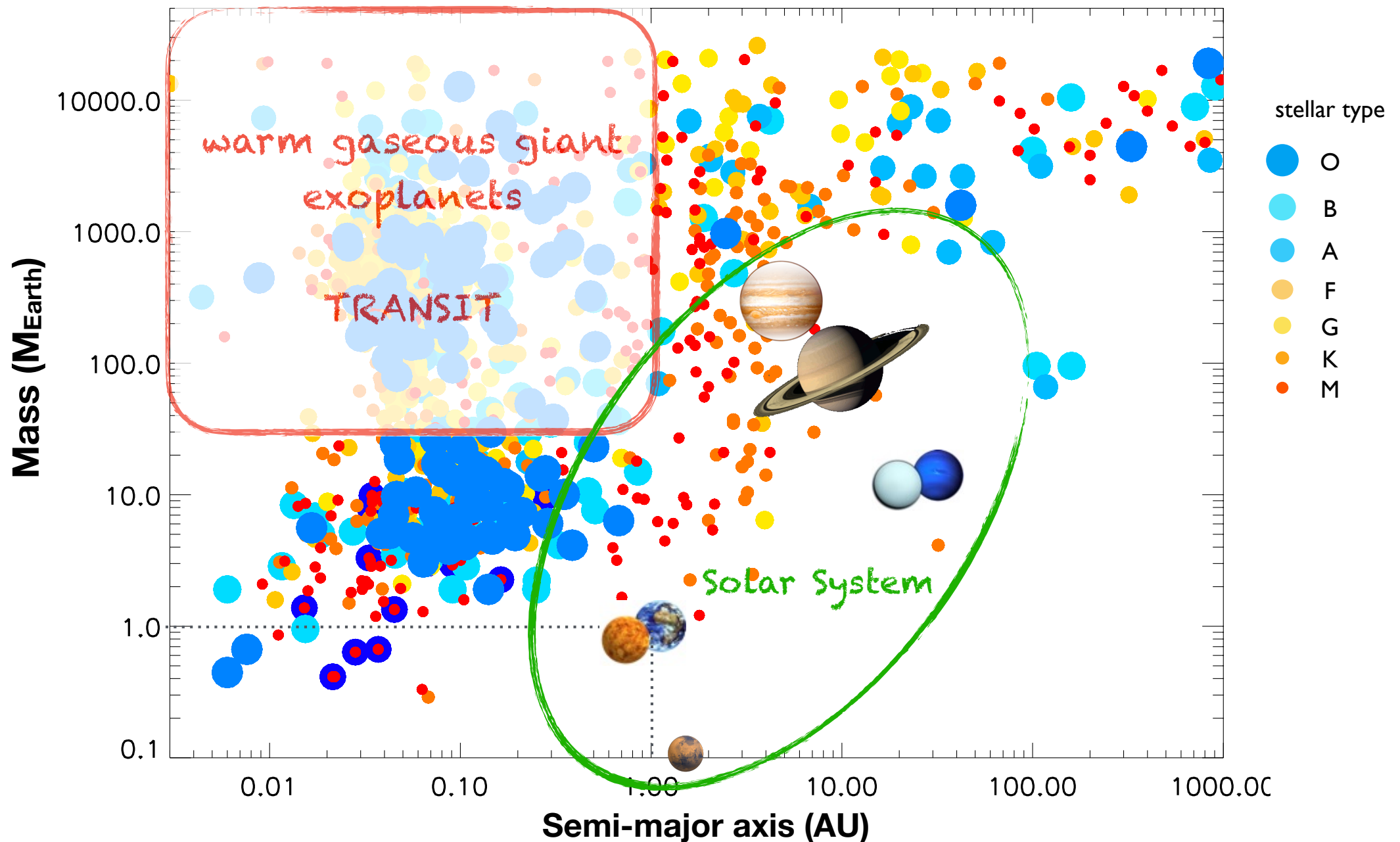
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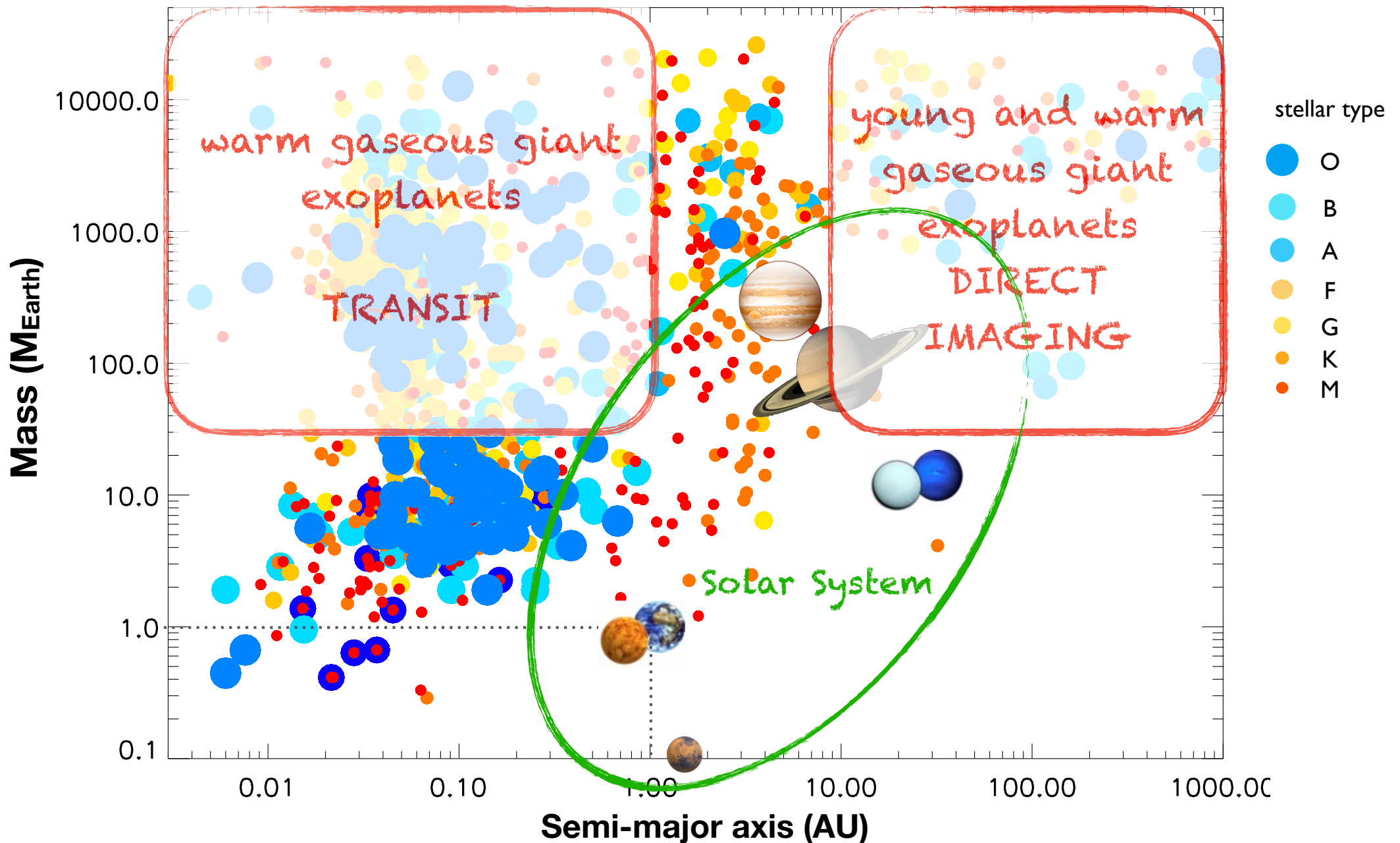




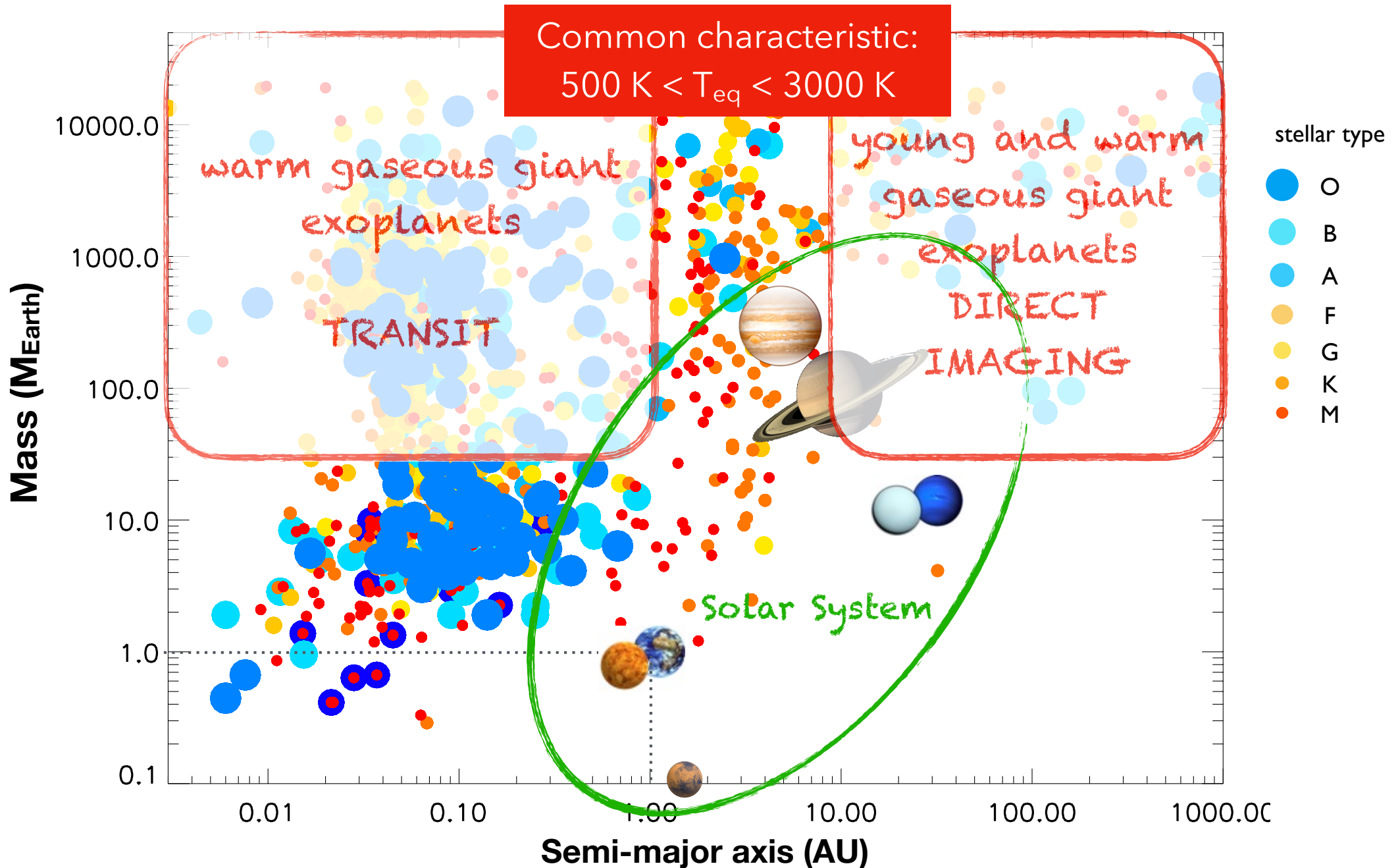
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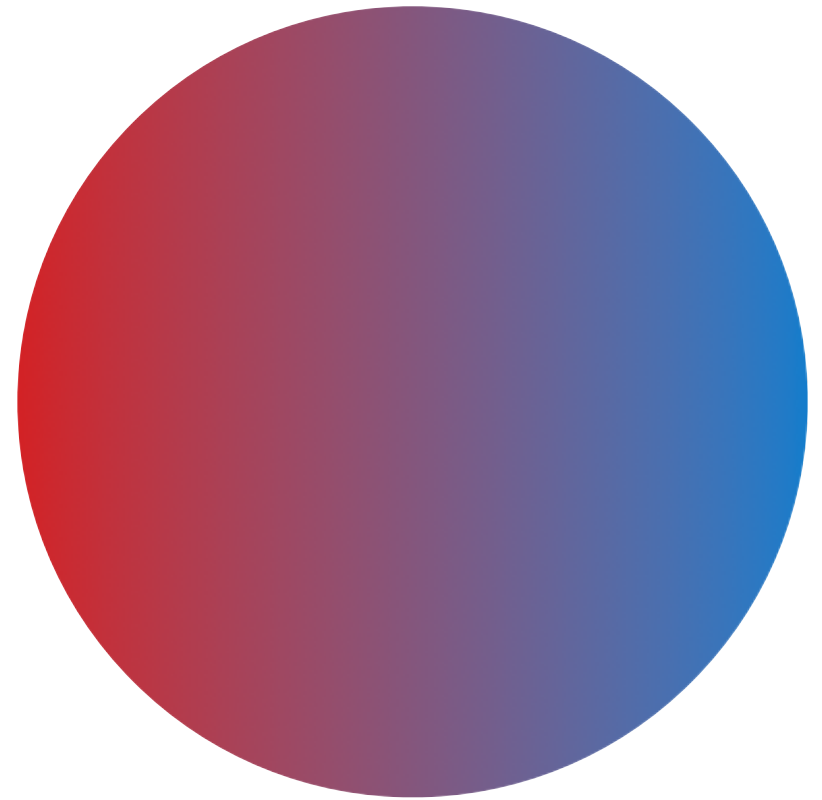
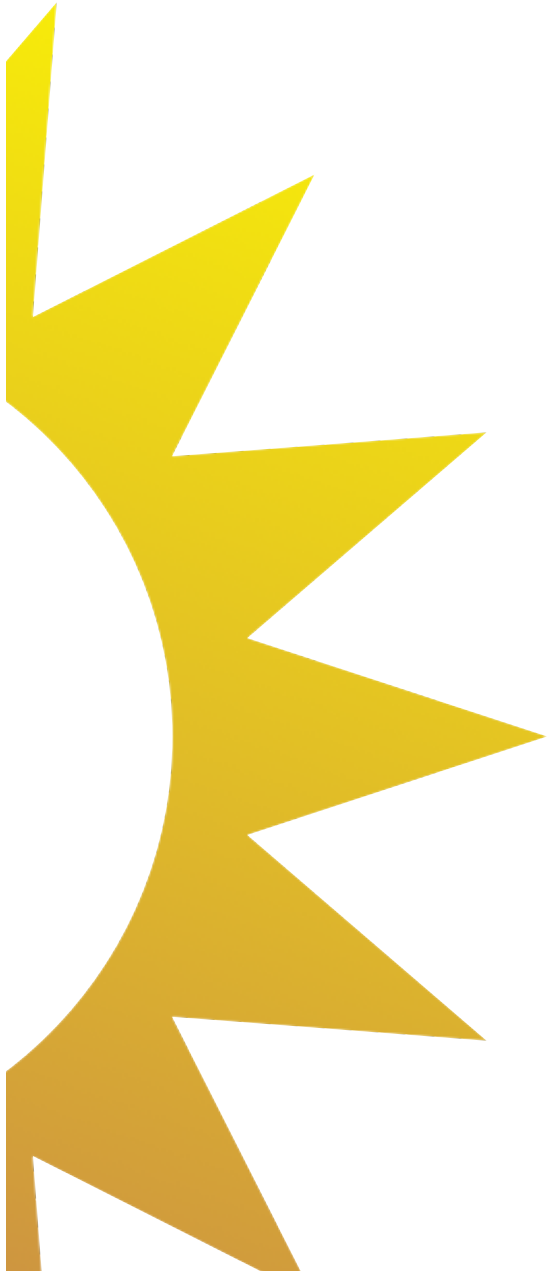


# Diversity of planetary worlds



# Out of equilibrium processes

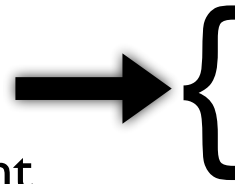
Thermochemical Equilibrium: depends only of P, T, elementary abundances



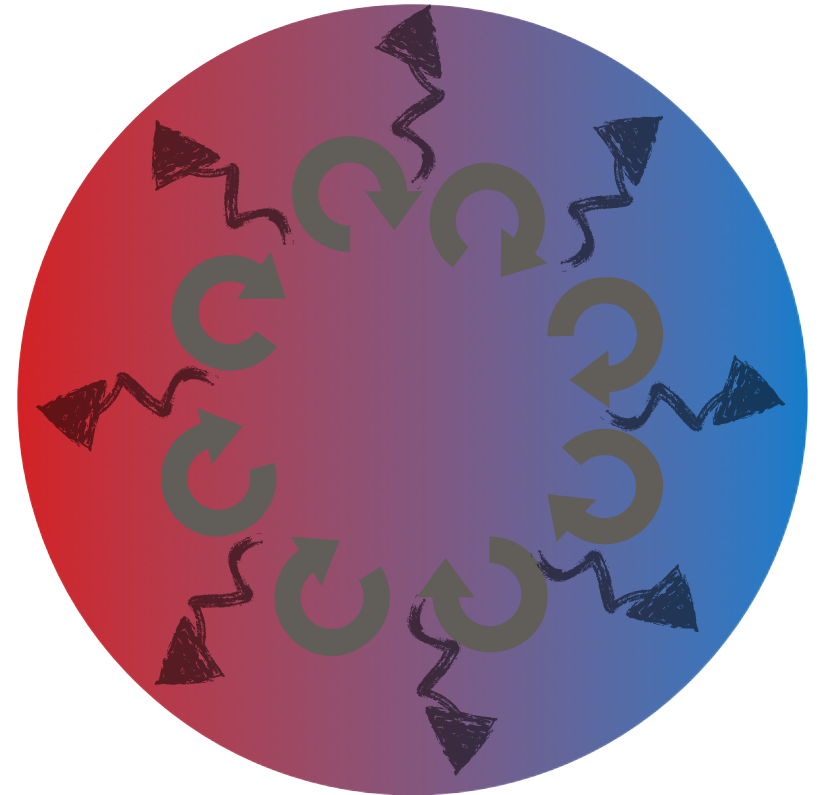
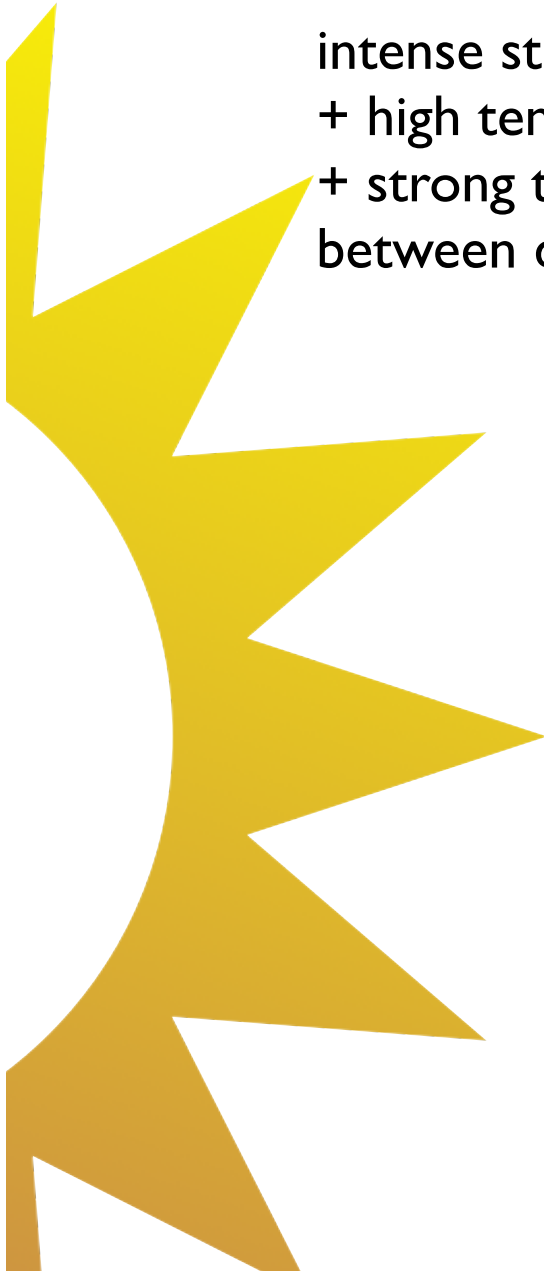
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Thermochemical Equilibrium: depends only of P, T, elementary abundances

intense stellar irradiation  
+ high temperatures  
+ strong temperature gradient  
between day and nightside



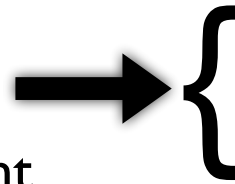
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- vigorous dynamic :
  - horizontale circulation (winds)
  - vertical mixing (convection, turbulence)



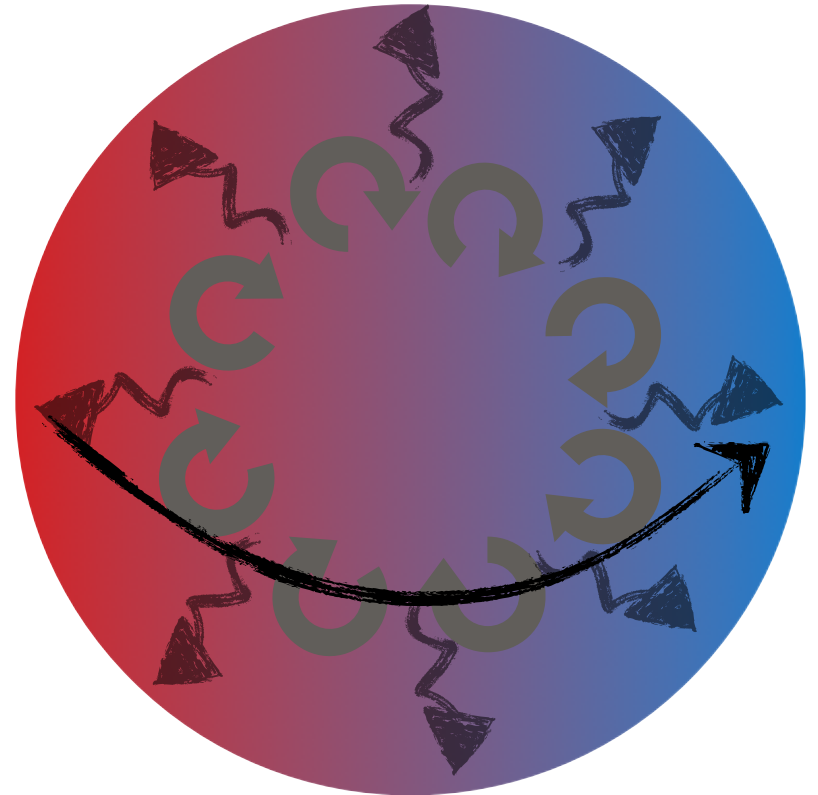
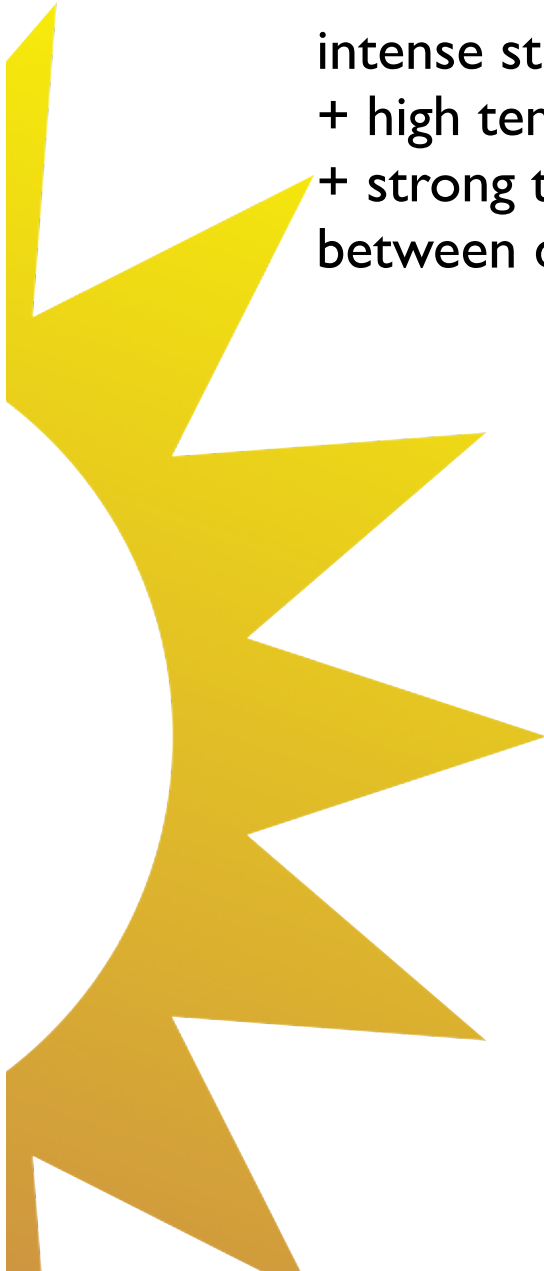
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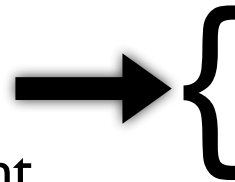
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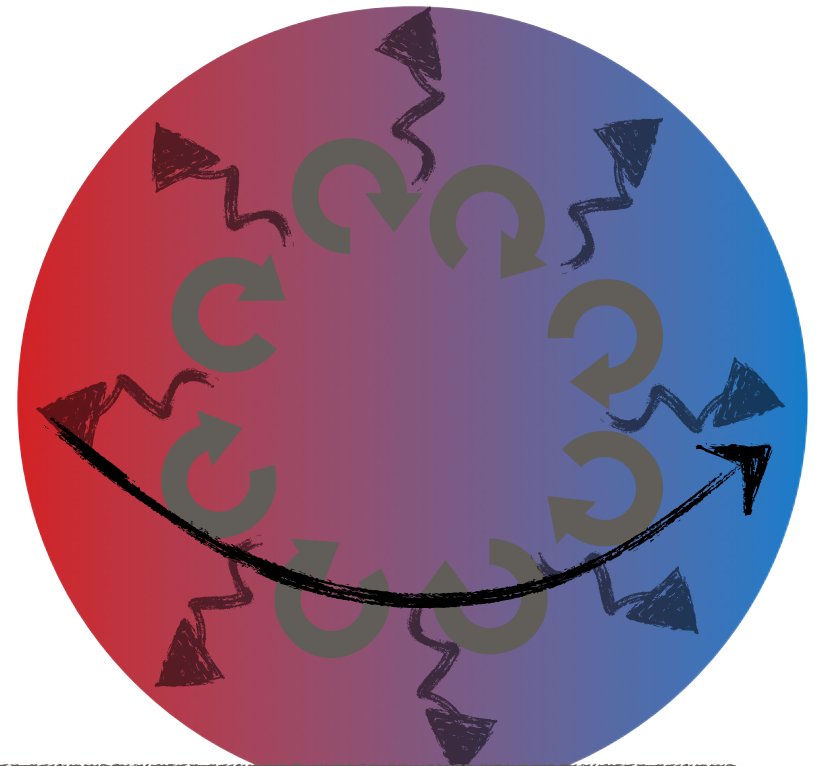
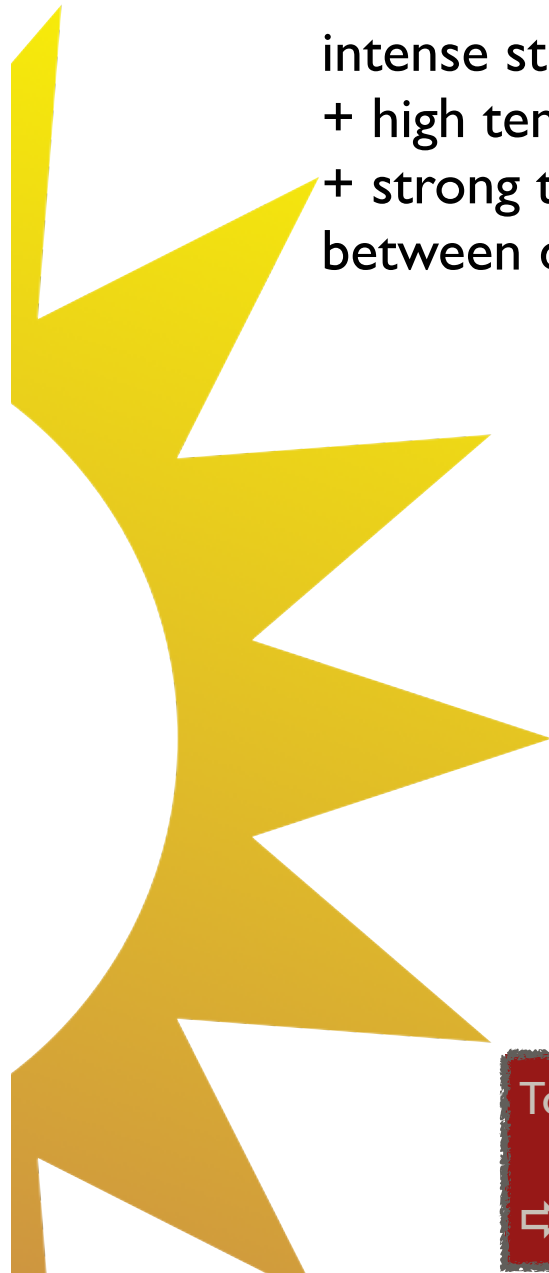
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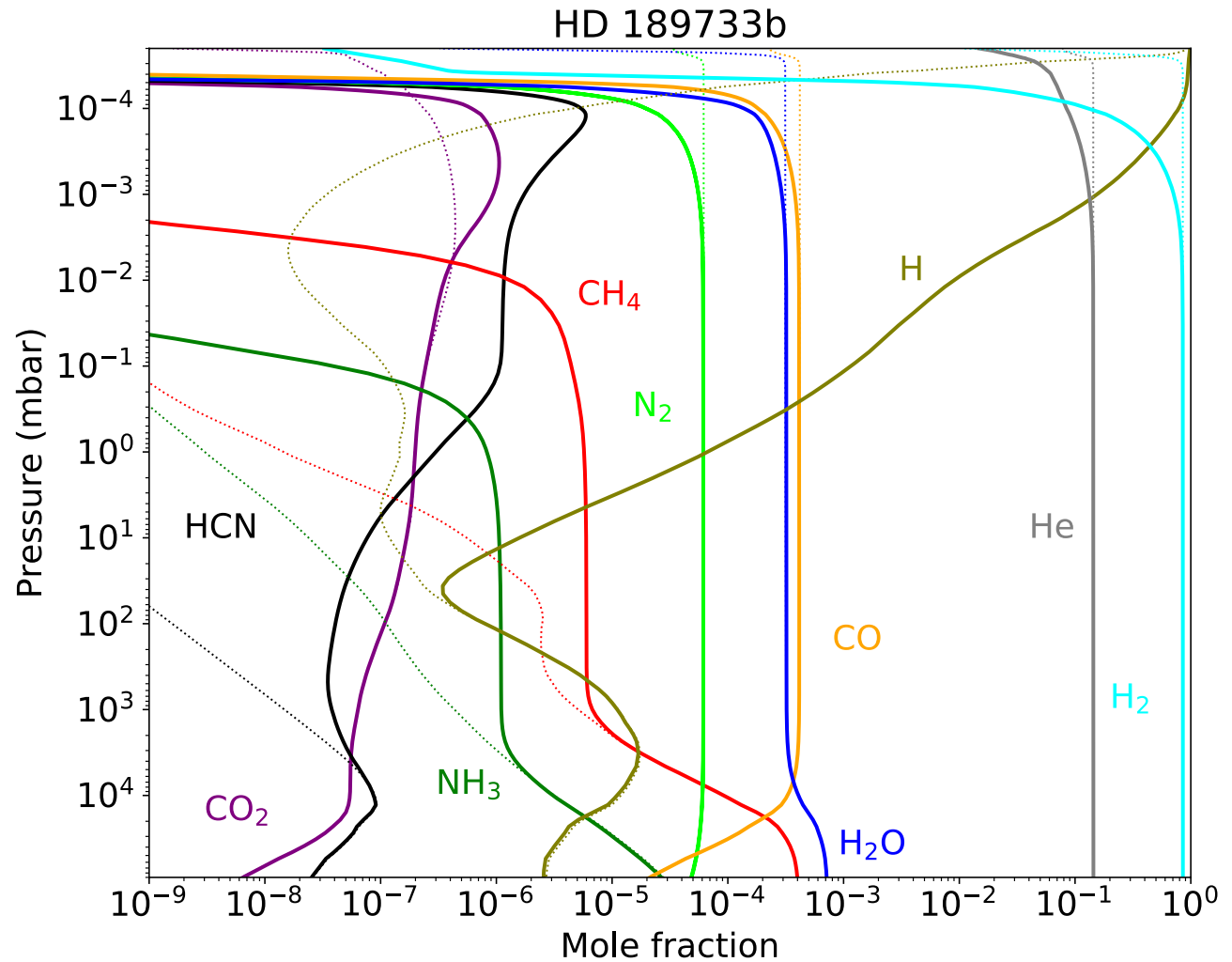
To interpret observations + to understand these atmospheres

⇒ **Need kinetic models !**

# Structure of giant gaseous exoplanets

- From their small density, we know that their atmospheres are dominated by Hydrogen ( $H_2$  or  $H$ ) and Helium

..... thermochemical equilibrium  
— kinetic model

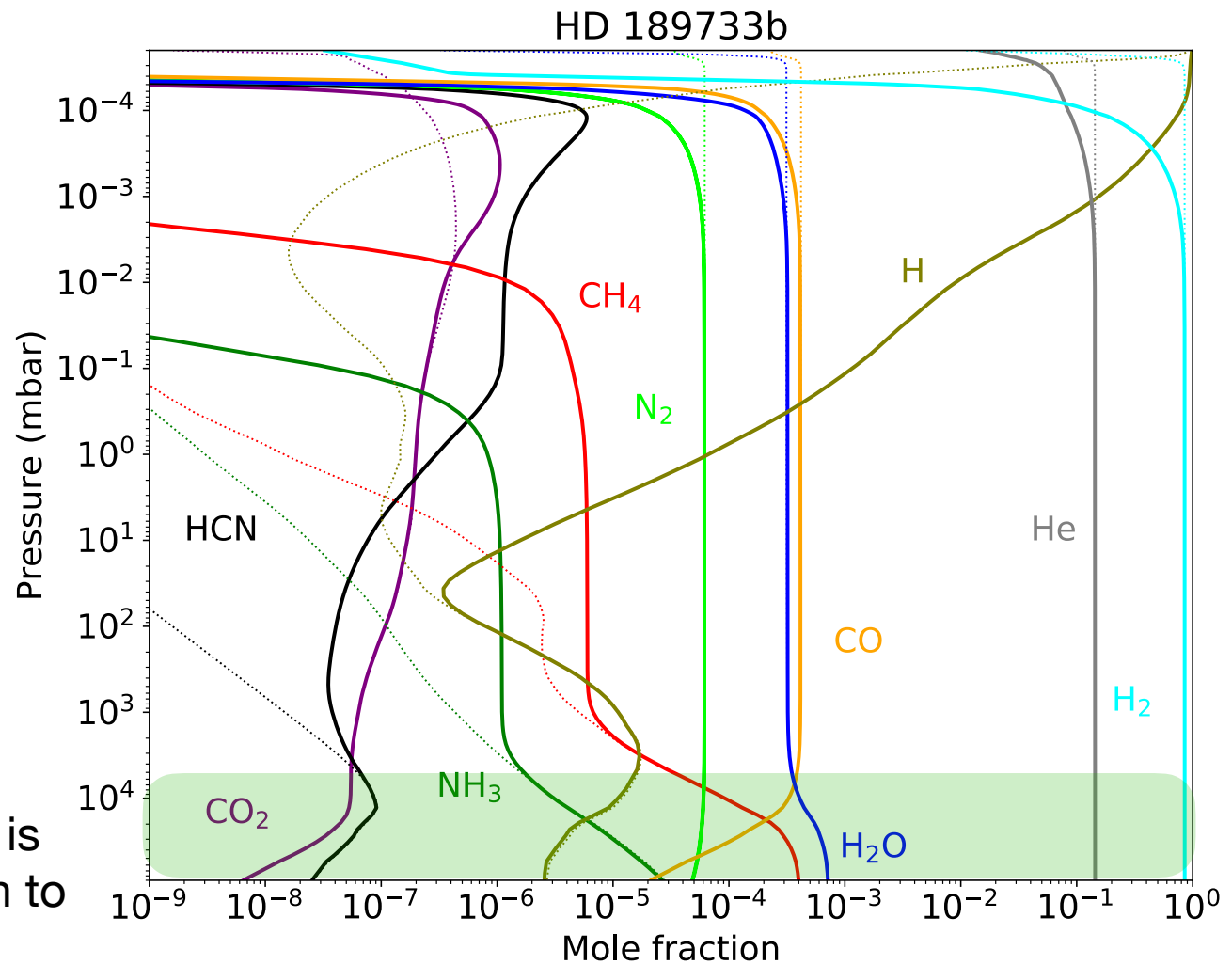




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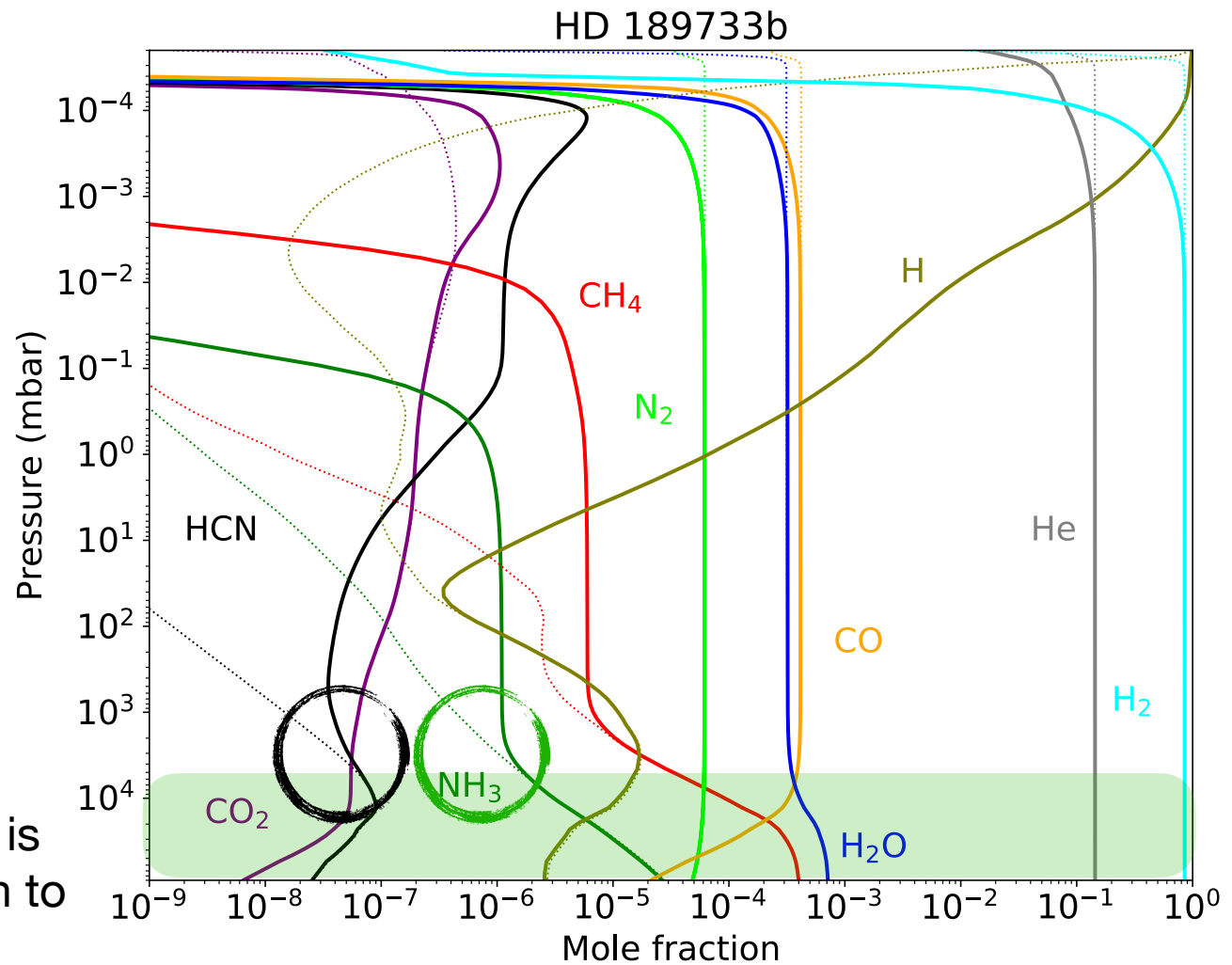


- Thermo equilibrium:** temperature is very high so kinetics is fast enough to reproduce thermo equilibrium

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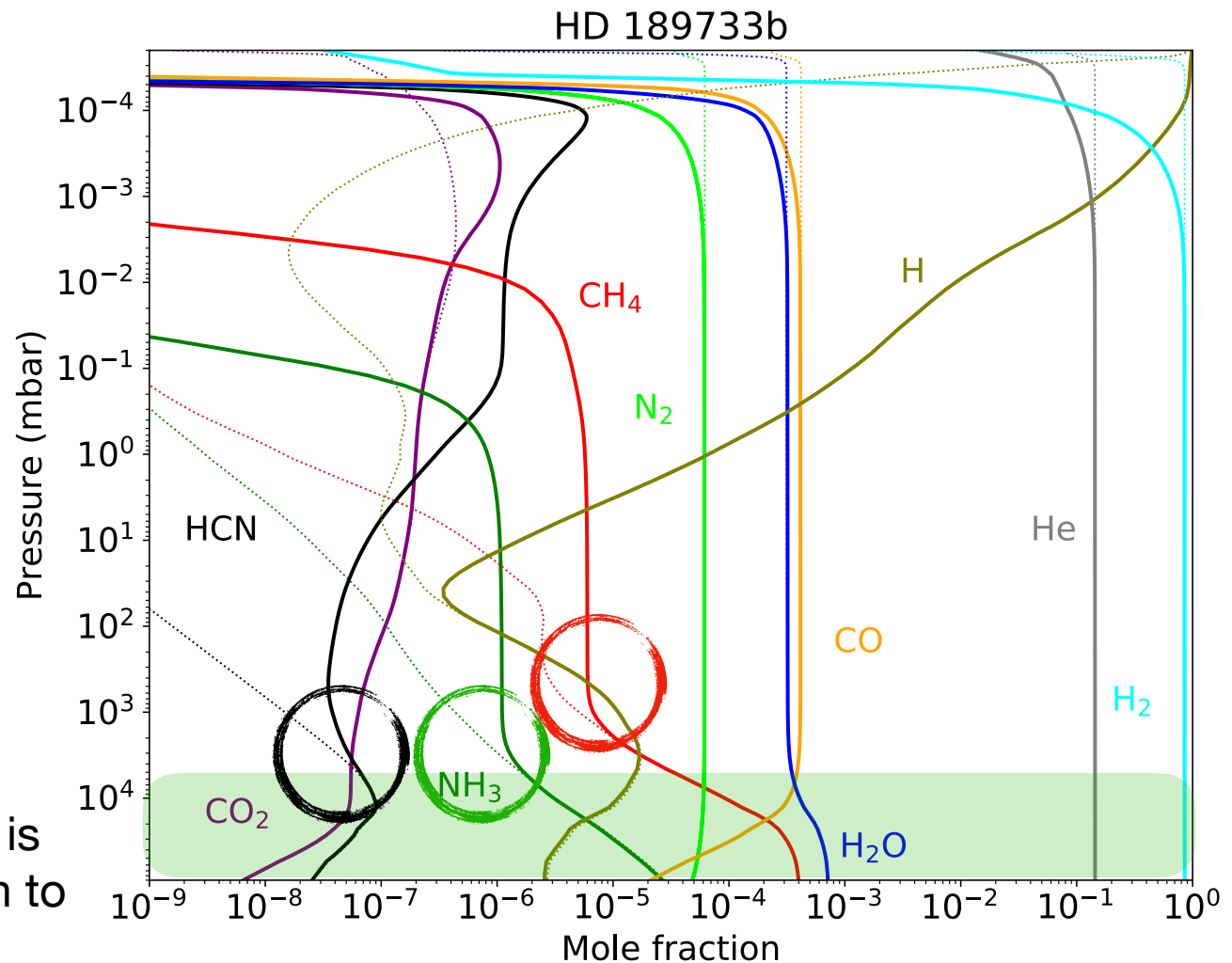
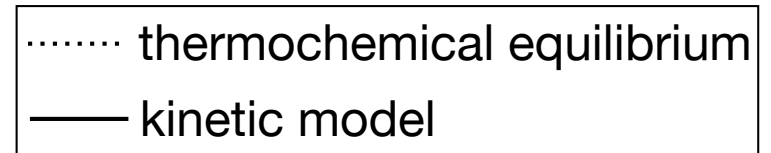
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- Quenching:** abundances depart from thermo equilibrium. They are frozen when  
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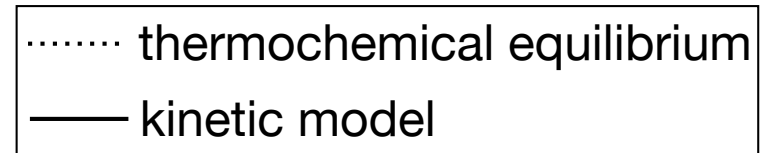
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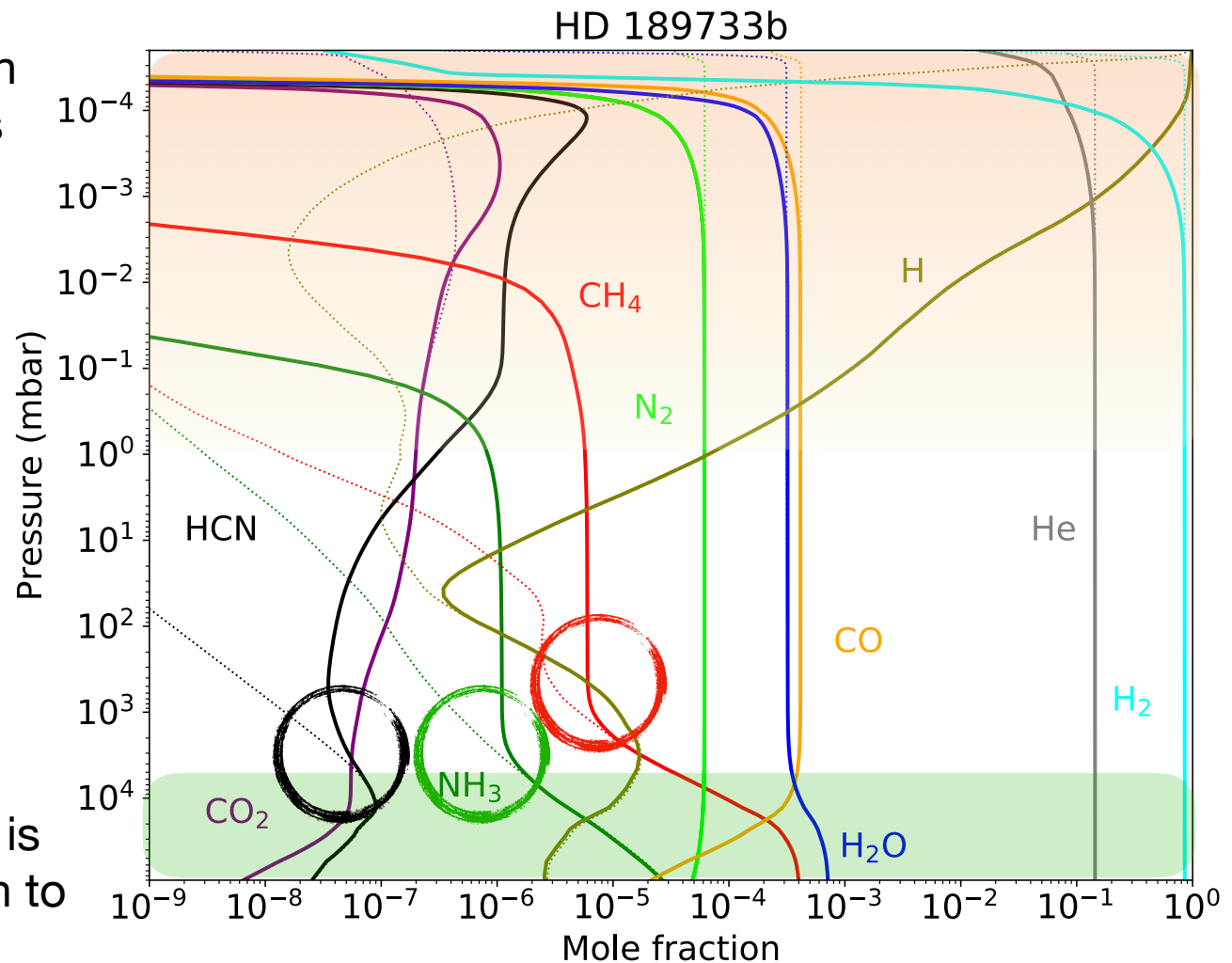
- Photodissociations:** UV irradiation from the star destroys or produces molecules.

- Quenching:** abundances depart from thermo equilibrium. They are frozen when

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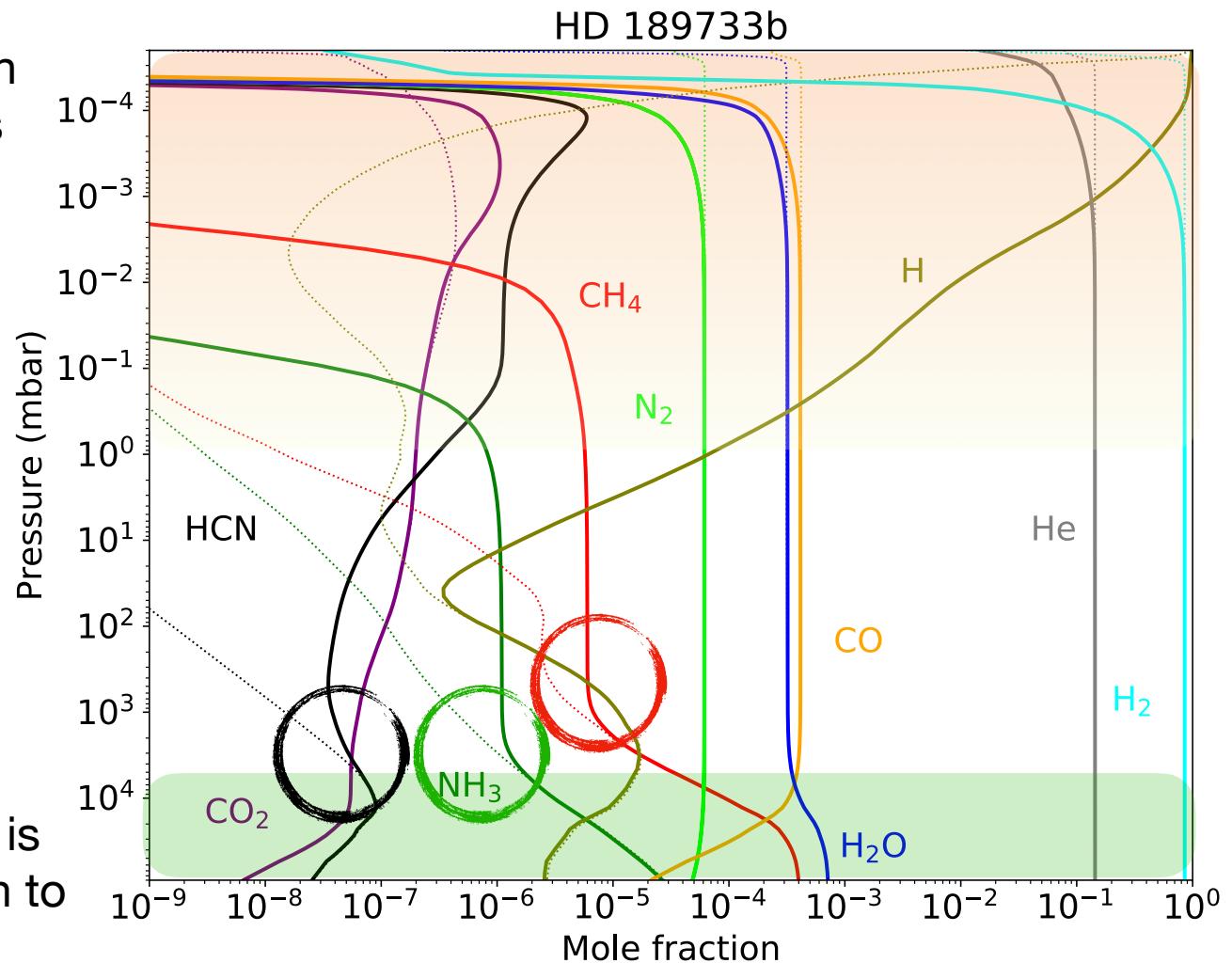


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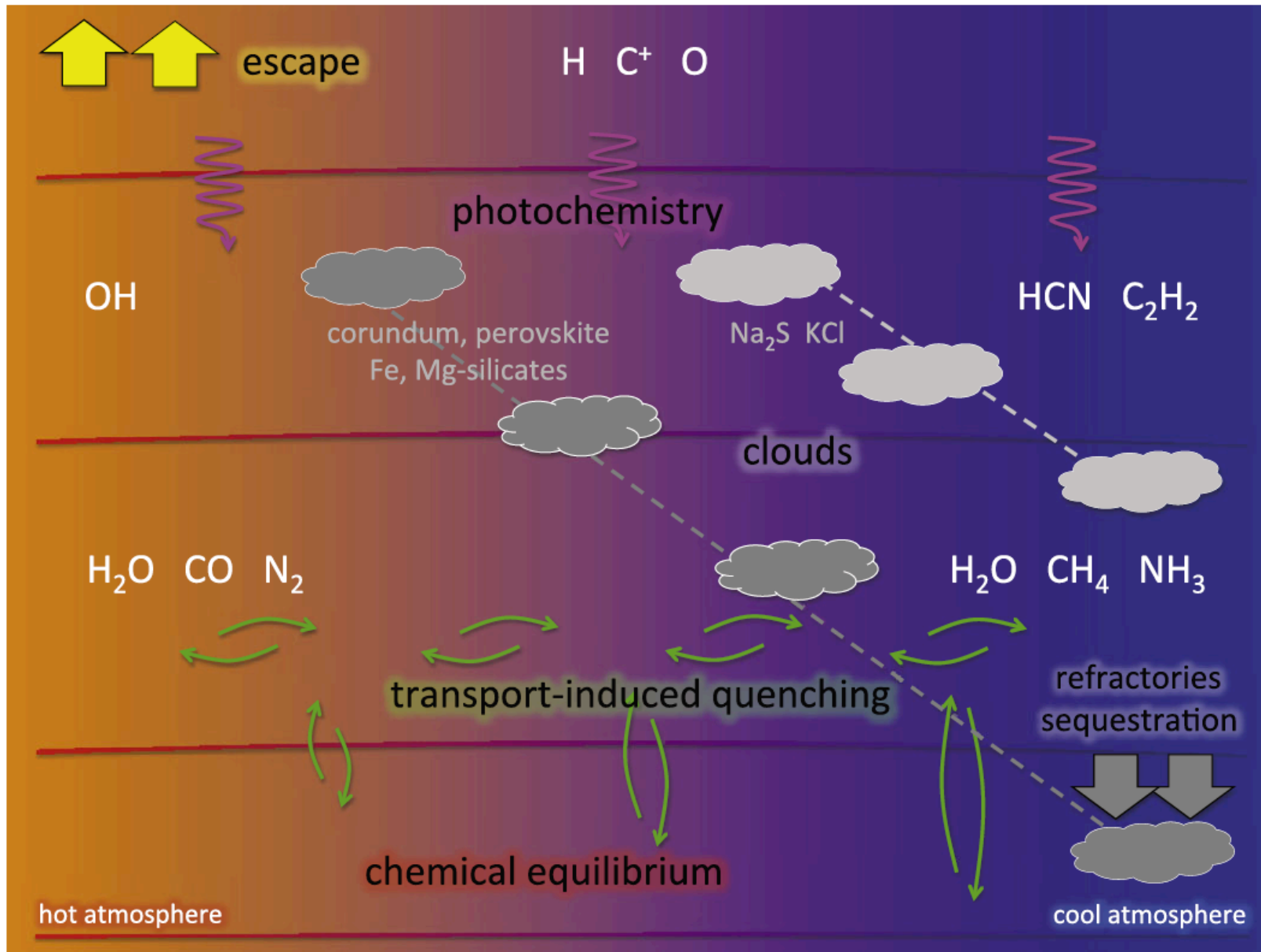
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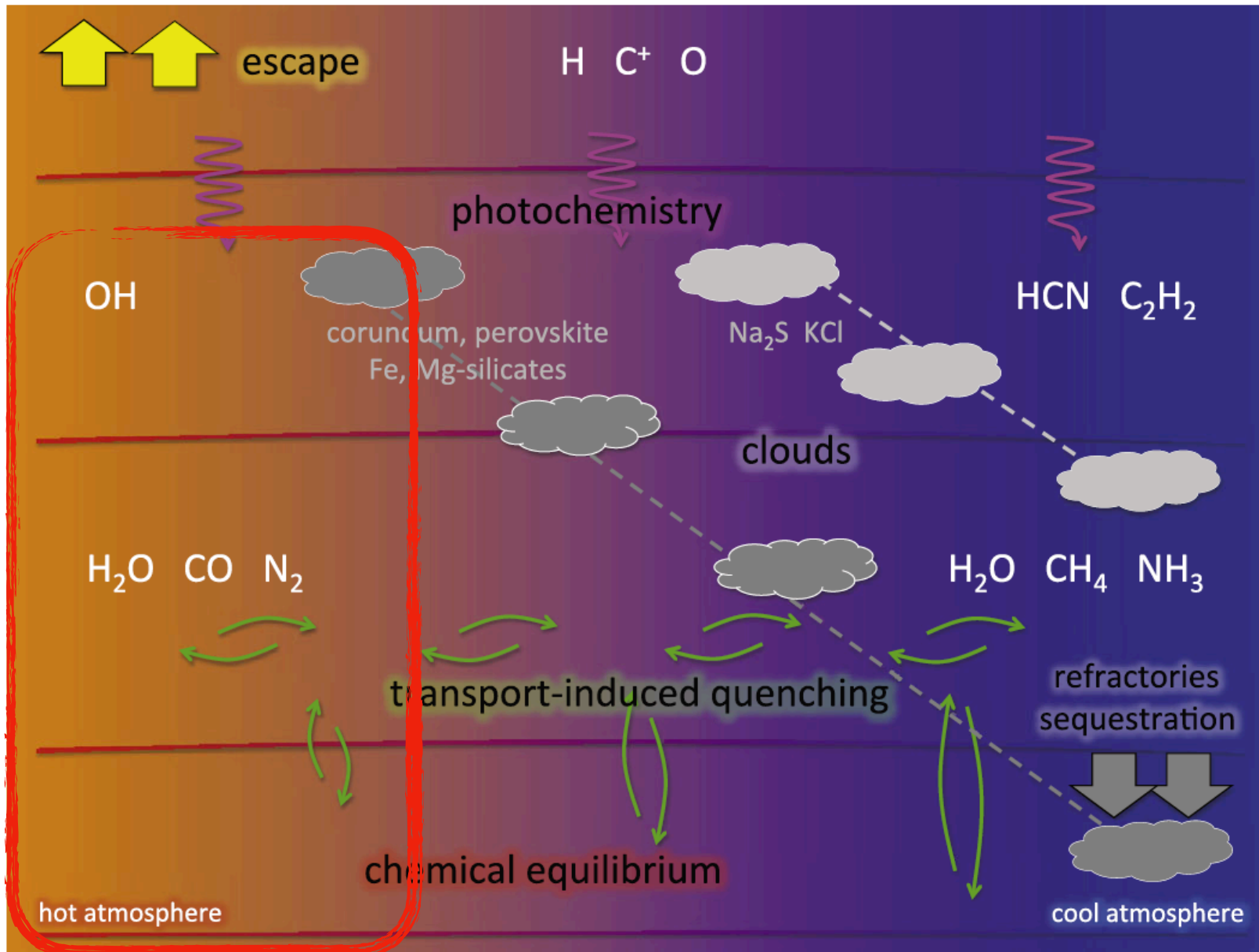
- Photodissociations:** UV irradiation from the star destroys or produces molecules. Effect can be seen as deep as 10/100 mbar
- Quenching:** abundances depart from thermo equilibrium. They are frozen when  $\tau_{chemical} > \tau_{dynamical}$ . This level depends on  $\tau_{chemical}$  so is proper to each species
- Thermo equilibrium:** temperature is very high so kinetics is fast enough to reproduce thermo equilibrium



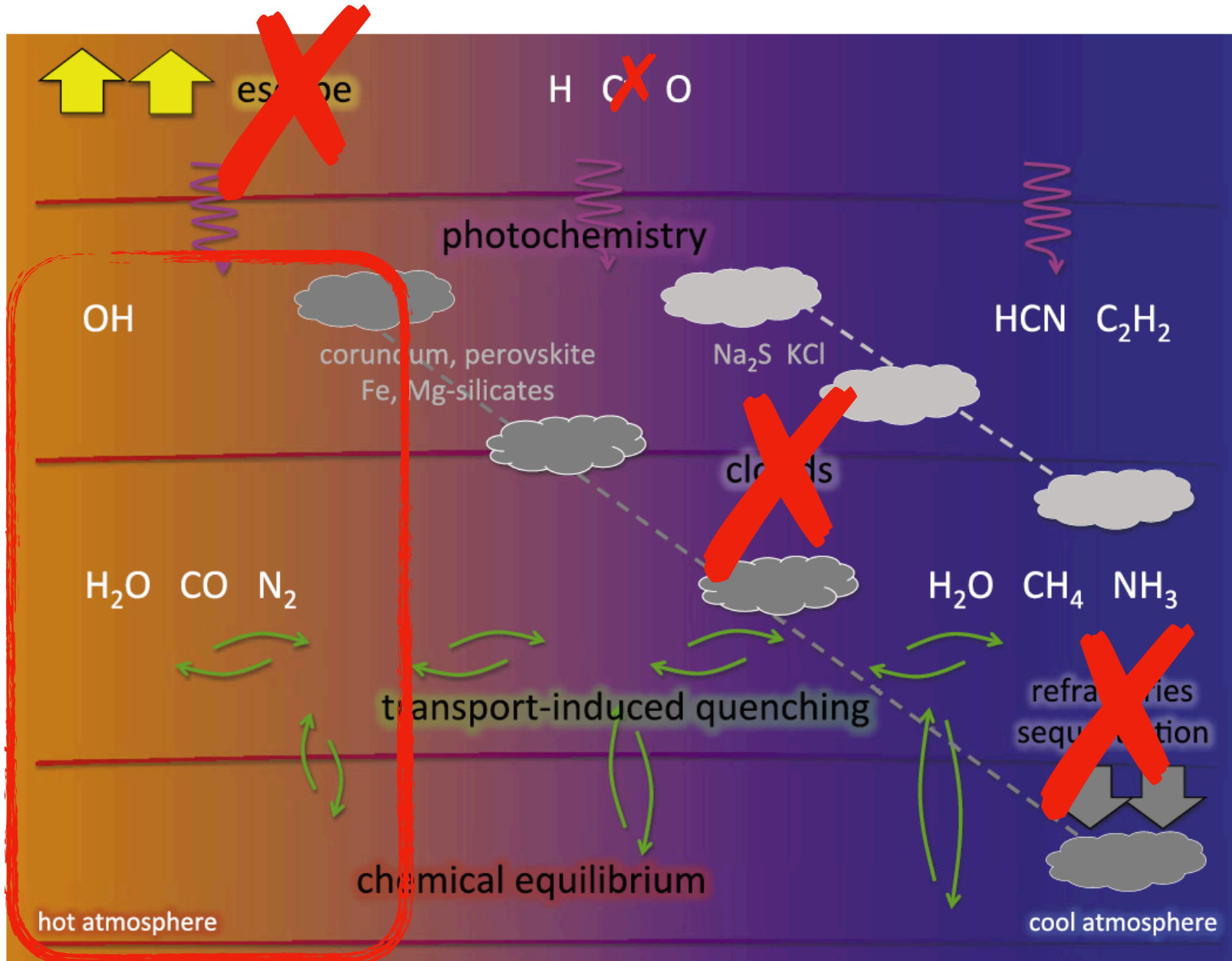
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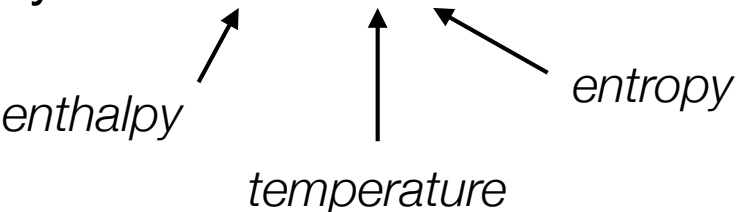
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# Thermodynamic

- In the deep region of hot/warm gaseous giant exoplanets atmospheres, because  $P$  and  $T$  are high, chemical composition corresponds to thermochemical equilibrium.
- The chemical composition in these regions can be calculated using the laws of thermodynamics, considering this region as a closed system.
- The Gibbs free Energy ( $G$ ) is the thermodynamic quantity the most appropriate to study and calculate this chemical equilibrium.

- The Gibbs free Energy is given by :  $G = H - TS$   


The diagram shows the equation  $G = H - TS$  with three arrows pointing to the variables: 'enthalpy' points to  $H$ , 'temperature' points to  $T$ , and 'entropy' points to  $S$ .

# Thermodynamic

- Consider one reaction occurring in a mixture of gases with constant  $P$  and  $T$ .
- The 2nd law of thermodynamics states that the total entropy of an isolated system can never decrease over time:

$$\Delta S_{tot} \geq 0 \text{ with } \Delta S_{tot} = \underbrace{\Delta S_{sys}}_{\text{chemical reaction}} + \underbrace{\Delta S_{ext}}_{\text{mixture of gases}}$$

- The variation of enthalpy of the system corresponds to the heat exchanged during the reaction:  $Q_P = \Delta H_{sys}$

and this variation of enthalpy is received by the exterior  $\Rightarrow \Delta S_{ext} = -\frac{Q_P}{T} = -\frac{\Delta H_{sys}}{T}$

- $\Delta S_{sys} - \frac{\Delta H_{sys}}{T} \geq 0 \Rightarrow \Delta H_{sys} - T\Delta S_{sys} \leq 0 \Rightarrow \boxed{\Delta G_{sys} \leq 0}$

- The reaction can occur only if the Gibbs Energy of the system decreases and the equilibrium state will be reached for the minimum of  $G_{sys}$ .

# Thermodynamic

- In a system composed of  $L$  species, the Gibbs Energy of the system can be expressed as a function of the partial Gibbs Energy (=chemical potential) of each species  $l$ :  $G_{sys} = \sum_{l=1}^L \mu_l N_l$

with  $\mu_l = g_l(T, P) + RT \ln N_l$  and  $N_l$  the number of moles of species  $l$

- The Gibbs Energy of species  $l$  is :  $g_l(T, P) = h_l(T) - Ts_l(T)$ .
- Let express  $h_l(T)$  and  $s_l(T)$  with the values at Normal conditions of Pressure ( $P^0 = 1.01325$  bar)  
 $h_l(T)$  does not depend on P =>  $h_l(T) = h_l^0(T)$  (at  $P^0$ )  
 $s_l(T)$  does depend on P => a term depending on pressure must be added:  
 $g_l(T, P) = h_l^0(T) - Ts_l^0(T) + RT \ln \frac{P}{P^0}$
- Finally, the total Gibbs Energy of the system is given by:

$$G_{sys} = \sum_{l=1}^L \left( h_l^0(T) - Ts_l^0(T) + RT \ln \frac{P}{P^0} + RT \ln N_l \right) \times N_l$$

# NASA coefficients

- The thermodynamic properties of species  $h_i^0(T)$  and  $s_i^0(T)$  can be computed numerically thanks to NASA polynomials.

```
H2O          20387H   20   1           G  0300.00   5000.00  1000.00   1
0.02672145E+02 0.03056293E-01-0.08730260E-05 0.12009964E-09-0.06391618E-13 2
-0.02989921E+06 0.06862817E+02 0.03386842E+02 0.03474982E-01-0.06354696E-04 3
0.06968581E-07-0.02506588E-10-0.03020811E+06 0.02590232E+02 4
```

- For each species, two sets of coefficients exist, corresponding to two ranges of temperature. In the format found in the literature, the first set of coefficients corresponds to the high temperature range (1000-6000 K), the second set to the low temperature range (300-1000 K)
- Originally, the format of these polynomials used 7 coefficients, but the update NASA polynomial format is using 9 coefficients. However, both format are still regularly used.

- 7-coefficients format :**

$$\frac{h_i^0(T)}{RT} = a_{1l} + \frac{a_{2l}T}{2} + \frac{a_{3l}T^2}{3} + \frac{a_{4l}T^3}{4} + \frac{a_{5l}T^4}{5} + \frac{a_{6l}}{T}$$

$$\frac{s_i^0(T)}{R} = a_{1l} \ln T + a_{2l}T + \frac{a_{3l}T^2}{2} + \frac{a_{4l}T^3}{3} + \frac{a_{5l}T^4}{4} + a_{7l}$$

- 9-coefficients format :**

$$\frac{h_i^0(T)}{RT} = -\frac{a_{1l}}{T^2} + \frac{a_{2l} \ln T}{T} + a_{3l} + \frac{a_{4l}T}{2} + \frac{a_{5l}T^2}{3} + \frac{a_{6l}T^3}{4} + \frac{a_{7l}T^4}{5} + \frac{a_{8l}}{T}$$

$$\frac{s_i^0(T)}{R} = -\frac{a_{1l}}{2T^2} - \frac{a_{2l}}{T} + a_{3l} \ln T + a_{4l}T + \frac{a_{5l}T^2}{2} + \frac{a_{6l}T^3}{3} + \frac{a_{7l}T^4}{4} + a_{9l}$$

# Equilibrium composition

- Reminder: the Gibbs free Energy of the system is :

$$G_{sys} = \sum_{l=1}^L (h_l^0(T) - Ts_l^0(T) + RT \ln \frac{P}{P_0} + RT \ln N_l) \times N_l$$

- With NASA coefficients, we are able to calculate each term of this formula.
- For an initial molecular composition (or initial elemental abundances), the set of  $N_l$  that permits to have the lower  $G_{sys}$  will correspond to the thermochemical equilibrium composition.
- This composition is found numerically, with a Newton-Raphson method for instance.

# Repartition of chemical elements



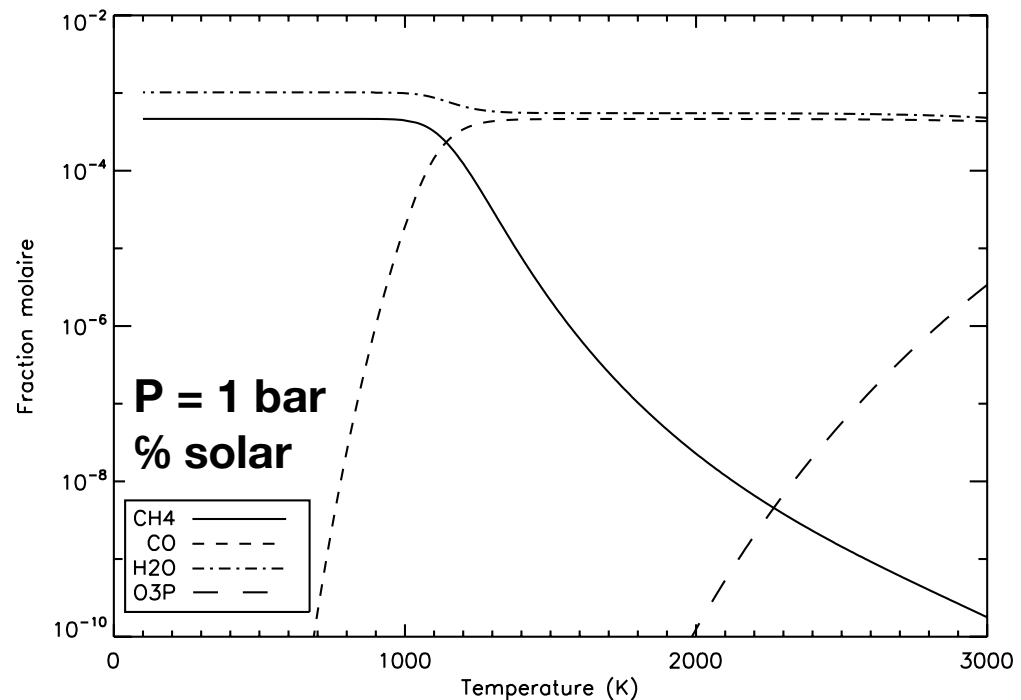
**Application** : Study the molecular composition of a mixture of gases as a function of T (between 200 and 2000K)

- P = 0.001 bar (2 groups)
- P = 1 bar (2 groups)
- P = 100 bar (2 groups)

- go on <http://navier.engr.colostate.edu/code/code-4/index.html>
- elements: C, H, O, N, He
- initial:  $y_{\text{H}_2} = 0.8317$ ,  $y_{\text{He}} = 0.1663$ ,  $y_{\text{C}} = 6.643 \times 10^{-4}$ ,  $y_{\text{O}} = 1.331 \times 10^{-3}$ ,  $y_{\text{N}} = 1.422 \times 10^{-4}$
- additional species: H, CH<sub>4</sub>, CO<sub>2</sub>, CH<sub>3</sub>, CO, H<sub>2</sub>O, O<sub>2</sub>, N<sub>2</sub>, NH<sub>3</sub>, HCN
- ➡ which are the dominant molecules as a function of T ?
- ➡ at which T does the transition for the main C-bearing species occur?
- ➡ same question for the main N-bearing species?

# Repartition of chemical elements

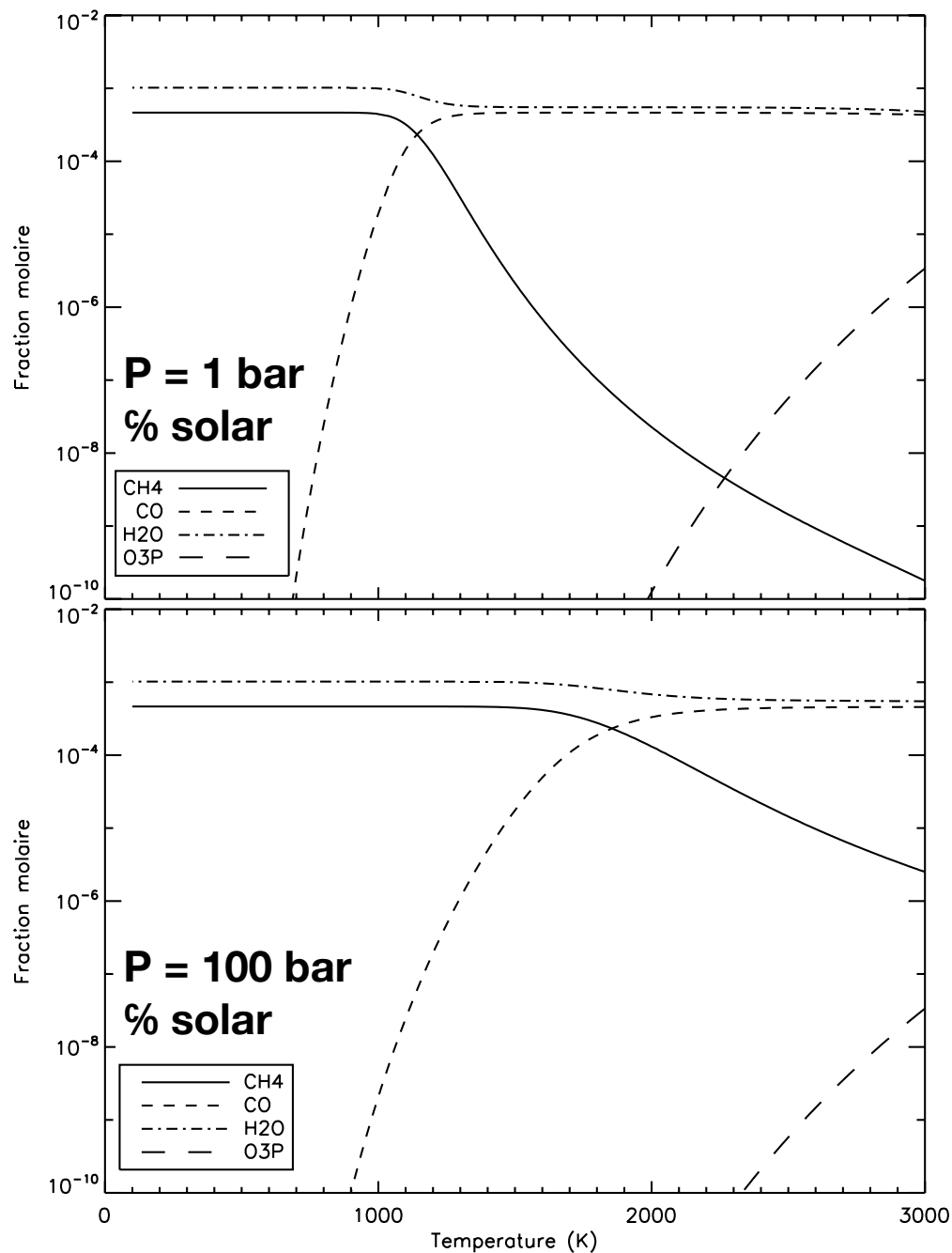
- We can thus determine how the chemical elements are distributed among the different species as a function of T:
- For **solar elemental abundances** ( $\% = 0.46$ ), Carbon is mainly under the form of  $\text{CH}_4$  at low T. At higher T, CO is the main C-bearing species. Transition occurs about **1100 K**.
- $\text{H}_2\text{O}$  is the main O-bearing species (up to 3000 K), but sees its abundance decrease when that of CO increases.





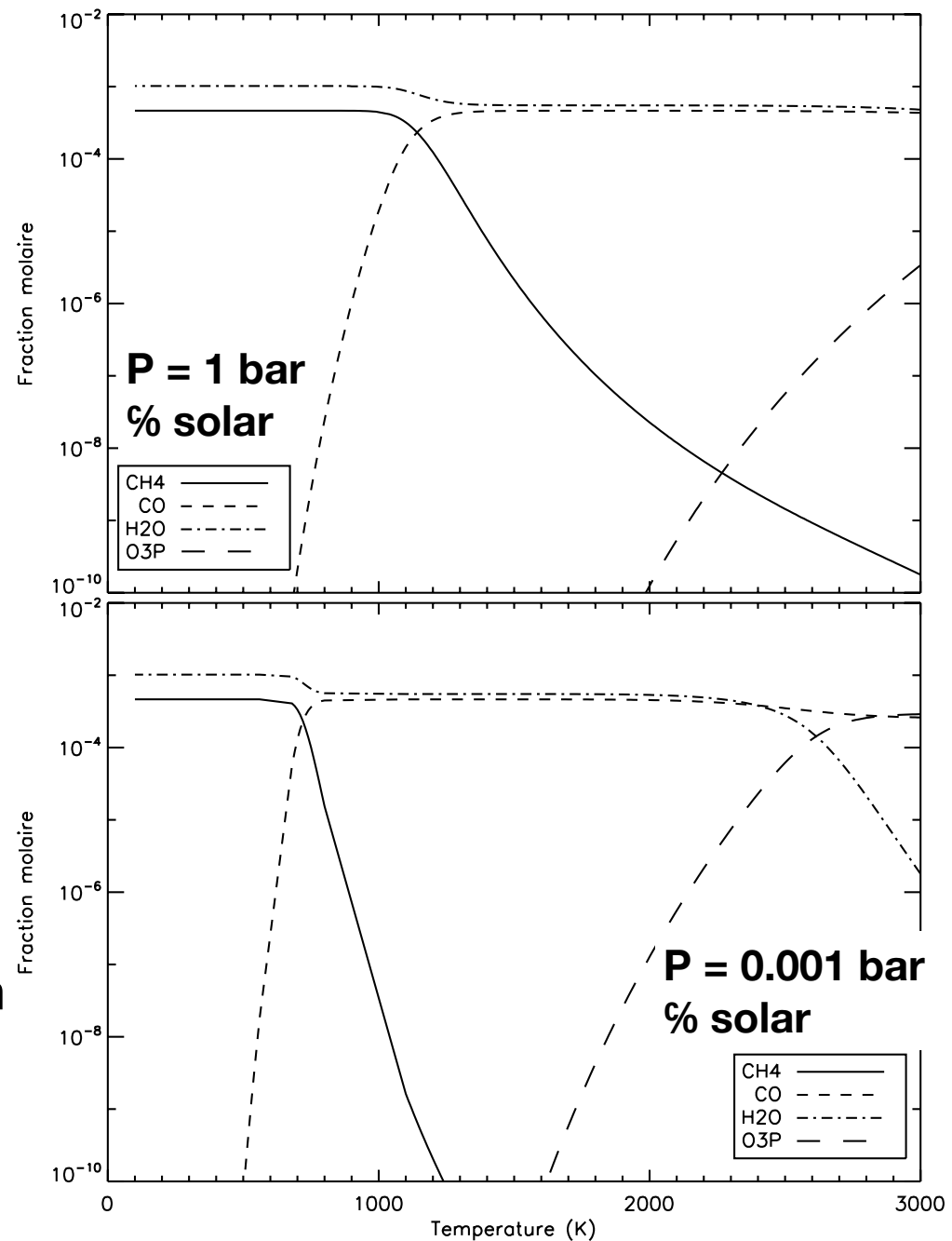
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- We can also see that  $P$  has an influence:
- At  $P = 100$  bar, transition between  $\text{CO}/\text{CH}_4$  occurs at higher  $T$  than at 1 bar:  **$\sim 1800$  K.**



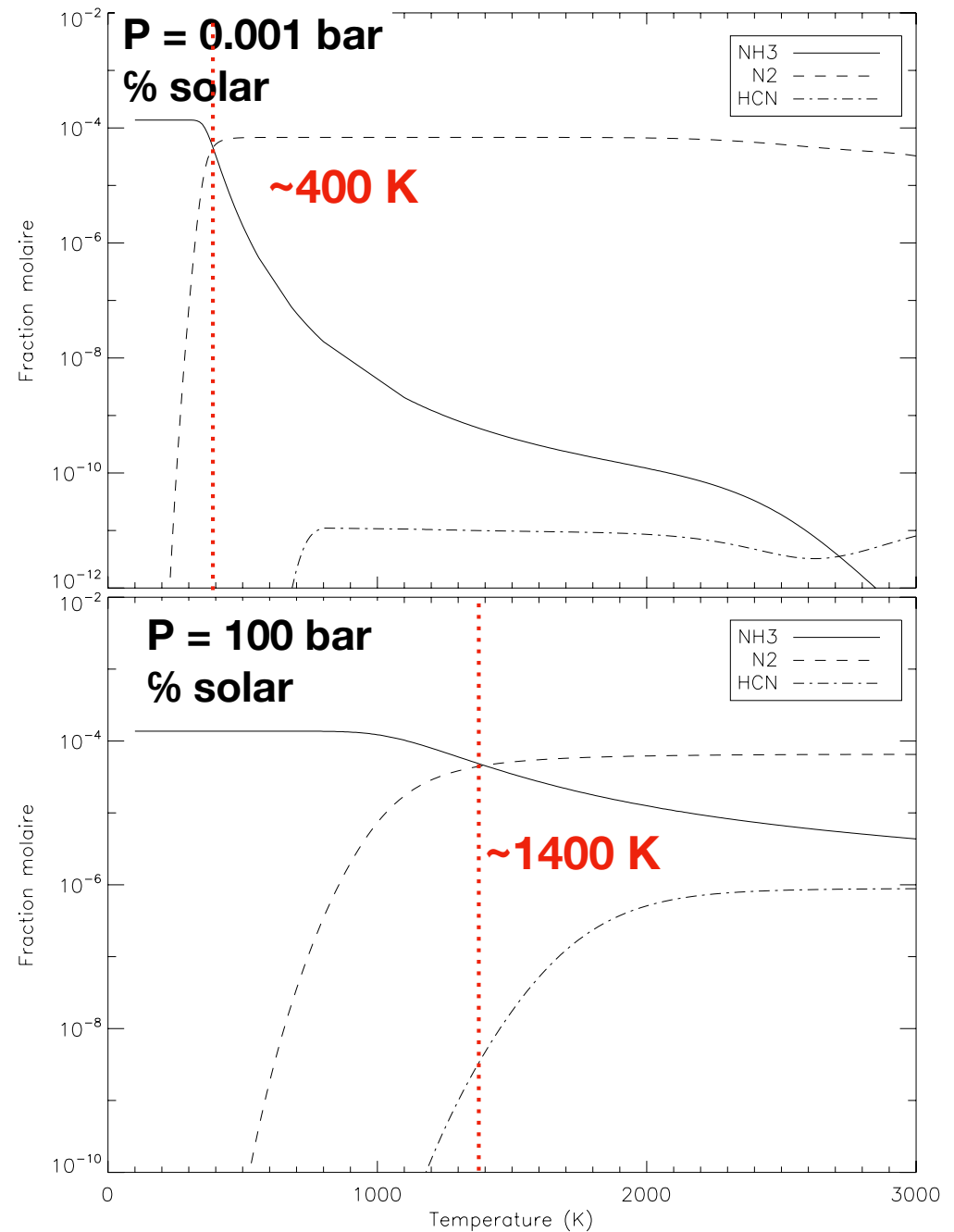
# Repartition of chemical elements

- Conversely, when  $P$  decreases transition between  $\text{CO}/\text{CH}_4$  occurs at lower  $T$ .  
At **0.001 bar**, transition happens at  **$\sim 700$  K**.
- $\text{CO}$  becomes more abundant than  $\text{H}_2\text{O}$  about 2500K.
- We notice the increase of molecular oxygen, which becomes the reservoir of oxygen after 2900 K.



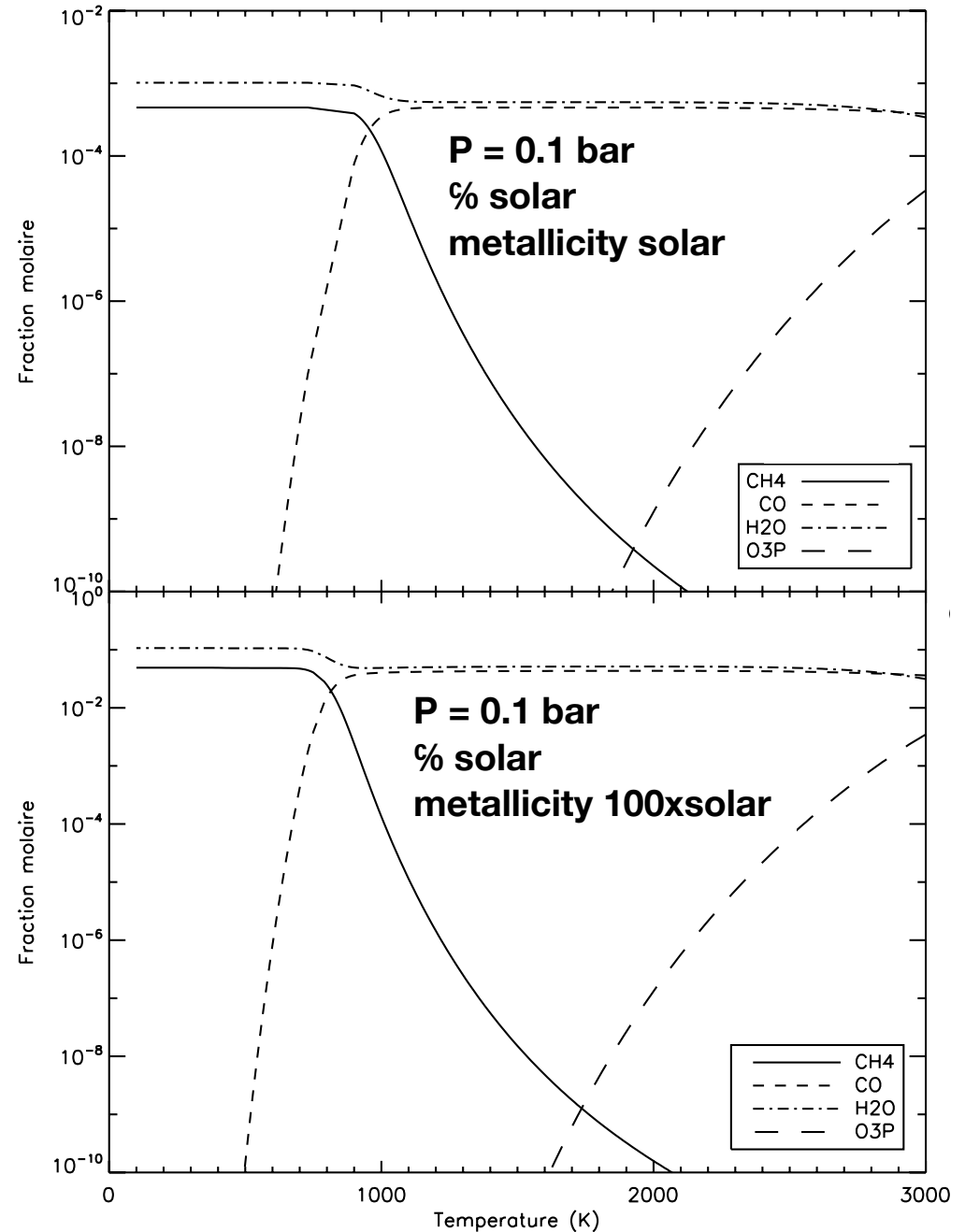
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- The same behaviour is observed for Nitrogen species,  $\text{NH}_3$  being the N-bearing species at low T,  $\text{N}_2$  at high T.
- Temperature of transition increases together with P.



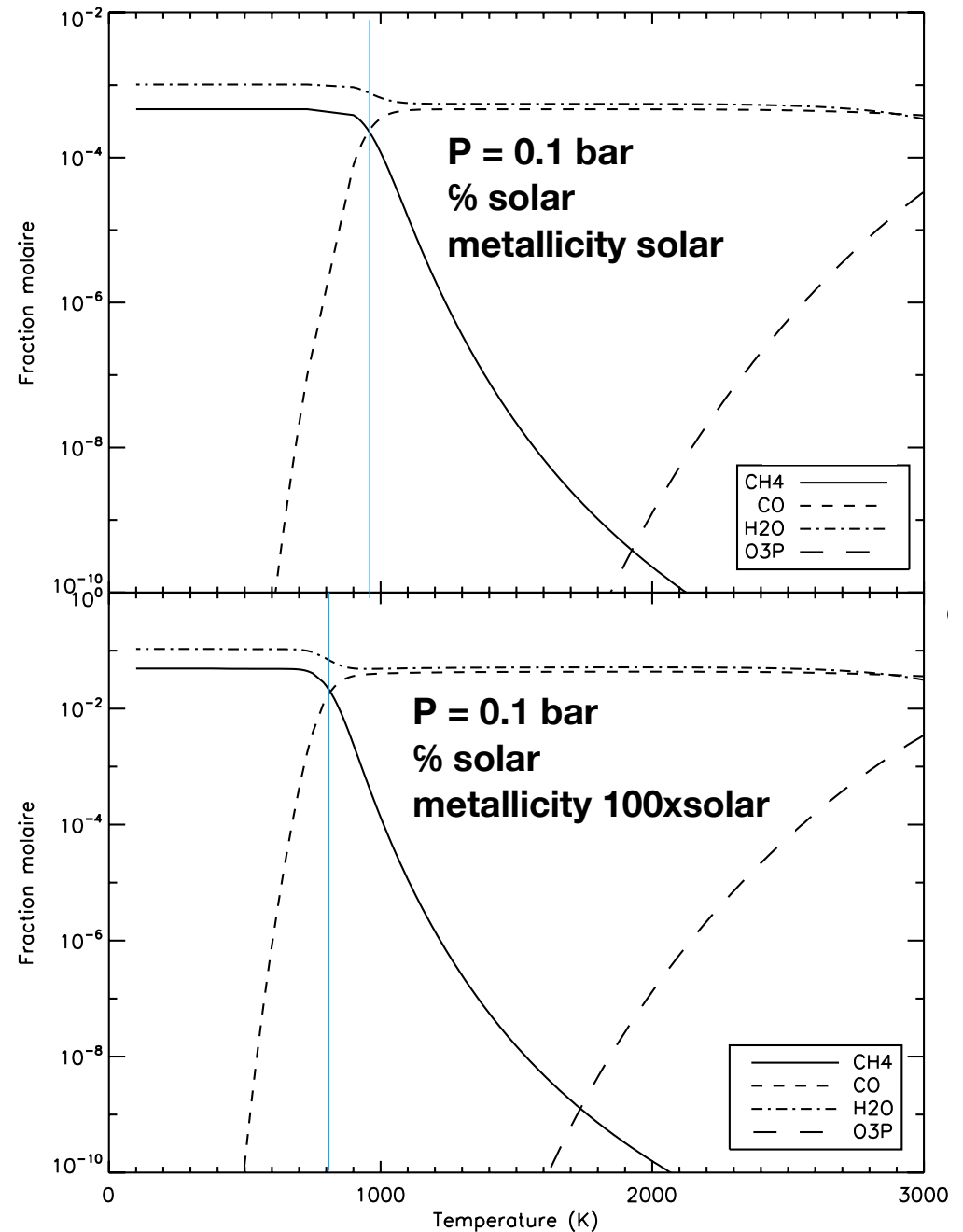
# Repartition of chemical elements

- For a given elemental composition, P and T determine the molecular composition.
- The elemental composition influences also the molecular composition (i.e. C/H, O/H, N/H)



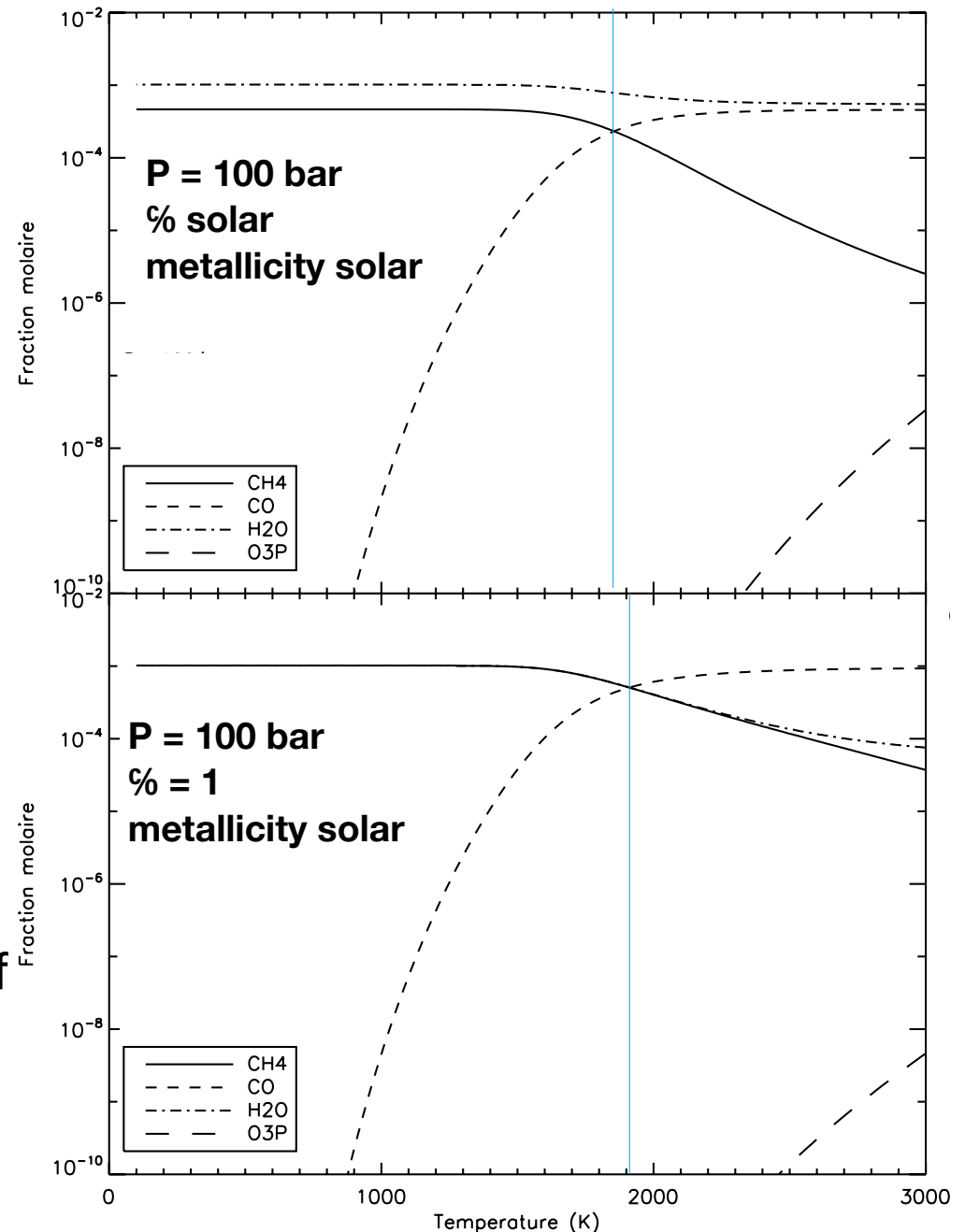
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# Repartition of chemical elements

- For a given elemental composition, P and T determine the molecular composition.
- The elemental composition influences also the molecular composition (i.e. C/H, O/H, N/H)
- An increase of the metallicity lowers the temperature of transition between CO / CH<sub>4</sub> (same for N<sub>2</sub>/NH<sub>3</sub>)
- An increase of the % ratio also slightly increases the temperature of transition.
- At high T and %=1, CO is the main C- and O-bearing species.



# Reaction quotient

- Thermodynamic is useful but does not give information on the time required to reach equilibrium. In planetary atmospheres, disequilibrium processes compete with chemical reactions, so ...

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- Let consider a reversible reaction of the general form  

$$\sum_{l=1}^L \nu_l' \chi_l = \sum_{l=1}^L \nu_l'' \chi_l$$
 with  $\nu_l'$  and  $\nu_l''$  the stoichiometric coefficients in the forward and reverse direction respectively

- At any time  $t$ , the reaction quotient is defined as

$$Q_R(t) = \prod_{l=1}^L a_l(t)^{\nu_l}$$

- The activity of a species  $a_l$  is a dimensionless quantity defined as the ratio of its partial pressure to its standard pressure ( $a_l = p_l/P^0$ ), its molecular fraction in a mixture ( $a_l = y_l/Y^0$ ), or its concentration in a mixture ( $a_l = c_l/c^0$ ).

\*for non-ideal gas, one must use the fugacity coefficient

\*\*  $P^0$ ,  $N^0$ , and  $Y^0$  are the standard pressure, standard number of moles, and standard mixing ratio, respectively



of the general form

coefficients in the forward and reverse directions

reaction quotient ( $Q_R$ ):

product of species  $\chi_l$  at instant  $t$

concentration » in a mixture.

function of its partial pressure

its mixing ratio ( $a_l = y_l/Y^0$ ) \*\*

fugacity coefficient ( $0 \leq \gamma_l \leq 1$ )

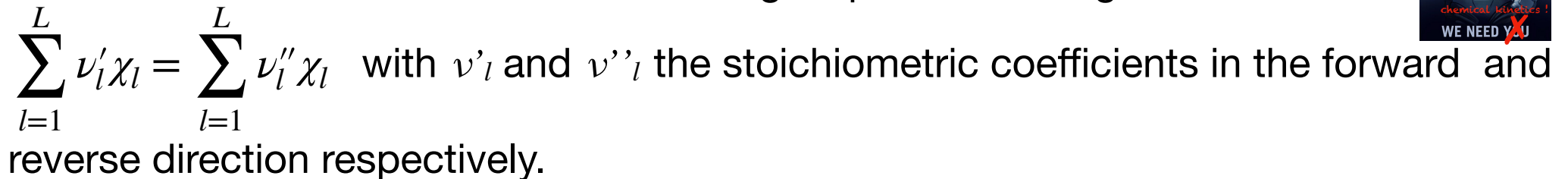
and 1

# Reaction quotient

- Thermodynamic is useful but does not give information on the time required to reach equilibrium. In planetary atmospheres, disequilibrium processes compete with chemical reactions, so **we need chemical kinetics....**



- Let consider a reversible reaction involving  $L$  species of the general form



- At any time  $t$ , the reaction is characterised by the **reaction quotient ( $Q_R$ )**:

$$Q_R(t) = \prod_{l=1}^L a_l(t)^{\nu_l} \quad \text{with } \nu_l = \nu''_l - \nu'_l \text{ and } a_l(t) \text{ the activity of species } \chi_l \text{ at instant } t$$

- The activity of a species corresponds to its « effective concentration » in a mixture. Dimensionless quantity that can be expressed\* as a function of its partial pressure ( $a_l = p_l/P^0$ ), its molecular concentration ( $a_l = n_l/N^0$ ), or its mixing ratio ( $a_l = y_l/Y^0$ ) \*\*

\*for non-ideal gas, one must multiply  $p_l$ ,  $n_l$  and  $y_l$  by the activity coefficient ( $0 \leq \gamma_l \leq 1$ )

\*\*  $P^0$ ,  $N^0$ , and  $Y^0$  are the standard values : 1 bar, 1 molecule.cm<sup>-3</sup>, and 1

# Reaction quotient

- Thermodynamic is useful but does not give information on the time required to reach equilibrium. In planetary atmospheres, disequilibrium processes compete with chemical reactions, so **we need chemical kinetics....**



- Let consider a reversible reaction involving  $L$  species of the general form

$$\sum_{l=1}^L \nu'_l \chi_l = \sum_{l=1}^L \nu''_l \chi_l \quad \text{with } \nu'_l \text{ and } \nu''_l \text{ the stoichiometric coefficients in the forward and reverse direction respectively.}$$

ex:  $A+B=C+2D$

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$$\Rightarrow Q_R(t) = \frac{a_C(t)a_D^2(t)}{a_A(t)a_B(t)}$$

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# Equilibrium constant

- The reaction quotient with the activity expressed in pressure units ( $Q_p$ ) is linked to Gibbs Energy through:  $\Delta G = \Delta G^0 + RT \ln Q_p$
- When the reaction reached an equilibrium, and thus the system does not evolve anymore,  $Q_p$  is called **equilibrium constant** and is noted  $K_p$  and  $\Delta G = 0$   
 $\Rightarrow \Delta G^0 = -RT \ln K_p$
- We obtain the expression of the equilibrium constant:  $K_p = \exp(-\Delta G^0/RT)$

that can be also expressed :  $K_p = \exp\left(\frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}\right)$

$$\text{with } \frac{\Delta S^0}{R} = \sum_{l=1}^L \nu_l \frac{s_l^0(T)}{R} \text{ and } \frac{\Delta H^0}{RT} = \sum_{l=1}^L \nu_l \frac{h_l^0(T)}{RT}$$

- ➡ The equilibrium constant of a reaction,  $K_p$ , can be calculated with NASA coefficients.

# Outline



- Introduction - Structure of exoplanet atmospheres
- Thermodynamics - Thermochemical equilibrium
- **Chemical kinetics**
- Photochemistry
- Tools: 1D kinetic models - ingredients + key results

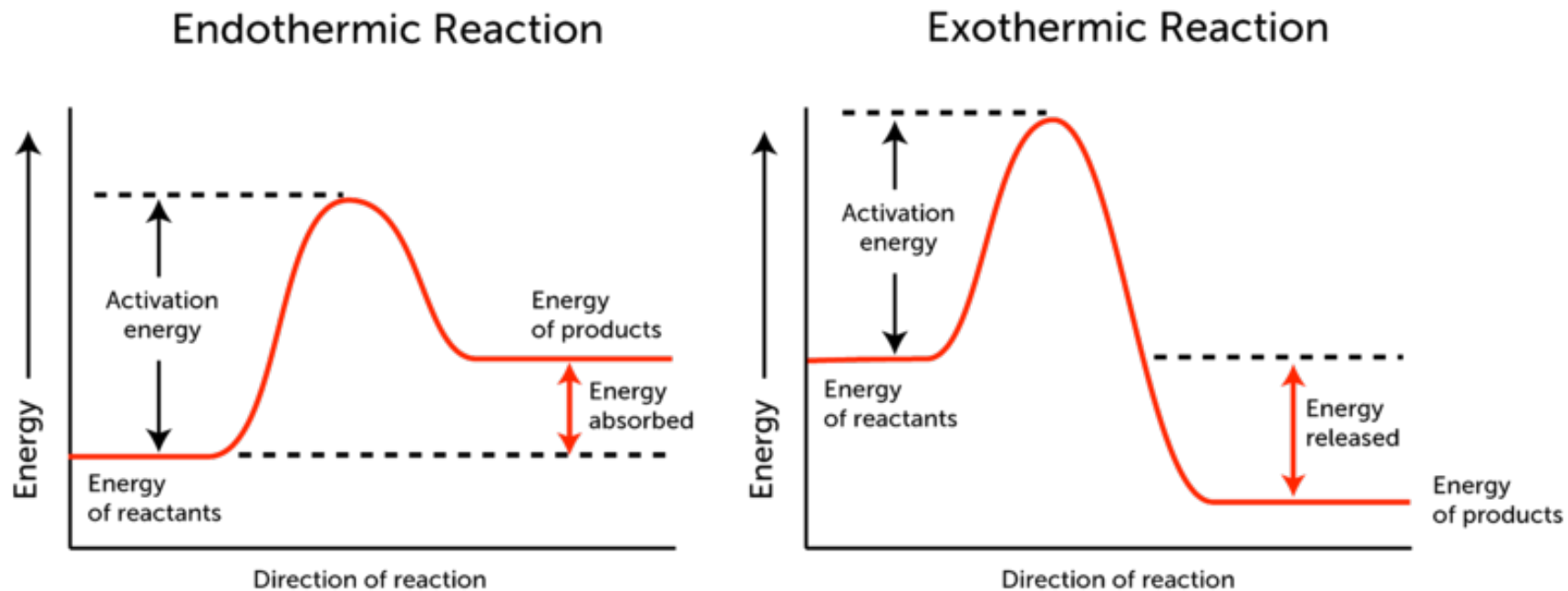
# Reaction rate

- We are still considering the reaction  $\sum_{l=1}^L \nu'_l \chi_l = \sum_{l=1}^L \nu''_l \chi_l$  **ex: A+B=C+2D**
- Conservation of matter imposes:  $-\frac{1}{\nu'_l} \frac{d[\chi_l]}{dt} = \frac{1}{\nu''_l} \frac{d[\chi_l]}{dt} = \nu$ , where  $[\chi_l]$  is the concentration of species  $\chi_l$  (molecule.cm<sup>-3</sup>) and  $\nu$  is the **reaction rate** (molecule.cm<sup>-3</sup>.s<sup>-1</sup>)  
**ex:  $\nu = k(T)[A][B]$**
- The reaction rate,  $\nu$ , is proportional to the concentration of species. The general formula postulated by Van't Hoff is  $\nu = k(T) \prod_l [\chi_l]^{\nu_l}$  with  $k(T)$  the **rate coefficient**.
- The **production/loss rates** of products/reactants are given by  $\pm \frac{d[\chi_l]}{dt}$   
 **$P_C = d[C]/dt = k[A][B]$**   
 **$L_A = -d[A]/dt = k[A][B]$**
- The chemical lifetime of a species destroyed by this reaction is  $\frac{[\chi_l]}{\nu}$   
 **$\tau_A = 1/k[B]$**

# Rate coefficient

- The rate coefficient is expressed with an Arrhenius law, or, more commonly, with the modified Arrhenius law:  $k(T) = AT^n \exp\left(-\frac{E_a}{RT}\right)$

$E_a$  is the *activation energy* of the reaction.



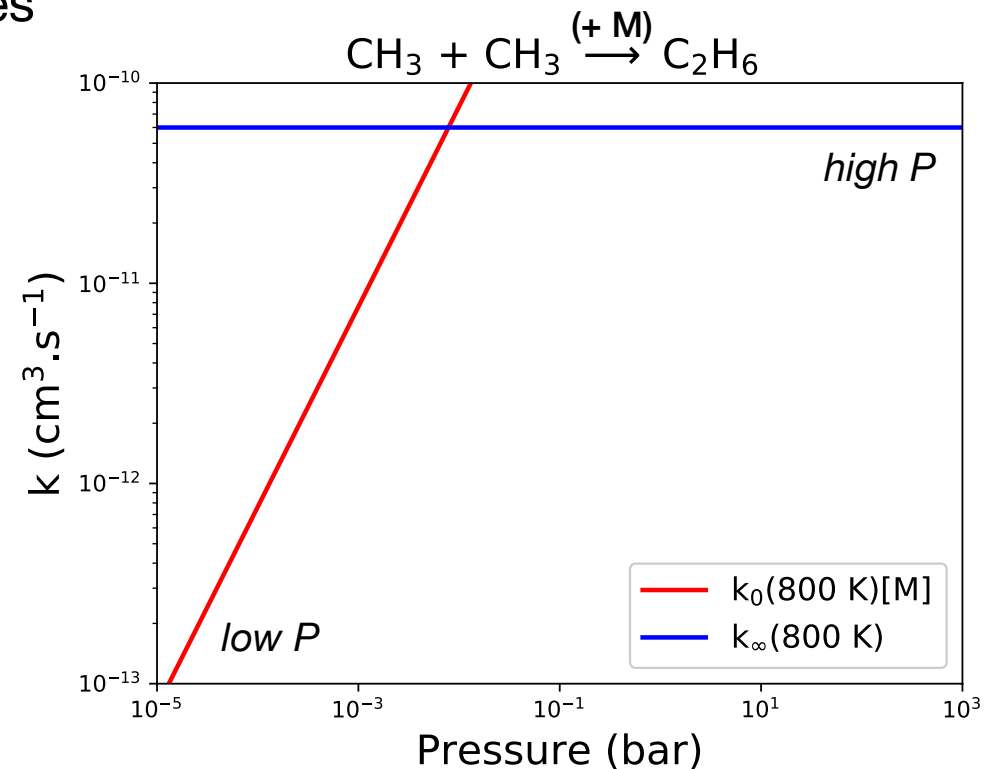


# Rate coefficient

- Units of  $k(T)$  depends on the type of the reaction:
  - Unimolecular:  $\mathbf{A \rightarrow B + C}$   
 $\nu = k(T)[A] \Rightarrow k(T) \text{ in } \text{s}^{-1}$
  - Bimolecular:  $\mathbf{A + B \rightarrow C + D}$   
 $\nu = k(T)[A][B] \Rightarrow k(T) \text{ in } \text{cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$
  - Termolecular:  $\mathbf{A + B + M \rightarrow AB + M}$   
 $\nu = k(T)[A][B][M] \Rightarrow k(T) \text{ in } \text{cm}^6 \cdot \text{molecule}^{-2} \cdot \text{s}^{-1}$
- A 3-bodies reaction is complex. It results from the association of 2 molecules:  
 $\mathbf{A + B \rightarrow AB^*}$   
followed by a deexcitation thanks to the collision with M (background gas):  
 $\mathbf{AB^* + M \rightarrow AB + M}$
- $\mathbf{AB^*}$  is not stable and will decay spontaneously if there is no collision with M:  
 $\mathbf{AB^* \rightarrow A + B}$

# Three-bodies reactions

- The probability that **AB\*** meets a **M** body is large at high P, because molecules are close to each other. In this case, the reaction rate does not depend on **[M]** and the reaction can be considered as bimolecular: **A+B→AB**  
⇒ In the high-pressure limit:  $v_{\infty} = k_{\infty}[A][B]$
- At low-pressure, the reaction rate is limited by the density of M.  
⇒ In the low-pressure limit:  $v_0 = k_0[A][B][M]$
- [M] is the sum of the density of each molecules (eventually weighted by their efficiencies)



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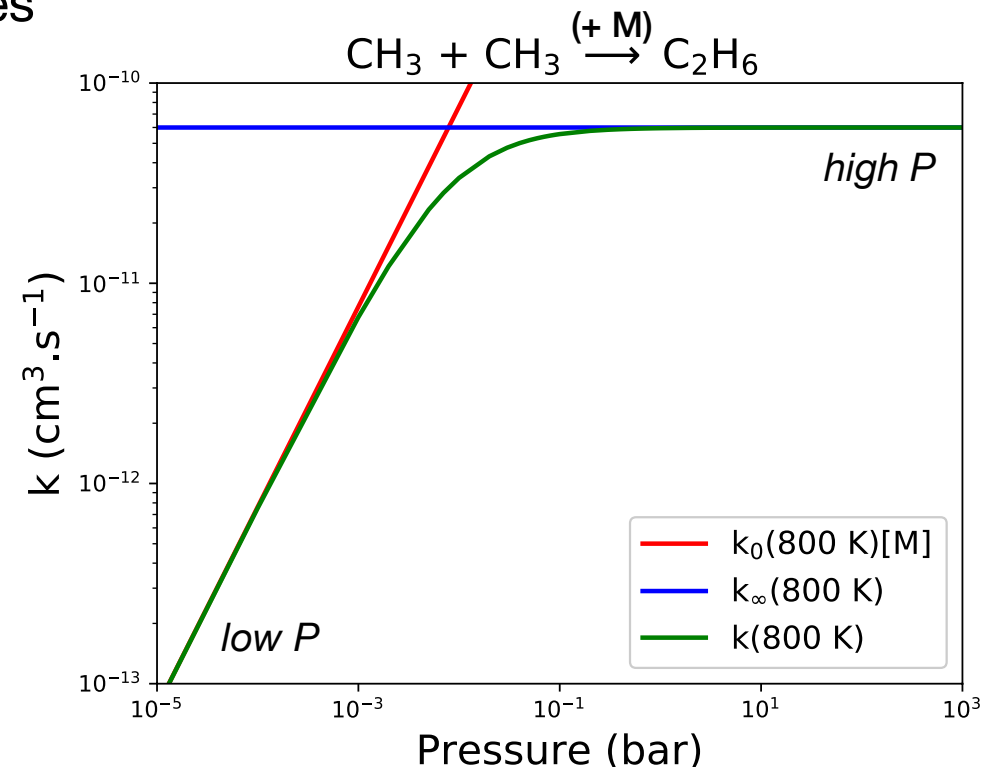
⇒ In the low-pressure limit:  $v_0 = k_0[A][B][M]$

- [M] is the sum of the density of each molecules (eventually weighted by their efficiencies)

- The transition region between the low- and high-pressure regimes is called « fall-off » region.  $k(T)$  is given by :

$$k(T) = k_{\infty} \left( \frac{P_r}{1 + P_r} \right) F$$

with the reduced pressure  $P_r = \frac{k_0[M]}{k_{\infty}}$



# Three-bodies reactions

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$\Rightarrow$  In the high-pressure limit:  $v_{\infty} = k_{\infty}[A][B]$

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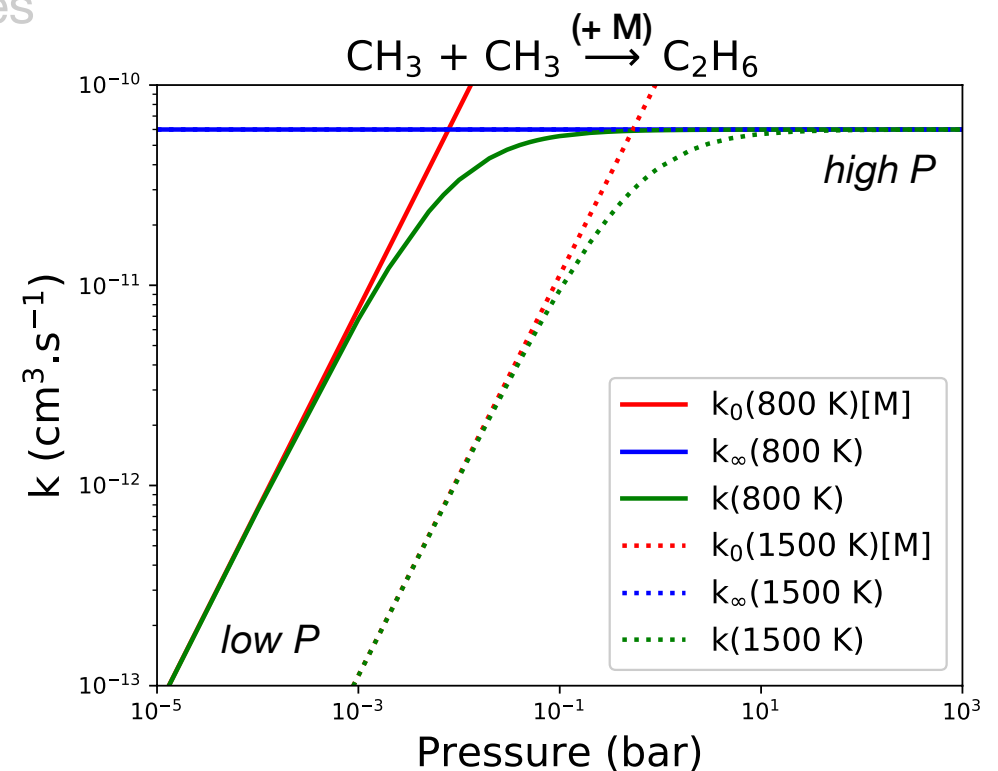
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**The notions of « low » and « high » pressure are temperature dependent !**



# Fall-off region

$$k(T) = k_{\infty} \left( \frac{P_r}{1 + P_r} \right) F$$

- Several formulations for  $F$  exist:

- Lindemann:  $F=1$      *Lindemann et al. 1922*

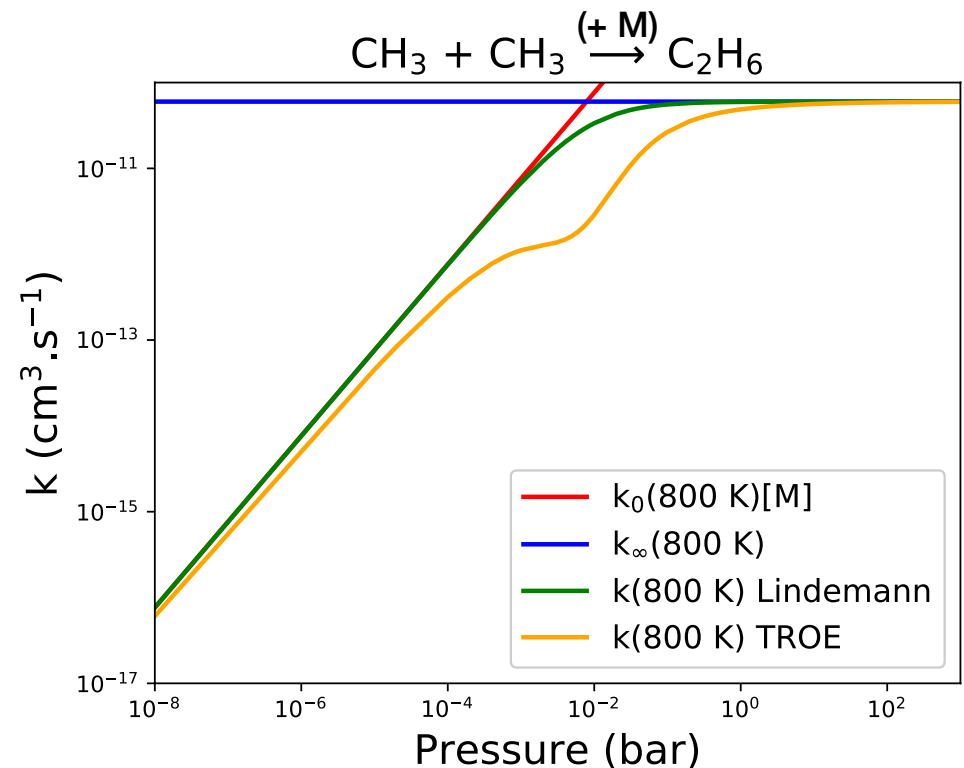
- Troe:  $\log_{10} F = \frac{\log_{10}(F_{cent})}{1 + \left[ \frac{\log_{10}(P_r) + c}{N - d(\log_{10}(P_r) + c)} \right]^2}$  with  $c = -0.4 - 0.67 \times \log_{10}(F_{cent})$   
 $N = 0.75 - 1.27 \times \log_{10}(F_{cent})$   
 $d = 0.14$   
*Troe 1989, 1983*  
*Gilbert et al. 1983*

and  $F_{cent} = (1 - a) \exp\left(-\frac{T}{T^{***}}\right) + a \exp\left(-\frac{T}{T^*}\right) + \exp\left(-\frac{T^{**}}{T}\right)$

- SRI:  $F = d \left[ a \exp\frac{-b}{T} + \exp\frac{-T}{c} \right]^X T^e$  with  $X = \frac{1}{1 + (\log_{10} P_r)^2}$      *Stewart et al. 1989*  
*Kee et al. 1996*

# Three-bodies reactions

- The different expressions for F allow a better description of the fall-off region
- The more common expression used to study planetary atmospheres is « Troe »



- A new method is appearing and consists in a logarithmic interpolation of rates coefficients specified at individual pressures.

The rate  $k$  at pressure  $P$  (with  $P_1 < P < P_2$ ) is given by :

$$\log k(P) = \log k(P_1) + (\log k(P_2) - \log k(P_1)) \frac{\log P - \log P_1}{\log P_2 - \log P_1}$$

# Reverse and forward rates

- The reaction  $\sum_{l=1}^L \nu'_l \chi_l = \sum_{l=1}^L \nu''_l \chi_l$  can occur in both directions (forward and reverse)



- The associated rate coefficients are  $k_f(T)$  and  $k_r(T)$ .

- The reaction rates are respectively  $v_f = k_f(T) \prod_l [\chi_l]^{\nu'_l}$  and  $v_r = k_r(T) \prod_l [\chi_l]^{\nu''_l}$

$$v_f = k_f(T) [A]^a [B]^b$$

$$v_r = k_r(T) [C]^c [D]^d$$

- When the reaction is at equilibrium  $v_f = v_r$  and thus  $\frac{k_f}{k_r} = \prod_l [\chi_l]^{\nu_l}$   $\frac{k_f}{k_r} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$

- One can recognise the equilibrium constant, with the activity expressed in term of molecular concentration. Expressed in term of pressure, we obtain:

$$\frac{k_f}{k_r} = \left( \frac{P^0}{k_B T} \right)^{\sum_l \nu_l} K_p \Rightarrow \frac{k_f}{k_r} = \left( \frac{P^0}{k_B T} \right)^{\sum_l \nu_l} \exp(-\Delta G^0 / RT)$$

$\Rightarrow$  knowing  $k_f$  only,  $k_r$  is calculated with NASA coefficients .... !

# Outline



- Introduction - Structure of exoplanet atmospheres
- Thermodynamics - Thermochemical equilibrium
- Chemical kinetics
- **Photochemistry**
- Tools: 1D kinetic models - ingredients + key results



# Photolyses

- Photodissociations occur in the upper atmosphere of irradiated exoplanets
- After the absorption of a photon, the molecule  $A$  is excited:  $A+h\nu \rightarrow A^*$
- Depending on the energy of the absorbed photon, the molecule  $A^*$  can dissociate and the photodissociation products can vary.
- The molecule  $A$  has  $N$  routes to photodissociate. At each wavelength, the probability that  $A$  dissociates through the route  $k$  is given by the branching ratio,

$$q_k(\lambda), \text{ verifying : } \sum_{k=1}^N q_k(\lambda) = 1.$$

|               | <i>Photodissociation route</i>                      | <i>branching ratio [<math>\lambda</math> range]</i> |
|---------------|---|---|
| For instance: | $\text{CH}_4+h\nu \rightarrow \text{CH}_3+\text{H}$ | <b>1.0 [6-151] ; 0.42 [121.6]</b>                   |
|               | $\rightarrow {}^1\text{CH}_2+\text{H}_2$            | <b>0.48 [121.6]</b>                                 |
|               | $\rightarrow {}^3\text{CH}_2+\text{H}+\text{H}$     | <b>0.03 [121.6]</b>                                 |
|               | $\rightarrow \text{CH}+\text{H}_2+\text{H}$         | <b>0.07 [121.6]</b>                                 |

Gans et al. 2011

# Photodissociation rate

- For these reactions, the rate coefficient is called the photodissociation rate and is noted  $J$ .

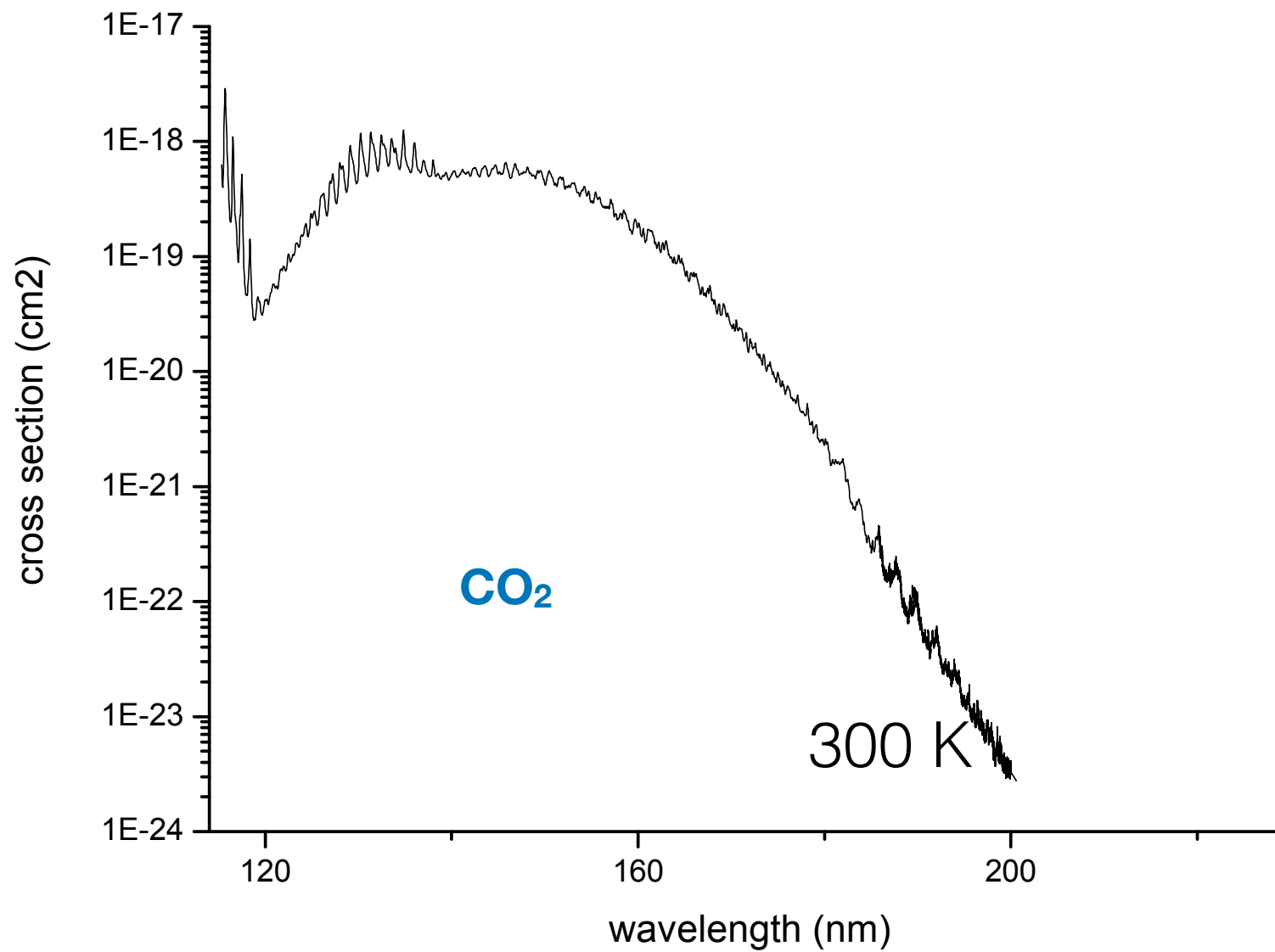
- For a molecule  $i$ , dissociating through the route  $k$ ,  $J_i^k(z) = \int_{\lambda_1}^{\lambda_2} \sigma_i^{abs}(\lambda) F(\lambda, z) q_k(\lambda) d\lambda$   
*absorption cross section of species i (cm<sup>2</sup>)*  
*Actinic flux (cm<sup>-2</sup>.s<sup>-1</sup>.nm<sup>-1</sup>)*

- The total photodissociation rate of the molecule  $i$  is the sum of the

photodissociation rate in each route:  $J_i(z) = \sum_{k=1}^N J_i^k(z)$

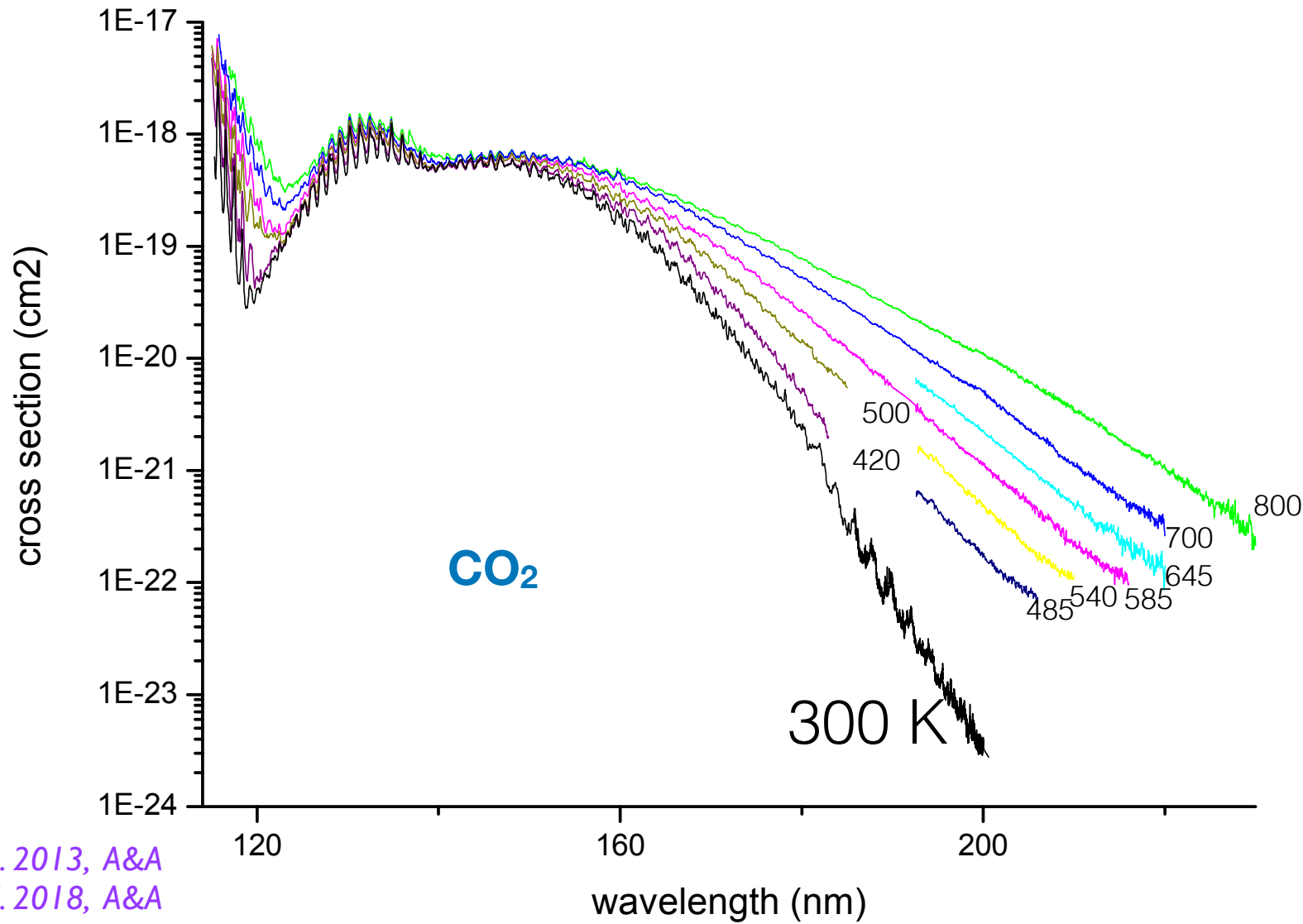
- Absorption cross sections and branching ratios are very important data to calculate the photodissociation rates. In reality these data depends on temperature, but their thermal dependency is badly quantified....
- Very few experimental measurements and not trivial to model theoretically

# VUV Absorption cross section



# VUV Absorption cross section

- When temperature increases, electrons are excited and can move to rovibrational levels of higher energy. Thus, transition to a higher electronic level requires less energy, so the absorption of photons of less energy (longer wavelength) increases



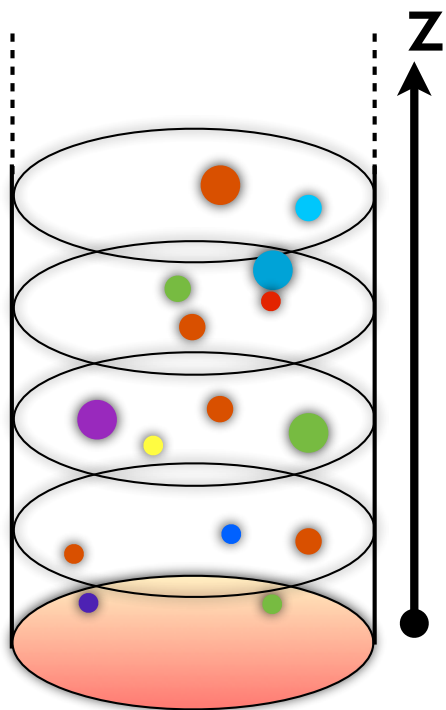
# Outline



- Introduction - Structure of exoplanet atmospheres
- Molecular Spectroscopy - Electronic, vibrational, rotational transitions
- Thermodynamics - Thermochemical equilibrium
- Chemical kinetics
- Photochemistry
- **Tools: 1D kinetic models - ingredients + key results**

# Thermo-photochemical model

- A thermo-photochemical model aims at reproducing all physical and chemical processes occurring in an atmosphere in order to study the evolution of its chemical compounds.
- Up to now, these models exist mainly in 1D.
- The atmosphere is represented by a column divided in several layers



- Each of these layers contains molecules that
  - photodissociate with UV radiation
  - react with each other
  - move from a layer to another thanks to mixing

- For each species and in each level, the thermo-photochemical model resolves the **continuity equation**, which describes the temporal evolution of the density of a species  $i$  at the altitude  $z$

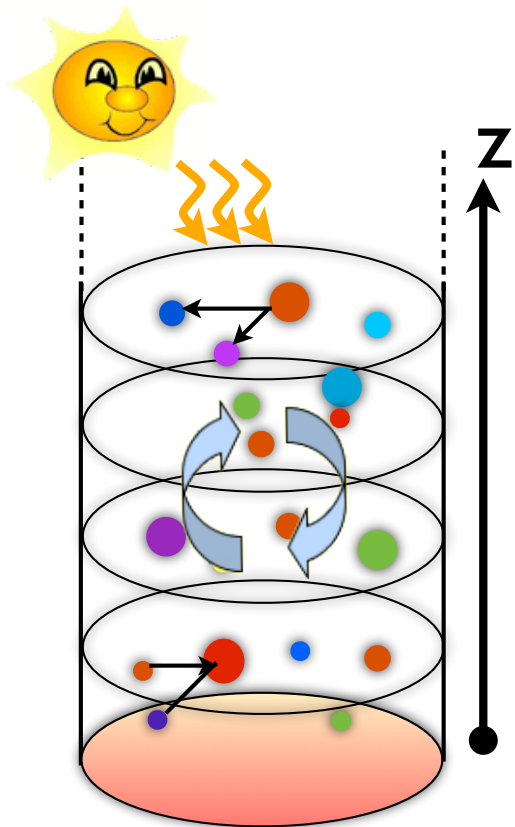
$$\frac{\partial n_i(z)}{\partial t} = P_i(z) - L_i(z) - \text{div}(\Phi_i(z)\vec{e}_z)$$

with  $P_i(z)$  the production rate ( $\text{cm}^{-3}\text{s}^{-1}$ )  
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➡ Large system of coupled differential equations

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# Continuity equation

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- Production ( $P_i$ ) and loss ( $L_i$ ) rates are calculated with formula of chemical kinetics (seen previously) and thanks to the chemical scheme, given as input.
- The flux ( $\Phi_i$ ) is calculated with the **diffusion equation**, taking into account molecular and eddy diffusions

$$\Phi_i(z) = -n_i(z)D_i(z) \left[ \frac{1}{n_i(z)} \frac{\partial n_i(z)}{\partial z} + \frac{1}{H_i(z)} + \frac{(1 + \alpha_i)}{T(z)} \frac{dT(z)}{dz} \right] - n_i(z)K(z) \left[ \frac{1}{y_i(z)} \frac{\partial y_i(z)}{\partial z} \right]$$

with  $D_i(z)$  the molecular diffusion coefficient ( $\text{cm}^2\text{s}^{-1}$ ),  $K(z)$  the eddy diffusion coefficient ( $\text{cm}^2\text{s}^{-1}$ ),  $\alpha_i(z)$  the thermal diffusion coefficient, and  $H_i(z)$  the scale height (cm)

- Ingredients necessary to run such model are:
  - information/data for diffusion
  - a chemical scheme
  - a thermal profile
  - a stellar flux



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# Molecular diffusion

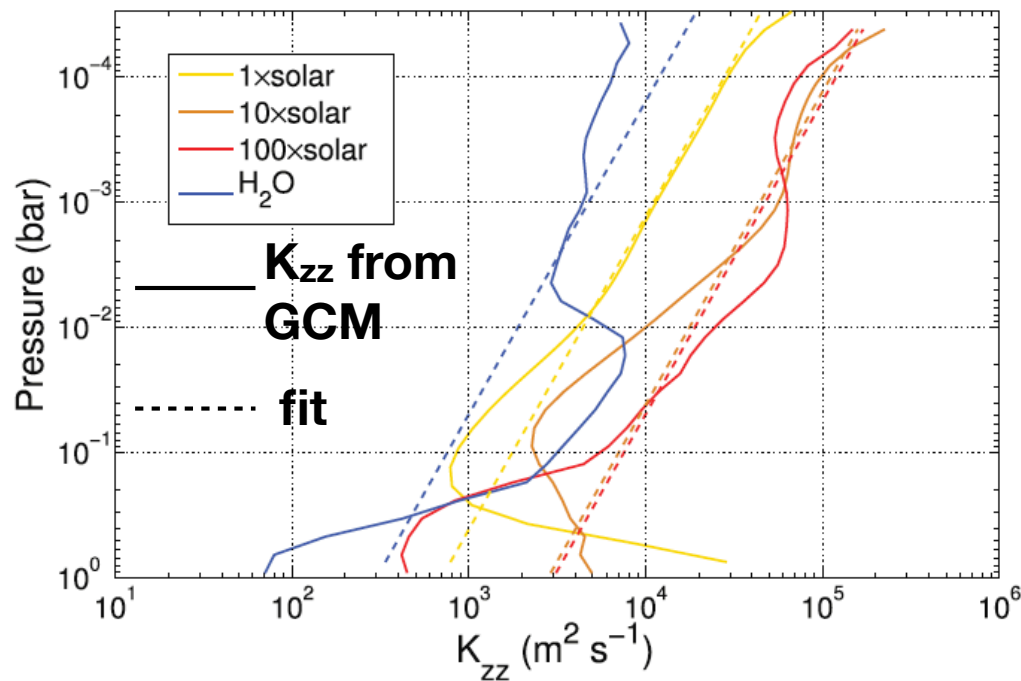
- In planetary atmospheres, made of a major molecule, minor molecules undergo molecular diffusion when their density depart from hydrostatic equilibrium.
- The induced flux is proportional to the molecular diffusion coefficient  $D_i$  of the minor species  $i$  in the major molecule.
- In atmospheres in which the background is formed by 2 compounds A and B (like hot Jupiters atmospheres, made mainly of He and H<sub>2</sub>), the minor species  $i$  diffuses in a binary mixing of gases with a coefficient  $D_{mix}$  given by:

$$D_{mix} = \left( \frac{y_A}{D_{iA}} + \frac{y_B}{D_{iB}} \right)^{-1} \quad \text{with } D_{iX} = \frac{0.00143T^{1.75}}{PM_{iX}^{1/2}[(\Sigma_v)_i^{1/3} + (\Sigma_v)_X^{1/3}]}$$

with  $P$  the pressure (bar),  $M_{iX}$  the reduced mass (kg), and  $\Sigma_v$  the sum of volumes of atomic diffusion of each atom of species  $i$  and  $X$

# Eddy diffusion

- The Eddy diffusion gathers all processes that tend to mix the atmosphere, whether at micro or macroscopic scale.
- For exoplanets, there is a very large uncertainty for this parameter.
- It can be set constant with altitude. In this case,  $K(z)$  is typically between  $10^7$ - $10^{12}$   $\text{cm}^2\text{s}^{-1}$
- It can be estimated from GCM, using tracers (*Parmentier et al. 2013, Charnay et al. 2015*)



**warm Neptune GJ 1214b** (Charnay et al. 2015)

$$K_{zz}(P) = K_{zz0} \times P_{\text{bar}}^{-0.4}$$

$$K_{zz0} = 7 \times 10^2 \text{ m}^2\text{s}^{-1} \text{ for } 1 \times \text{ solar metallicity}$$

$$K_{zz0} = 2.8 \times 10^3 \text{ m}^2\text{s}^{-1} \text{ for } 10 \times \text{ solar metallicity}$$

$$K_{zz0} = 3 \times 10^3 \text{ m}^2\text{s}^{-1} \text{ for } 100 \times \text{ solar metallicity}$$

$$K_{zz0} = 3 \times 10^2 \text{ m}^2\text{s}^{-1} \text{ for pure water case}$$

# Continuity equation

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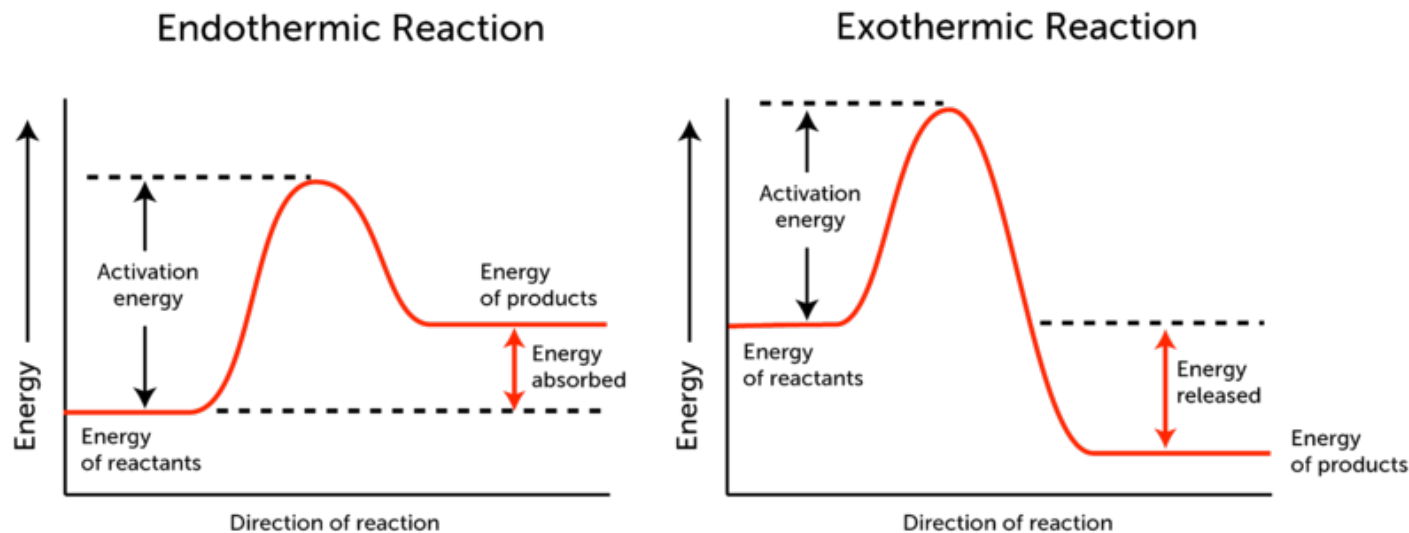
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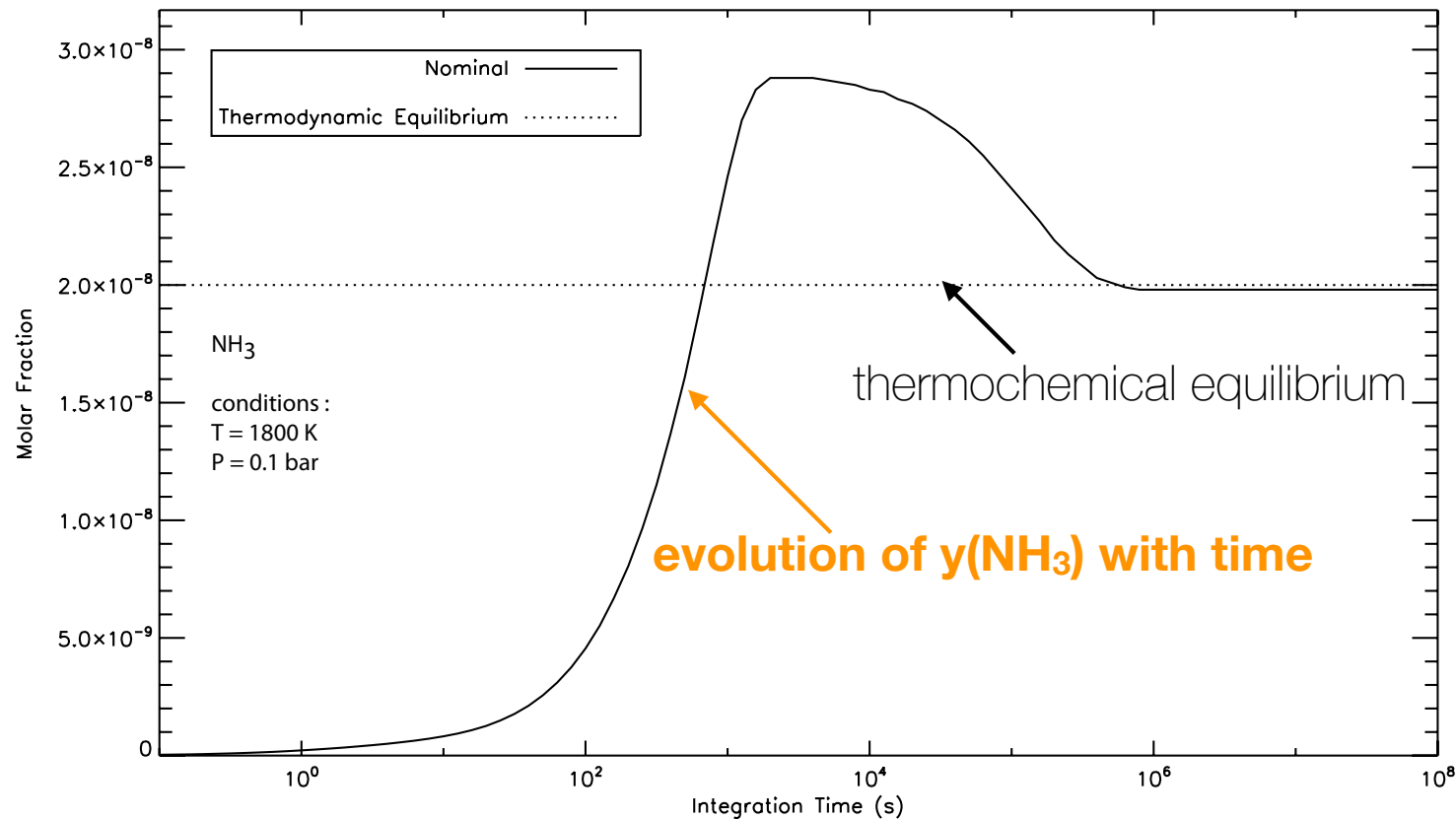
- To calculate the production and loss rates, the thermo-photochemical model needs a list of species and reactions, with the corresponding coefficients (Arrhenius, TROE,...)  
→ a **chemical scheme/network**
- The first chemical scheme used to study hot Jupiters atmosphere was one developed for Jupiter's atmosphere (applied to HD 209458b by Liang et al. 2003, 2004).  
→ scheme made for low temperature atmospheres  
→ lack of endothermic reactions that cannot be neglected at high temperature  
→ thermochemical equilibrium was not reproduce in the deep atmosphere
- For System solar planets (i.e. cold) endothermic reactions are not included because very slow. Lower boundaries conditions are set to fix mixing ratios.



# Chemical scheme

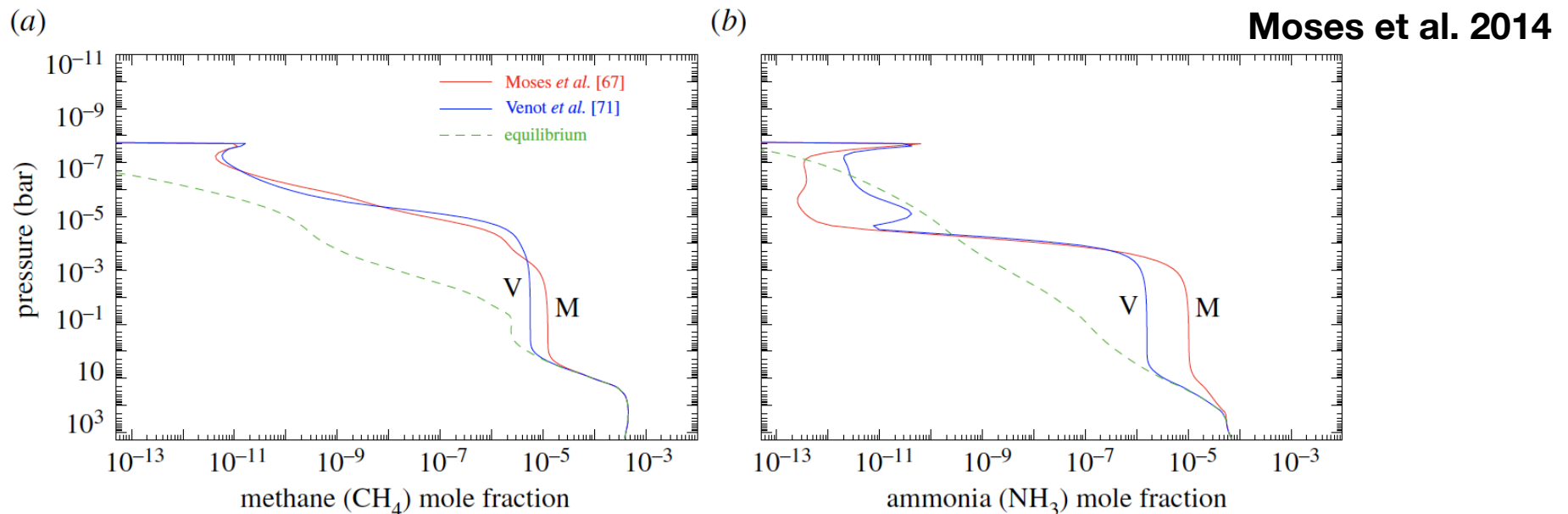
- In hot exoplanet atmospheres, no need of boundaries conditions if thermochemical equilibrium is reproduced
- **All reactions must be reversed thanks to the equilibrium constant** (calculated with

NASA coefficients): 
$$\frac{k_f}{k_r} = \left( \frac{P^0}{k_B T} \right)^{\sum_i \nu_i} K_p$$



# Chemical scheme

- To create the chemical scheme, no real rules:
  - usually/historically, made manually adding reactions found in literature to each others
  - developed from Jupiter's or Earth's model (depending on kind of planets studied)  
(*Moses et al. 2011, Kopparapu et al. 2012, Hu et al. 2012,...*)
  - uncertainty on the completeness of these schemes....
- other approach: use chemical schemes validated experimentally in combustion field  
(*Venot et al. 2012, 2015, 2020*)
- Depending on the scheme used, differences in the predicted abundances can occur  
→ quenching does not occur at the same level





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- Depending on the scheme used, differences in the predicted abundances can occur  
→ quenching does not occur at the same level
- For models focusing on the deep/middle atmosphere ( $P \geq 10^{-8}$  bar), only neutral species need to be included in the chemical scheme
- Models for the upper atmosphere (thermosphere) need to include ions and electrons  
(*Yelle 2004, Garcia Munoz 2007, Koskinen et al. 2013*) and some models couple neutral and ions chemistry (*Lavvas et al. 2014, Rimmer et al. 2014, 2016*)

# Continuity equation

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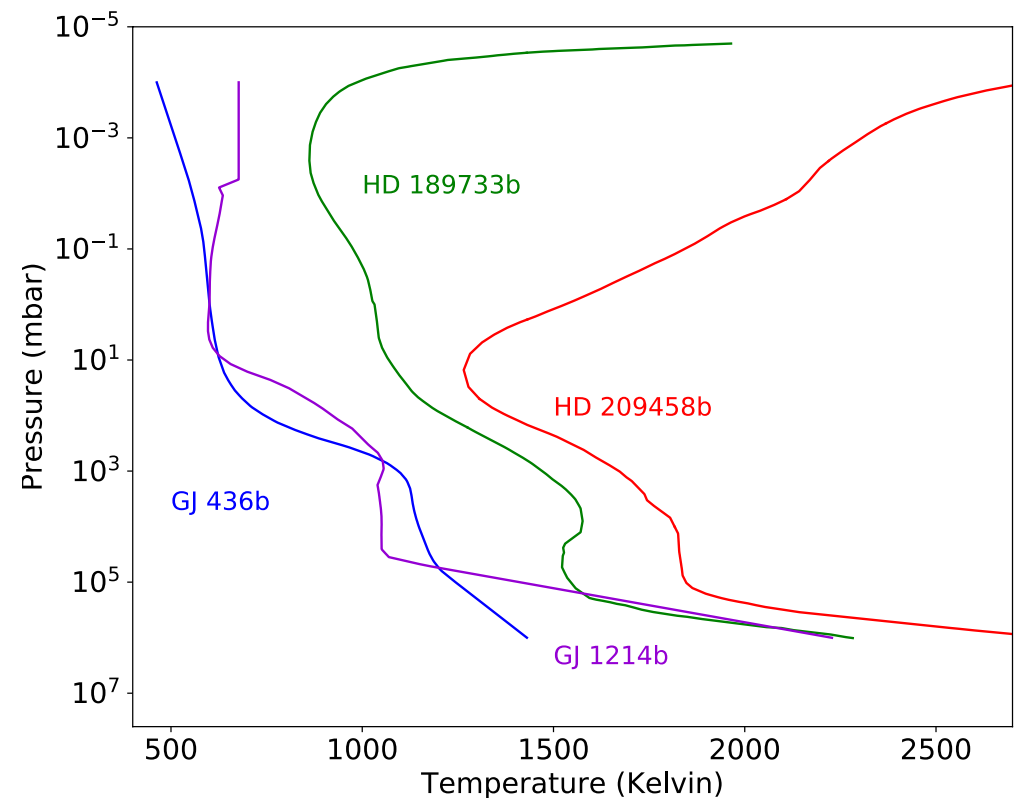
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# Thermal profile

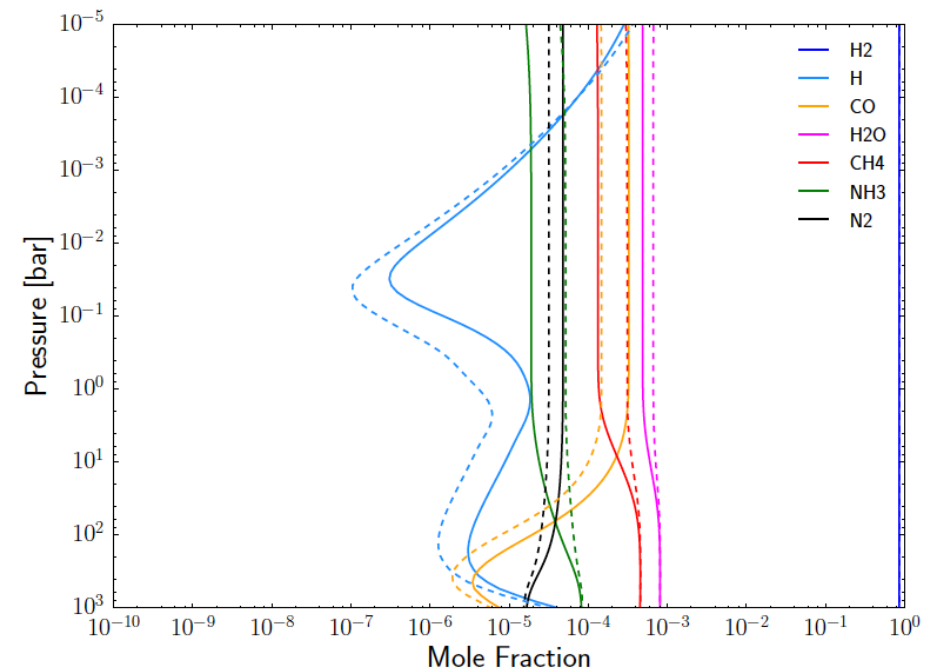
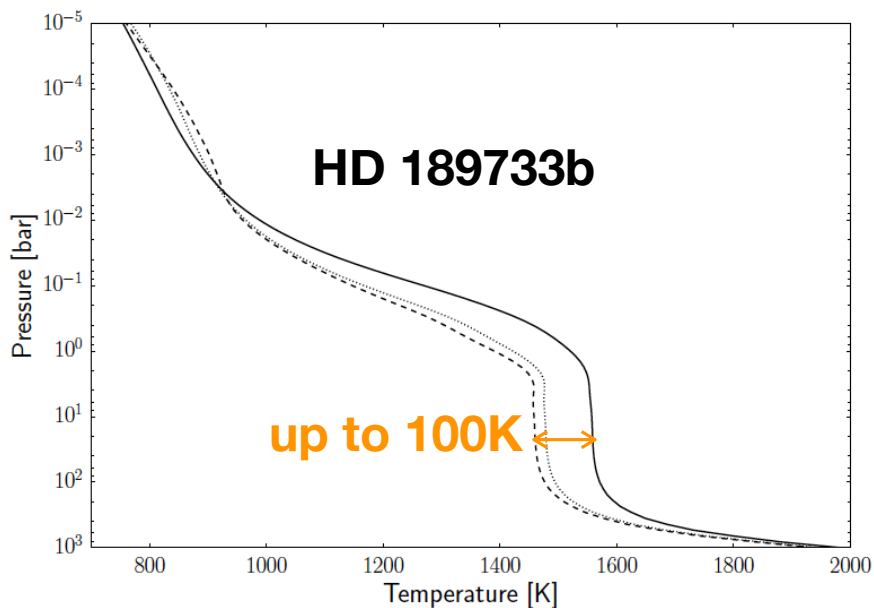
- In most kinetic models, the thermal profile is a fix input parameter
- The PT profile comes from theoretical models (GCMs or 1D/2D radiative-convective models) or is derived from observations (with a retrieval code)
- Temperature between 500 and 3000 K for hot gaseous giant planets
- Temperature inversion are possible

Case of HD 209458b: first, thermal inversion was invoked to explain observations by Spitzer (e.g. Knutson+2008, Madhusudhan & Seager 2009, Line+2014) but Diamond-Lowe+2014 analysed the same data with a new method and found that thermal inversion was no longer necessary. Then the analyse of high-precision HST data (Line+2016) confirm that no thermal inversion exist in this planet...



# Thermal profile

- The limitation of using fix profiles is that the change of chemical composition (and thus opacity of the atmosphere) is not taken into account leading to a non-consistent result.
- Up to now, only one fully-consistent kinetic model has been developed (*Drummond et al. 2016*)
- Impact on the temperature (up to 100 K) and the chemical composition



— initial PT (consistent with thermo equilibrium)  
- - - final PT (consistent with disequilibrium)

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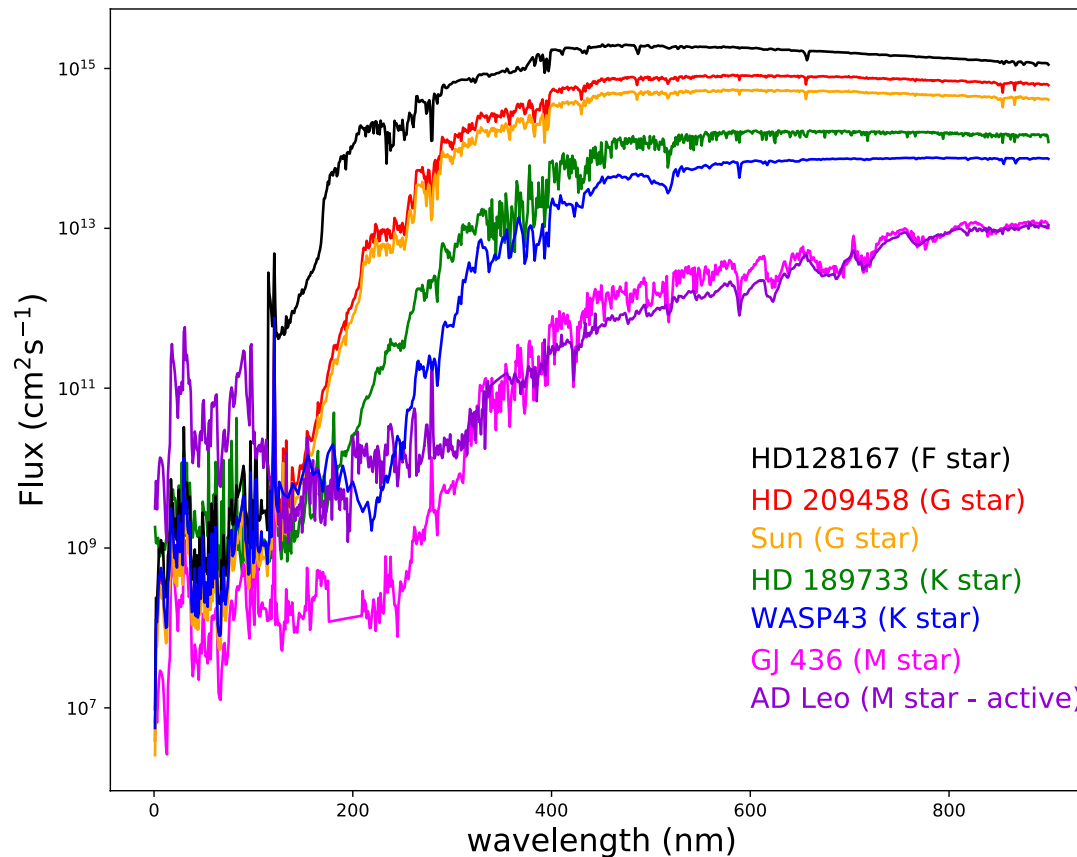
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# Stellar flux

- In thermo-photochemical model, the UV-vis stellar flux is needed to calculate photodissociation rates
- Unlike the Sun, the stellar flux of other stars in this range is rarely known.
- Need to use proxy for which observations are available, eventually combined to theoretical models (e.g. X-exoplanets, Phoenix, Kurucz)

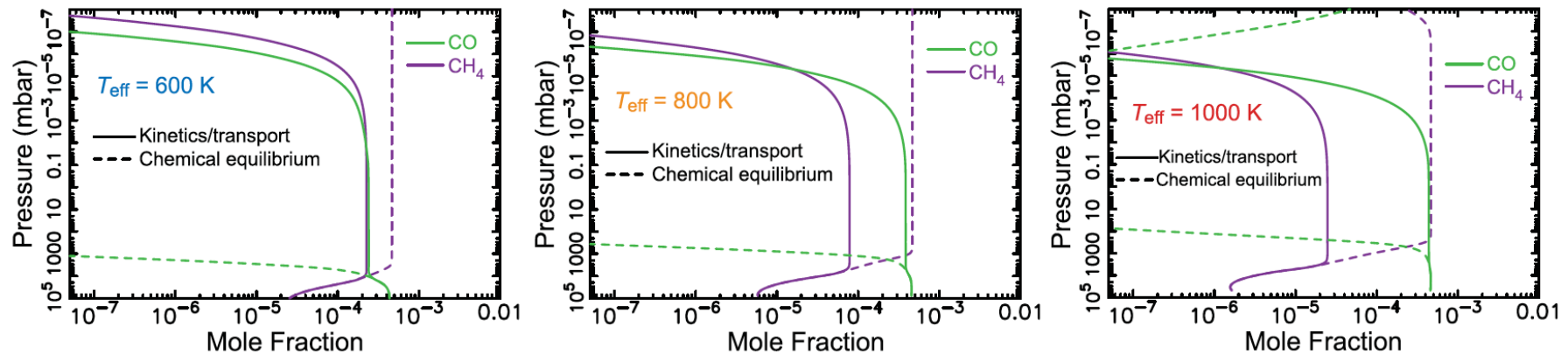


**flux normalized at 1 AU**



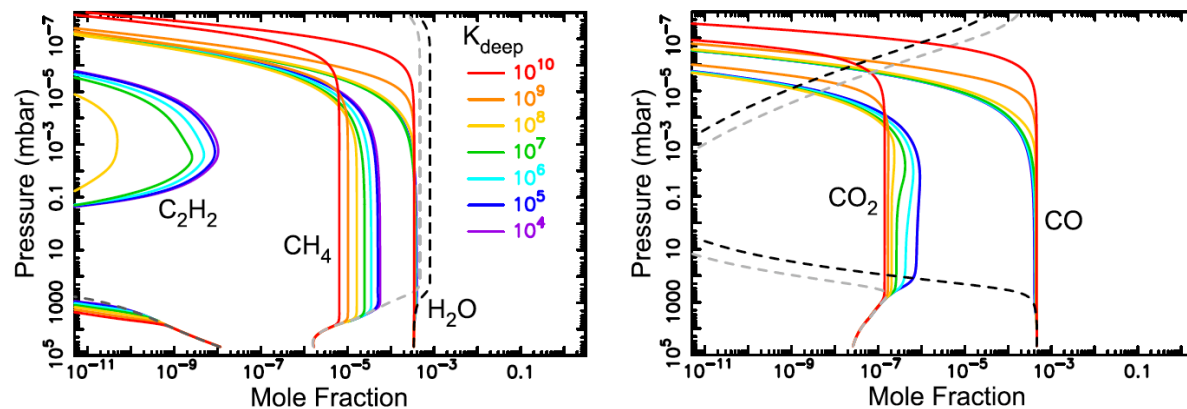
# Some key results...

- In the deep atmosphere CO converted to CH<sub>4</sub> through the net reaction:  
 $\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$  (detailed pathways vary depending on chemical schemes)
- The CO/CH<sub>4</sub> ratio is :
  - strongly modified by mixing compared to what is predicted by equilibrium
  - very dependent on effective temperature of the planet



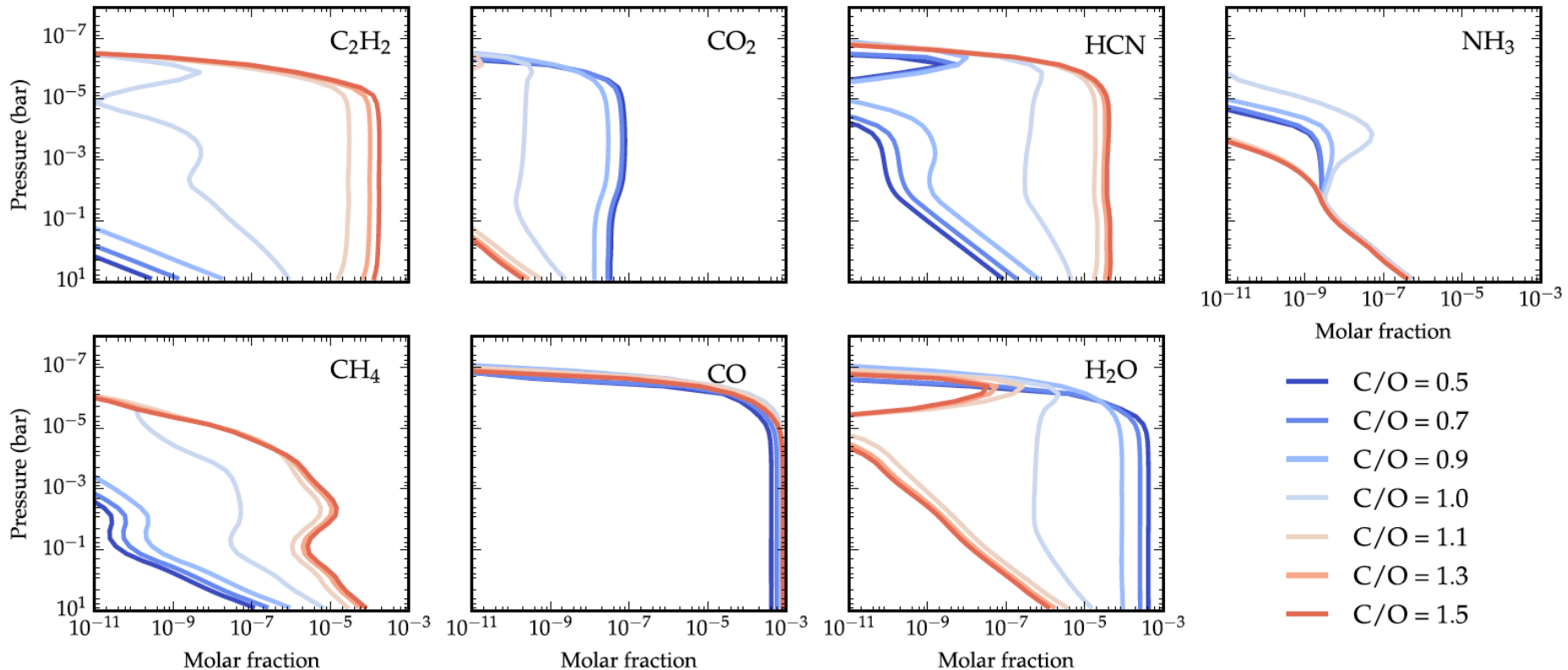
Young Giant Planets  
 Moses et al. 2016

- very dependent on Eddy diffusion coefficient



# Carbon-Oxygen ratio

- in hot atmospheres ( $T \gtrsim 800\text{K}$ ) molecular abundances are very dependent on the % ratio of the atmosphere

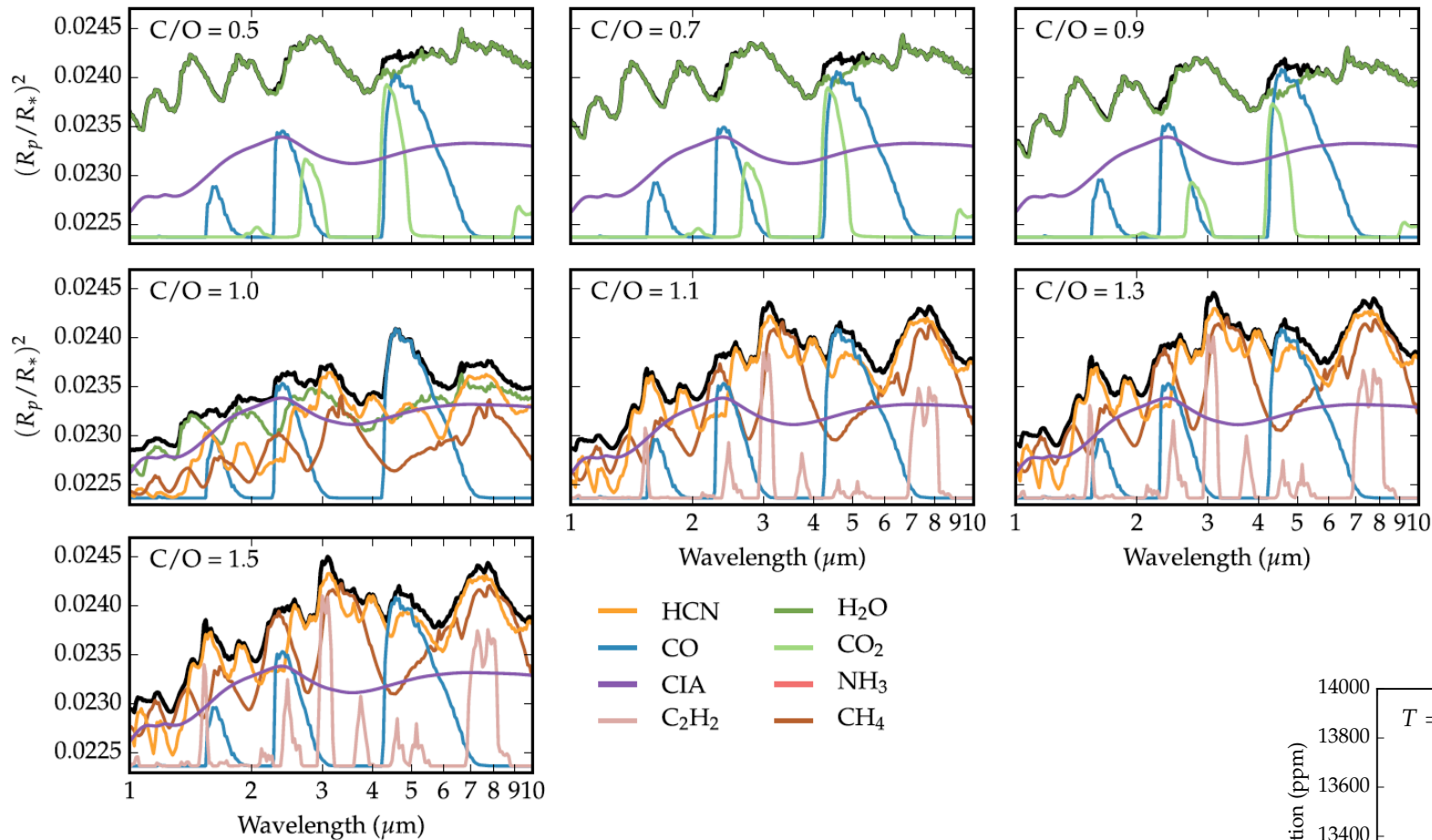


hot jupiter  
Rocchetto et al. 2016

- low %: dominated by  $\text{H}_2\text{O}$ ,  $\text{CO}$ ,  $\text{CO}_2$
- high %: dominated by  $\text{CO}$ ,  $\text{C}_2\text{H}_2$ ,  $\text{HCN}$ ,  $\text{CH}_4$

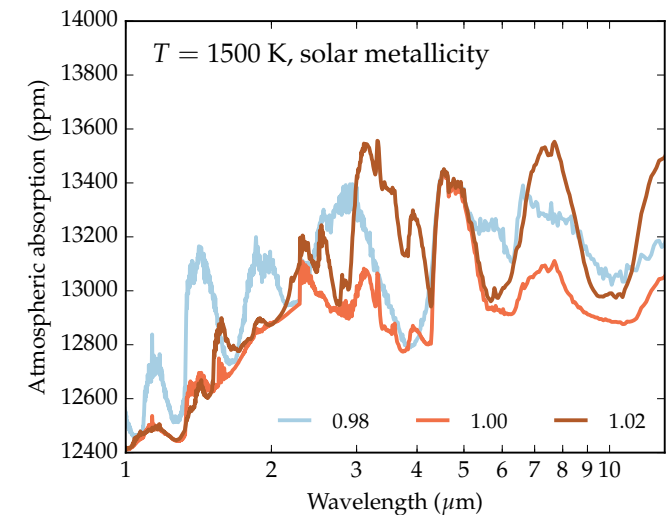
# Carbon-Oxygen ratio

- The differences of composition are visible on spectra



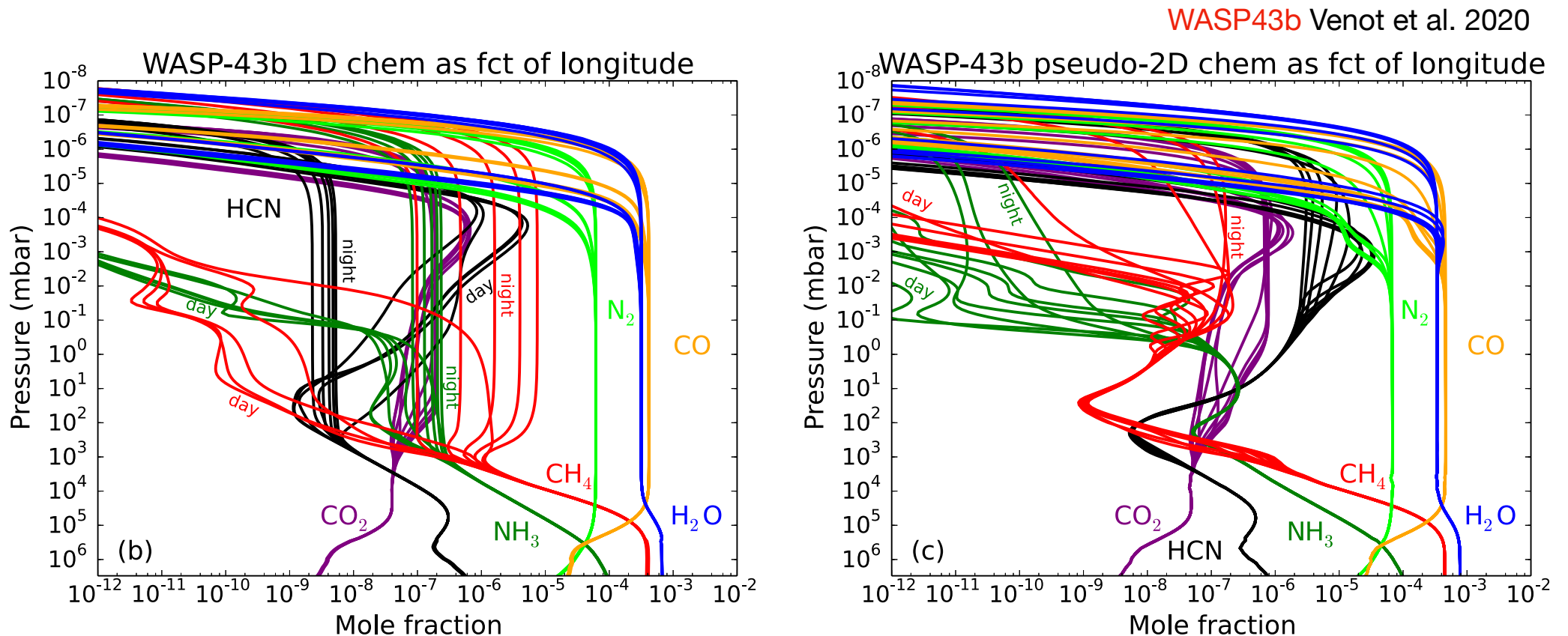
hot jupiter  
Rocchetto et al. 2016

- Change of shape happens drastically around  $\text{C/O}=1$




# Towards 3D kinetic models

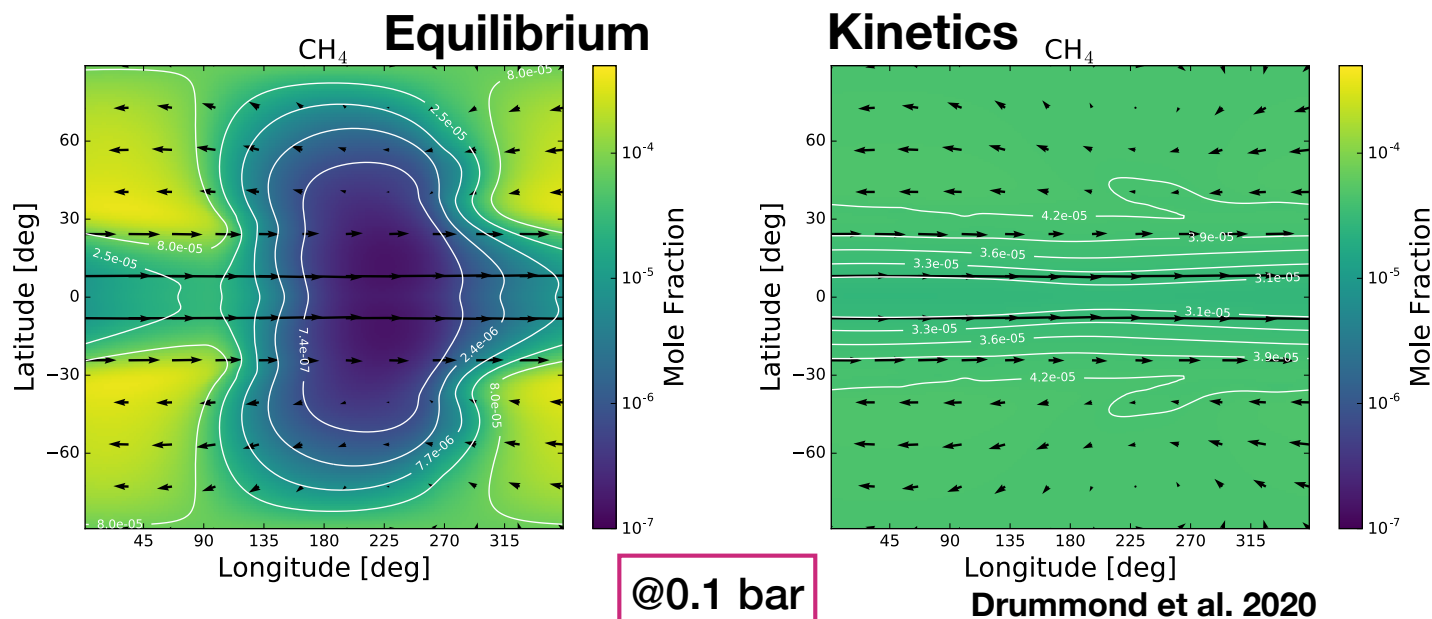
- Results presented are found with 1D models, taking into account vertical mixing only, but horizontal mixing has importance (i.e. Agúndez+ 2014; Venot+ 2020)



- With pseudo 2D model, we find that at equator, homogenisation of abundances, close to that of the dayside, or in-between day/night abundances, as for CH<sub>4</sub>

# Towards 3D kinetic models

- But what about other latitudes ?
- Need a real 3D kinetic model, but the major issue is the huge computational time required by a GCM included a set of 2000 reactions...
- solution: to use a reduced chemical scheme (less complete but enough to study major species - Venot et al. 2019, 2020)
- Very new model developed by B. Drummond at  EXETER



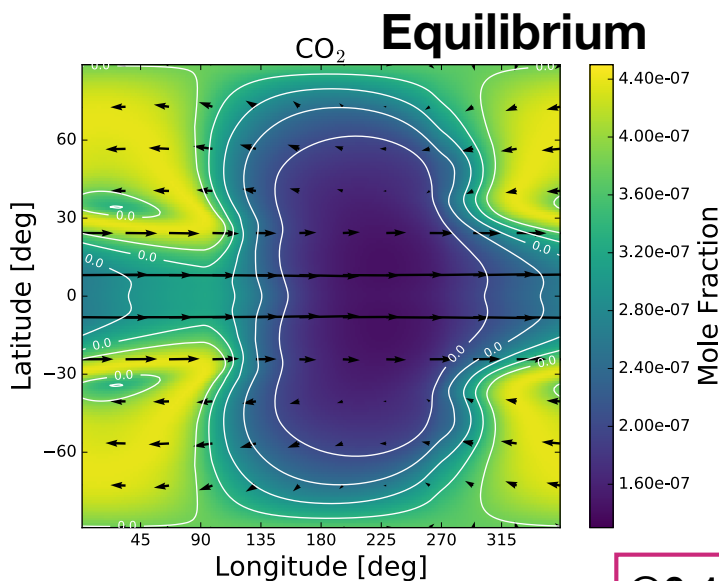
**homogenisation of  
abundances for CH<sub>4</sub>  
and HCN**

# Towards 3D kinetic models

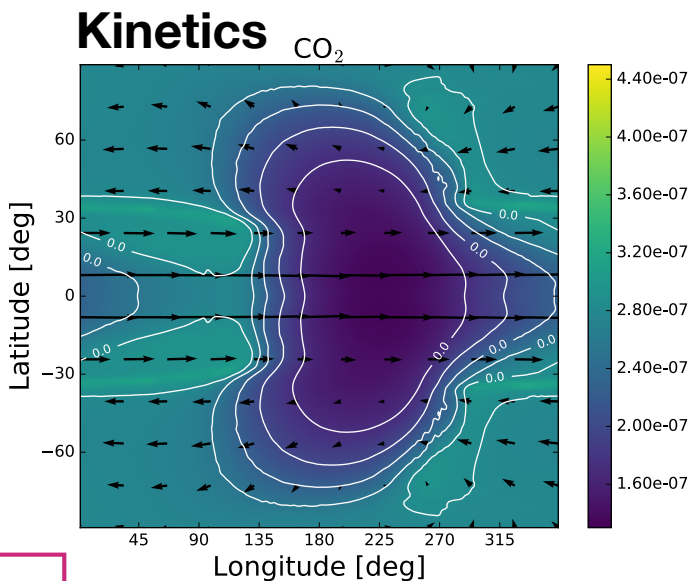
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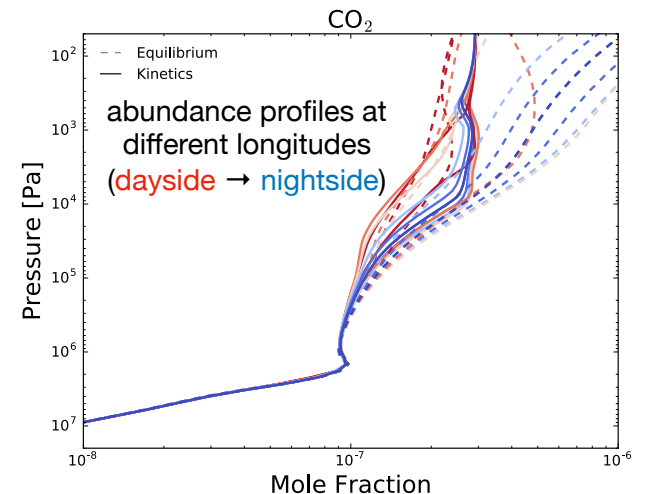
for CO<sub>2</sub>, abundance at the nightside terminator decreases but there is still a significant horizontal gradient



@0.1 bar

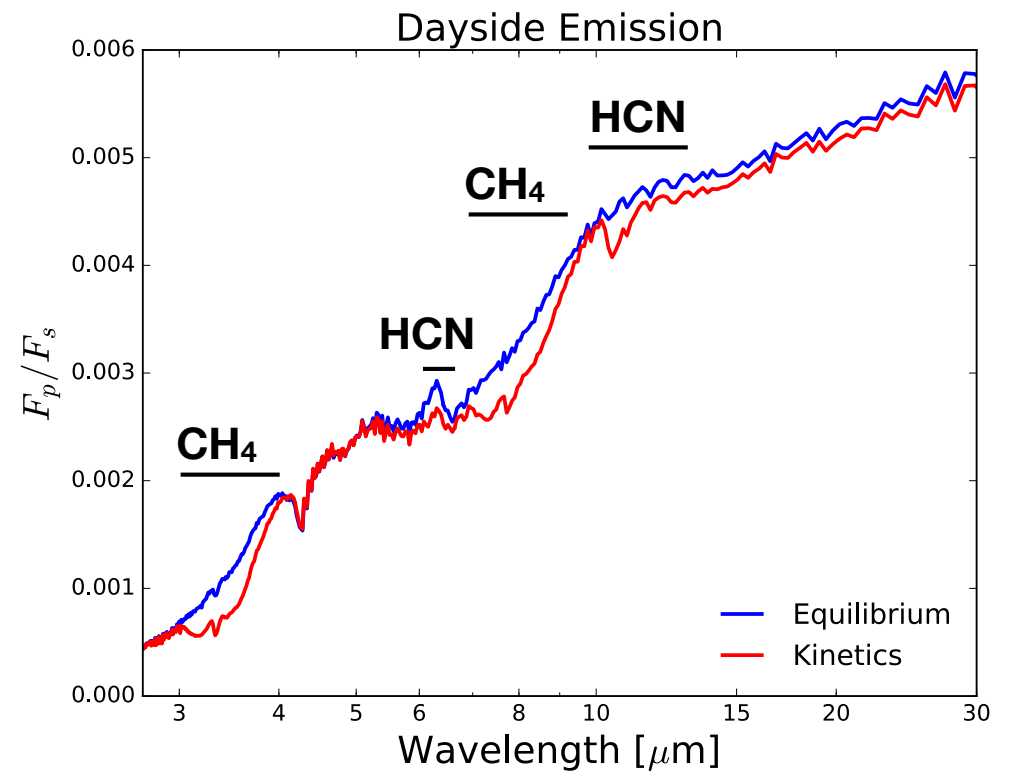
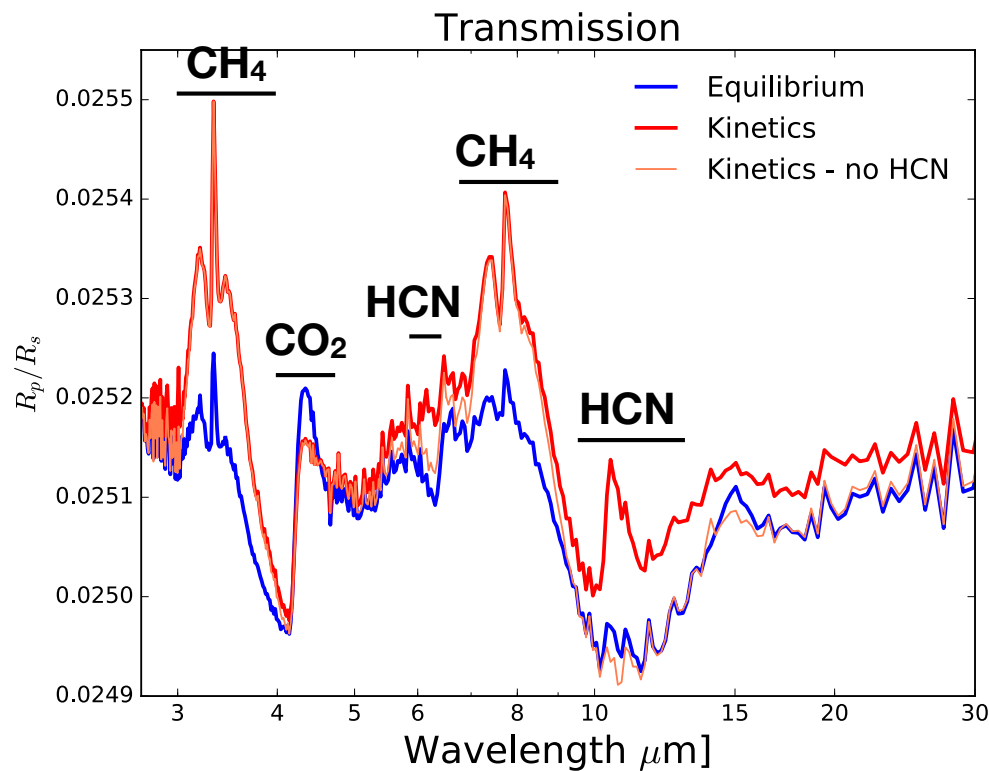


Drummond et al. 2020



# Towards 3D kinetic models

- The effects of 3D kinetics should be visible on the observations thanks to the spectral signature of CH<sub>4</sub>, HCN and CO<sub>2</sub>





# Planetary Atmospheres - Thermo and Photochemistry

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