외계행성 대기
Exoplanetary Atmospheres

Lecture 11: Composition of a Planetary Atmosphere I
Chemistry and Photochemistry

2026 November 23 (Monday)

Based on: Chapter 4 of Seager, *Exoplanet Atmospheres* (2010)

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Outline – Lecture 11

Why Composition Matters

Earth and Jupiter as Examples

Chemical Equilibrium

Departures from Chemical Equilibrium

Photochemistry

Summary

Composition Shapes the Spectrum

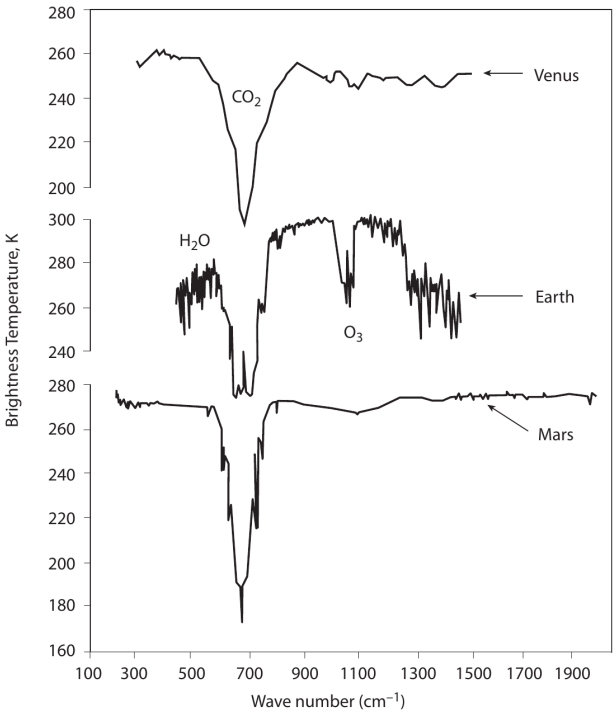


Figure 1: Infrared spectra of Venus, Earth, and Mars. Seager (2010), Fig. 4.1.

- **The spectrum is our only probe** of an exoplanet atmosphere.
- **Different gases absorb at different wavelengths**, so the dips in the spectrum tell us which gases are present.
  - All three terrestrial planets show a strong CO_2 band near $15\,\mu$m (≈ 667 cm^{-1}).
  - Earth also shows H_2O and O_3 features.
- **What the spectrum does *not* show:** abundant gases with weak or no features (e.g. N_2, O_2, H_2, He) are nearly invisible.
- **Today's question:** which atoms and molecules are in a planetary atmosphere, and why?

From Elements to Molecules

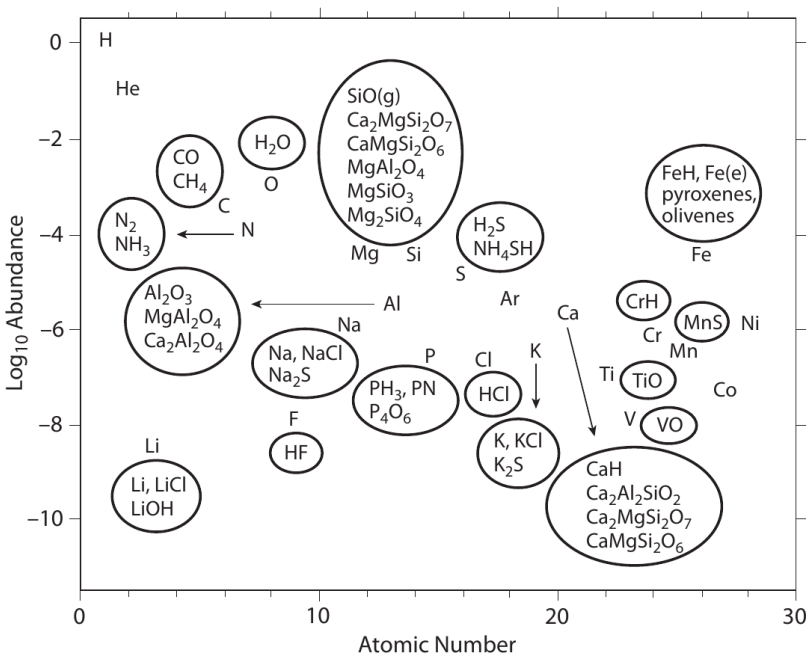


Figure 2: Dominant gas and condensate species for each element. Seager (2010), Fig. 4.2.

- **Step 1:** the **elemental abundances** of the planet (set by how it formed).
- **Step 2:** temperature T and pressure P decide how the atoms combine:
  - C $\rightarrow$ CH_4 (cool) or CO (hot),
  - O $\rightarrow$ H_2O, CO, or silicates,
  - N $\rightarrow$ NH_3 or N_2.
- **Step 3:** if it is cold enough, some gases **condense** into liquid or solid particles, i.e. **clouds**.
- **Only a handful of molecules dominate** planetary spectra, and the same ones appear on many planets: CH_4 on all giant planets, CO_2 on Venus, Earth, and Mars.

Mixing Ratio: How We Count Gases

- **Number density** n: the number of molecules per unit volume.
- **Mixing ratio** (volume mixing ratio) of a gas g:

$$\boxed{X_g = \frac{n_g}{n_{\text{total}}}}$$

  - Example: O_2 in Earth's air has $X = 0.209$; CH_4 has about 1.7 ppm (parts per million by volume).
  - X can change with altitude when a gas is not well mixed.
  - On giant planets X is sometimes defined relative to n_{H_2} instead of n_{total}.
- **Abundance is not the same as importance.** The absorbing power of a gas is

$$\text{absorbing power} \propto n \times \sigma \quad (\sigma = \text{absorption cross section}).$$

  - Homonuclear molecules (N_2, O_2) have **very small** σ.
  - Molecules with different atoms (CO_2, CH_4, H_2O) have **much larger** σ: a small abundance can still dominate the spectrum.

Earth's Atmosphere: The Bulk Gases

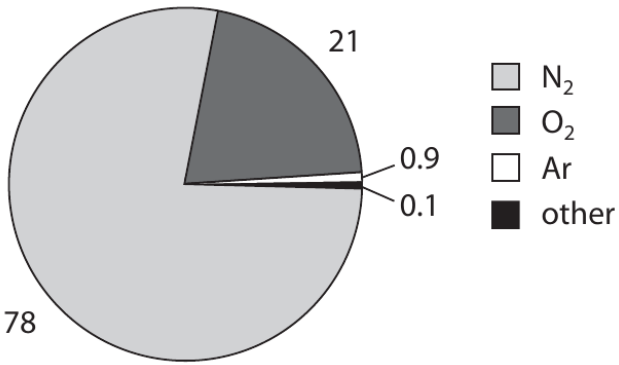


Figure 3: Earth's atmosphere by volume (%): N_2 78, O_2 21, Ar 0.9, other 0.1. Seager (2010), Fig. 4.3.

- **N_2 (78.1%):** inert, does not react with the surface, and too heavy to escape, so it stayed.
- **O_2 (20.9%):** made by **photosynthetic life**. Because of O_2, Earth's air is **far from chemical equilibrium**.
- **CO_2:** much of it dissolved in the ocean and ended up in limestone, so only a trace remains.
- **Hydrogen:** any early H_2 **escaped to space**.

The atmosphere we see today is the end product of long **evolution** (see Lecture 12).

Earth's Atmosphere: The Trace Gases That Matter

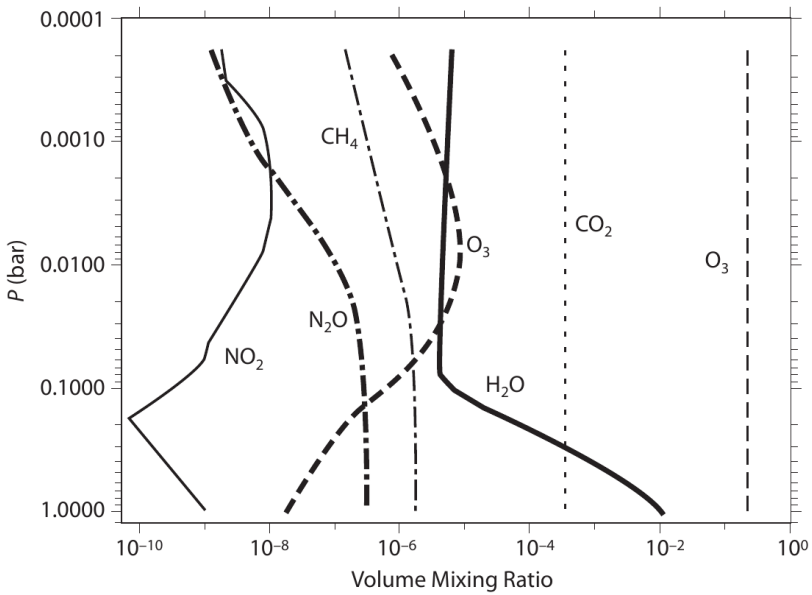


Figure 4: Earth's mean gas mixing ratios versus pressure. Seager (2010), Fig. 4.4.

- **The greenhouse gases are not the most abundant gases:** H_2O, CO_2, CH_4, N_2O are rare, but strong absorbers.
- **Water vapor** is the strongest greenhouse gas.
  - A few % near the surface, < 10 ppm by 40 km.
  - It **freezes out** in the cold upper troposphere.
- **Ozone (O_3)** lives in the stratosphere. It is made by **photodissociation of O_2** (UV light), which defines the stratosphere.

Jupiter's Atmosphere: A Primitive Atmosphere

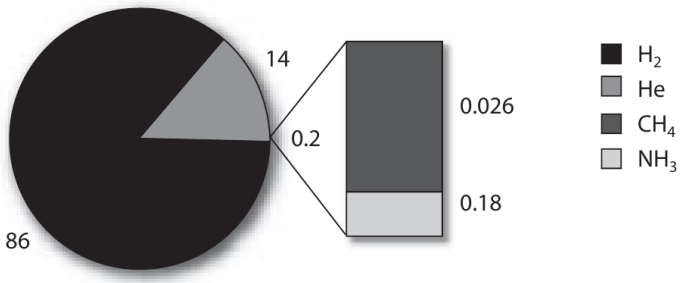


Figure 5: Jupiter's atmosphere by volume (%): H_2 86, He 14, CH_4 0.2, NH_3 0.03. Seager (2010), Fig. 4.5.

- **Hydrogen-rich:** Jupiter formed from the hydrogen-dominated solar nebula and was massive enough to **keep every gas** it collected.
- It is called **primitive**: almost no evolution, with elemental abundances close to those of the Sun.
- **H_2 (86.2%) and He (13.6%)** are inert (apart from collision-induced absorption) and show no deep features.
- **CH_4** is only 2.1×10^{-3} as abundant as H_2, yet it **dominates the visible spectrum**.
- Gases are **well mixed**; **ammonia and water ice clouds** remove those gases above the cloud decks.

Giant Planets: Methane Everywhere

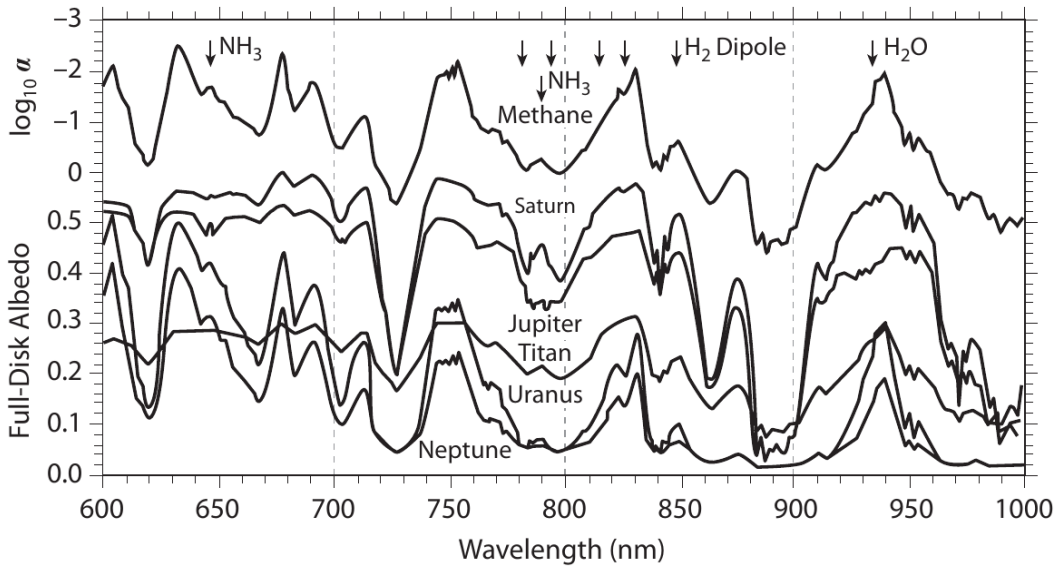


Figure 6: Visible reflection spectra of the giant planets and Titan. The top curve is the methane absorption coefficient. Seager (2010), Fig. 4.6.

- The **same methane bands** (e.g. near 890 nm) appear on every giant planet and on Titan.
- **Deep dips** in the albedo coincide with strong CH_4 absorption.
- Weaker features from NH_3, H_2O, and the H_2 dipole are also marked.
- **Take-away:** a weak gas can control the color of a planet.

Giant Planets Differ From the Sun in Carbon

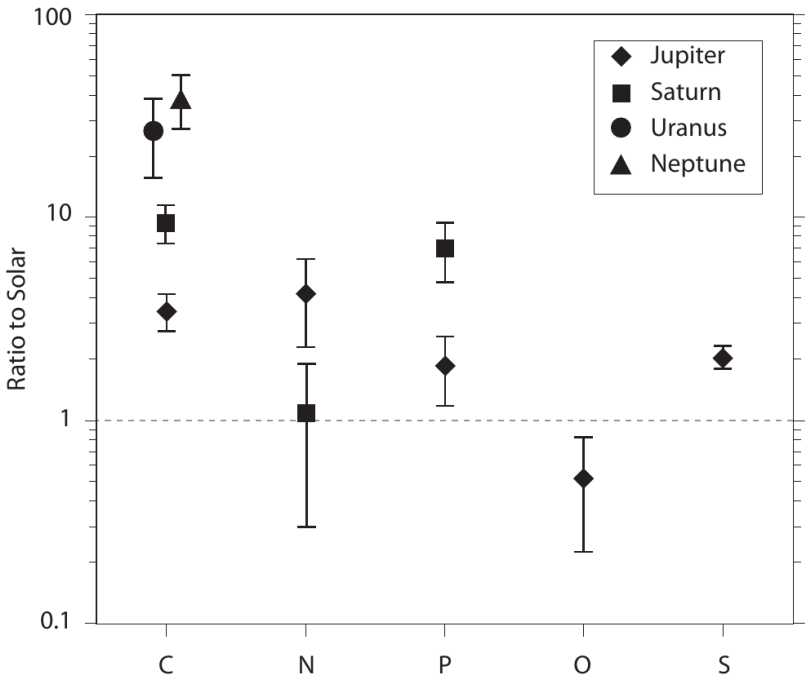


Figure 7: Elemental abundances of the giant planets relative to solar. Seager (2010), Fig. 4.7.

- To first order all solar-system giant planets **resemble solar composition**.
- **But there is a trend:** the carbon abundance (relative to solar) **increases with the planet's semimajor axis**: Jupiter $<$ Saturn $<$ Uranus, Neptune.
- Hints that the outer planets accreted more **heavy elements** (ices) compared to hydrogen.
- For exoplanets we have no such direct measurements, so we start from **an assumed elemental composition** and compute the chemistry.

What Is Chemical Equilibrium?

- **Problem:** for exoplanets we have no detailed spectra or probes. A first guess is to
  1. adopt an **elemental composition** (e.g. solar), and
  2. assume **chemical equilibrium**.
- **Chemical equilibrium:** the number densities of all atoms and molecules in a closed system **stop changing**.
  - Reactions still happen microscopically, but forward and backward rates **balance**.
  - For an atmospheric layer, the "closed system" is the atoms, molecules, and solids in that layer.
- **Goal:** given T, P, and the elemental abundances of a layer, find which molecules exist.
- **Big assumption:** the layer had **enough time** to reach equilibrium. (We revisit this later.)

Why the Gibbs Free Energy?

- **First law of thermodynamics** (energy conservation):

$$\mathrm{d}U = T\,\mathrm{d}S - P\,\mathrm{d}V$$

  ($T\,\mathrm{d}S$ = heating, $P\,\mathrm{d}V$ = work done by the system).

- **Problem:** in an exoplanet atmosphere we cannot measure entropy S or volume V. What we *can* infer from spectra are T and P.

- **Fix:** define a new quantity that uses T and P as its natural variables:

$$\boxed{G \equiv U + PV - TS} \quad \Longrightarrow \quad \boxed{\mathrm{d}G = V\,\mathrm{d}P - S\,\mathrm{d}T}$$

- **Cautions:**
  - G is not a measurable property of matter.
  - G has units of energy but is an **energy potential** ("Gibbs function"), **not** a conserved energy.

Equilibrium = Minimum of G

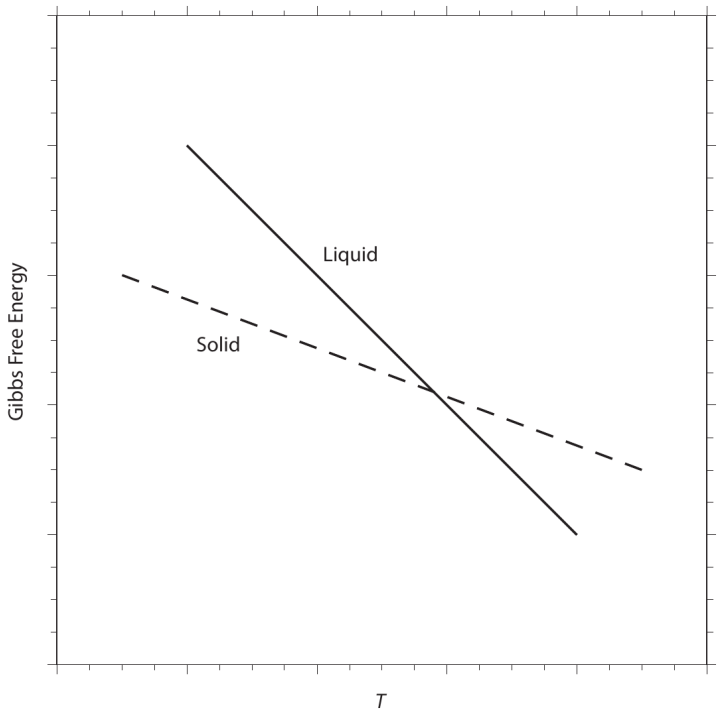


Figure 8: Gibbs free energy of liquid and solid water. The curves cross at 273 K. Seager (2010), Fig. 4.8.

- **Second law:** entropy of a closed system never decreases, $T\,\mathrm{d}S \geq \mathrm{d}Q$. At **constant** T **and** P this gives

$$\boxed{\mathrm{d}G \leq 0}$$

- **Picture:** G is like the height of a ball in a valley. The system keeps rolling **downhill** ($\mathrm{d}G < 0$) until it reaches the bottom, where $\mathrm{d}G = 0$: **equilibrium**.

- **One-component example (water):** at each temperature, the phase with the **lower** G wins.
  - $T < 273$ K: ice has lower G.
  - $T > 273$ K: liquid has lower G.

Many Species: Minimizing G Numerically

- **With several species,** the first law needs a new term for changing particle numbers N_i (chemical potential μ_i):

$$\mathrm{d}U = T\,\mathrm{d}S - P\,\mathrm{d}V + \sum_i \mu_i\,\mathrm{d}N_i.$$

- **Gibbs energy of the gas mixture** (from tabulated $g_i^0(T)$ and the ideal gas law):

$$G = \sum_i n_i \left[g_i^0(T) + RT \ln P_i \right], \qquad \frac{G}{RT} = \sum_i n_i \left[\frac{g_i^0(T)}{RT} + \ln P + \ln \frac{n_i}{N} \right]$$

  (n_i = moles of species i, $N = \sum n_i$, $P_i/P = n_i/N$, R = universal gas constant).

- **Constraint:** atoms are conserved, $\sum_i a_{ij}\, n_i = b_j$ (a_{ij} = atoms of type j in molecule i, b_j = total moles of element j).

- **Solution:** the non-negative set $\{n_i\}$ that minimizes G/RT. Codes handle hundreds of species, including **ions** (extra charge constraint) and **solids** (add their g^0, no pressure term).

- **Clouds:** once cloud particles form, they remove elements, and the gas is re-minimized with the remaining elements.

Example: NH_3 or N_2?

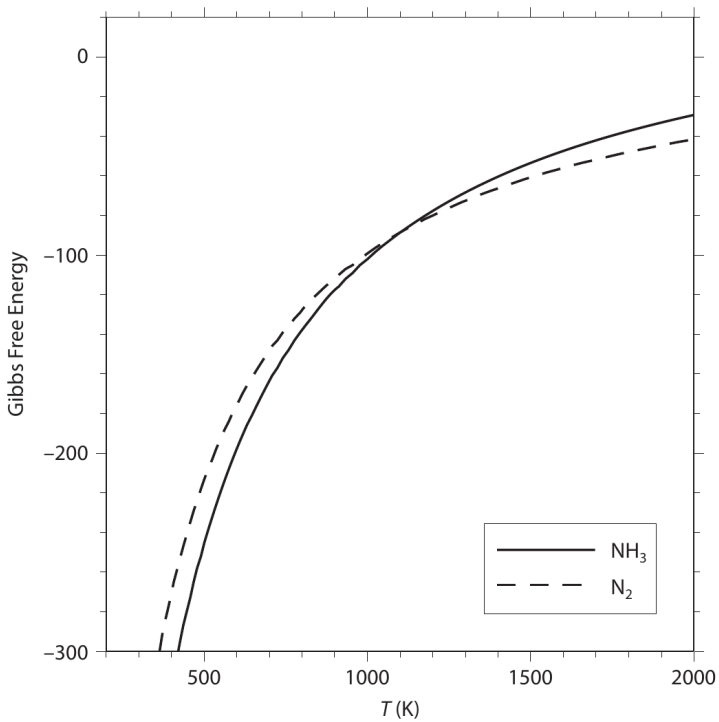


Figure 9: Gibbs free energies of NH_3 and N_2 versus temperature. Seager (2010), Fig. 4.17.

- **Rule of thumb:** the species with the **lower** G is favored.
- The two curves are close and **cross near** 1100–1200 **K** in this plot.
- But the full answer needs **the pressure term** $RT \ln P_i$ too: it shifts the balance, because converting $N_2 + 3H_2 \rightarrow 2NH_3$ reduces the number of molecules.
- **Results of equilibrium chemistry:**
  - Jupiter, Saturn: H_2 dominant; carbon as CH_4.
  - Hot Jupiters (solar abundances): carbon as **CO**, nitrogen as N_2.

When Is Equilibrium Reached?

- **Rule:** a closed system reaches equilibrium if it has **enough time**.
- **Reactions are faster at high T and high P**, so:
  - **Deep, hot layers** $\rightarrow$ chemical **equilibrium** is a good approximation.
  - **Upper, cool, low-density layers** $\rightarrow$ **disequilibrium** is common.
- **Solar-system planets** show disequilibrium everywhere (e.g. Earth's O_2).
- **Brown dwarfs** are good laboratories: failed stars with $T_{\rm eff} \approx 600$–2000 K, similar to hot Jupiters, but **heated from the interior** instead of by a star.

Two Brown-Dwarf Examples of Disequilibrium

- **Nitrogen:** equilibrium says NH_3 should dominate in the cool upper layers, but observed NH_3 is about **10 times lower**.

$$N_2 + 3H_2 \leftrightarrow 2NH_3$$

- **Carbon:** CH_4 should dominate in the upper layers, but **CO is over-abundant**.

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O$$

- **Why?** The N_2 triple bond and the CO double bond have **large binding energies**: they are **hard to break**, so the reactions toward NH_3 and CH_4 proceed very slowly.

- **Vertical mixing** (convection or eddies) **dredges up** N_2 and CO from the hot deep layers **faster** than the reactions can convert them.

- **Jupiter** has the same effect: CO should not exist in its cold upper atmosphere, so its presence proves **deep vertical mixing**.

The Quench Level

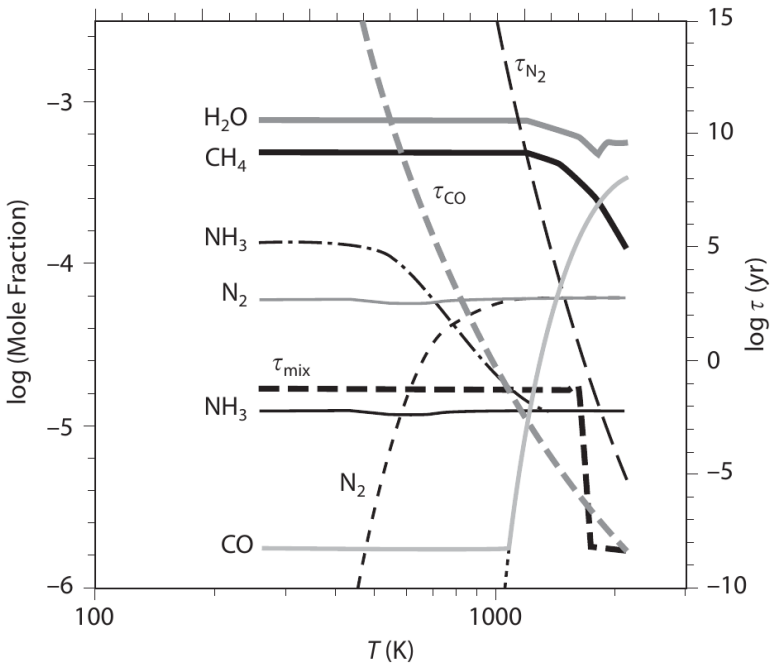


Figure 10: Chemical profile of the brown dwarf Gl 570D. Seager (2010), Fig. 4.9.

- Compare two timescales (not to be confused with optical depth): τ_{chem} (time to reach equilibrium) and τ_{mix} (time to mix vertically).
- **Deep layer:** $\tau_{\text{chem}} < \tau_{\text{mix}}$, so reactions win and the gas is in equilibrium.
- **Upper layer:** $\tau_{\text{chem}} > \tau_{\text{mix}}$, so mixing wins and abundances are **frozen** at their deep values.
- **Quench level:** the boundary $\tau_{\text{chem}} = \tau_{\text{mix}}$. Each species has its own.
- **Mixing time:**

$$\tau_{\text{mix}} \sim \begin{cases} H^2/\kappa_{\text{E}} & \text{radiative zone,} \\ H/v_{\text{c}} & \text{convective zone,} \end{cases}$$

with H the scale height, κ_{E} the eddy diffusion coefficient, v_{c} the convective velocity. Convective mixing is **much faster**.

Photochemistry: Starlight Changes the Chemistry

- **Stellar UV photons** can **photodissociate** molecules in the upper atmosphere.
- The resulting atoms may **escape to space** or **recombine** into a different molecule.
- **Where is it important?**
  - **Low-mass planets** (like Earth): light gases escape, and deep layers are never hot enough to rebuild the destroyed molecules.
  - **Massive planets** (Jupiter, Saturn): escape is negligible, and fast reactions deep down **re-form** the molecules, so composition is little changed.
- **Only the upper atmosphere:** photodissociation cross sections are strong at EUV ($\sim$ 10–100 nm) and UV ($\sim$ 100–320 nm), so starlight is absorbed **well above the millibar level**.

The Photochemical Rate Equation

- For each species i at altitude z, write a **budget** of sources and sinks:

$$\boxed{\frac{\partial n_i}{\partial t} + \frac{\partial \phi_i}{\partial z} = P_i(z) - n_i(z)\, L_i(z)}$$

  - n_i: number density, ϕ_i: vertical **flux** (mixing),
  - P_i: **production** rate, L_i: **loss** rate (from chemistry, photolysis, surface sources, escape).

- The equations of different species are **coupled**: a real network has $\gtrsim 100$ reactions.

- **Photodissociation rate** (units s^{-1}):

$$J(z) = \int_0^\infty \sigma(\nu)\, F_{\mathrm{act}}(\nu)\, \mathrm{d}\nu$$

  σ = cross section, F_{act} = **actinic flux** (flux from all directions, attenuated as it goes down).

A Toy Model: One Atom, One Molecule

- **Reactions** (M = any third body):

$$\mathrm{A_2} + h\nu \xrightarrow{J} \mathrm{A} + \mathrm{A}, \qquad \mathrm{A} + \mathrm{A} + M \xrightarrow{K} \mathrm{A_2} + M$$

- **Steady state** ($\partial/\partial t = 0$):

$$J[\mathrm{A_2}] = K[\mathrm{A}]^2 \quad \Longrightarrow \quad \boxed{[\mathrm{A}] = \sqrt{\frac{J[\mathrm{A_2}]}{K}}}$$

- **Conservation** of the total amount of A (input of the model):

$$[\mathrm{A}] + 2[\mathrm{A_2}] = A_{\mathrm{total}}$$

- Two equations, two unknowns $\Rightarrow$ solve for $[\mathrm{A}]$ and $[\mathrm{A_2}]$.

- **Meaning:** strong UV (large J) $\Rightarrow$ more atoms; fast recombination (large K) $\Rightarrow$ more molecules.

A Real Example: Ozone in Earth's Stratosphere

Formation:

$$\mathrm{O} + \mathrm{O_2} + M \xrightarrow{K_{12}} \mathrm{O_3} + M$$

$$\mathrm{O_2} + h\nu\,(\lambda < 242\ \mathrm{nm}) \xrightarrow{J_2} \mathrm{O} + \mathrm{O}$$

Destruction:

$$\mathrm{O_3} + h\nu\,(\lambda < 1100\ \mathrm{nm}) \xrightarrow{J_3} \mathrm{O} + \mathrm{O_2}$$

$$\mathrm{O} + \mathrm{O_3} \xrightarrow{K_{13}} 2\,\mathrm{O_2}$$

Photochemical equilibrium (below 75 km):

$$\boxed{[\mathrm{O_3}] \simeq [\mathrm{O_2}]\sqrt{\frac{J_2\,K_{12}\,[M]}{J_3\,K_{13}}}}$$

- **High up:** lots of UV $\Rightarrow$ J_3 large $\Rightarrow$ **little ozone**.
- **Slightly lower:** longer-wavelength UV reaches here, J_2 is large $\Rightarrow$ **ozone forms**: the ozone layer.

In general a photochemical network cannot be reduced to one analytic formula; computer codes are used.

Mixing and Photochemistry in Real Atmospheres

- **Layers are connected by vertical mixing.** In the photochemical region it is **not convection** (that is deeper), and **not molecular diffusion** (that is higher).

- It is **eddy diffusion**, described by one coefficient κ_E ($m^2 s^{-1}$):

$$\phi_i = -\kappa_E \frac{\partial n_i}{\partial z}$$

  Jupiter, Saturn: $\kappa_E \approx 10^3$–10^5 $m^2 s^{-1}$. For exoplanets it is a **free parameter** spanning several orders of magnitude.

- **Photochemistry shapes real worlds:**
  - **Early Venus:** water vapor photodissociated and H escaped, helping to lose the oceans.
  - **Jupiter, Saturn:** UV splits CH_4, and C and H recombine into hydrocarbon **hazes** that mute the blue.
  - **Hot Jupiters:** observed CO_2 is thought to be photochemical, since equilibrium predicts very little.

Summary: Composition and Chemistry

- **Composition** sets spectral features, but **abundance** $\neq$ **visibility**: strong absorbers (CO_2, CH_4, H_2O) can dominate with small $X_g = n_g/n_{\text{total}}$.
- **Earth:** N_2 (78%) and O_2 (21%), with O_2 made by life. **Jupiter:** primitive, H_2 (86%) and He (14%), with CH_4 controlling the visible spectrum.
- **Chemical equilibrium:**
  - Given elements, T, and P, the molecules are found by **minimizing the Gibbs free energy** $G = U + PV - TS$ (with $dG \leq 0$ at constant T, P).
  - Good in **deep, hot** layers: CH_4 on Jupiter, CO and N_2 on hot Jupiters.
- **Disequilibrium:** strong bonds (N_2, CO) make conversion slow; **vertical mixing** freezes deep abundances above the **quench level** where $\tau_{\text{chem}} = \tau_{\text{mix}}$.
- **Photochemistry:** stellar UV splits molecules in the upper atmosphere. Rate equation $\partial n_i/\partial t + \partial \phi_i/\partial z = P_i - n_i L_i$; most important for **low-mass planets**; produces **ozone**, **hazes**, and unexpected species such as CO_2.