Chemistry in Exoplanet Atmospheres

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Image credit: Dana Berry

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Why should you care?

Clues to planet formation/evolution

Clues to current processes

Chemistry affects observations

*Image credit: Alexandra Angelich, NRAO/AUI/NSF*

Line et al. (2013)
Three main chemical processes affect atmospheric composition on exoplanets. Each of these processes dominate in thermal regimes or atmospheric regions.
Thermochemical Equilibrium

- First-order prediction of composition, especially for hot planets
- Convenient: depends only on $T$, $P$, and relative elemental abundances. Some analytic solutions for simple cases available (e.g., Burrow & Sharp 1999, Heng et al. 2016, Woitke et al. 2021)
- Several public-domain codes and databases available

from Paul Mollière’s ERS theory talk

from Moses et al. (2013b)

from Fegley & Lodders (1996)
Thermochemical equilibrium also helps you predict where clouds should form (e.g., Morley et al. 2012); cloud formation can affect gas abundance ratios (e.g., Visscher et al. 2010, Helling et al. 2016, Woitke et al. 2021).

Moses et al. (2021), with original figure concept from Lodders & Fegley (2006)
Transport-induced quenching will matter for any planet with temperature gradients whose atmosphere gets hot enough, e.g., $T \geq \sim 800\text{-}1000\ \text{K}$, somewhere (e.g., at depth or on the dayside).
Photochemistry

from Moses et al. (2000)

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Photochemical Models

Solve the continuity equations:  

$$\frac{\partial n_i}{\partial t} + \nabla \cdot (n_i \mathbf{v}_i) = P_i - L_i$$

In 1D, $n_i v_i = n_i w_i$ = vertical flux $\phi_i$ based on “eddy” and molecular diffusion

Inputs to photochemical models:

- reactions and rate coefficients,
- thermodynamic parameters,
- UV cross sections and photodissociation/photoionization pathways,
- stellar flux,
- planetary and orbital parameters,
- atmospheric structure,
- wind fields and/or diffusion coefficients

Non-linear system of coupled partial differential equations. Solve using finite-difference techniques.
Photochemical models can give you results pertaining to all three main chemical regimes in exoplanet atmospheres.

Infamous spaghetti plots!

*Graph:*

- 51 Eri b
- $T_{\text{eff}} = 700$ K, $\log(g) = 3.5$, 1x solar
- $K_{zz(\text{deep})} = 2 \times 10^6$
- Pressure (bar) vs. Volume Mixing Ratio
- Species: $C_2H_2$, $C_2H_6$, $C_6H_6$, $C_2H_4$, $O_2$, $NO$, $OH$, $HCN$, $CO_2$, $CH_4$, $H_2O$, $NH_3$, $N_2$, $CO$
Giant Planets (including Neptunes)

Credit: NASA, ESA, CSA, Leah Hustak (STScI), Joseph Olmsted (STScI)

Credit: Gemini Observatory/AURA/ Lynette Cook

Credit: ESO VLT/P. Weilbacher (AIP)

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Giant Planets: Thermospheres

Extended thermospheres

Powered by absorption of XUV radiation from the host star

Greatly increases the planet’s cross section during transit in some UV/Vis spectral lines

Close-in giant exoplanets – and really any close-in planet with H-bearing molecules in the lower atmosphere – will have very hot, hydrodynamically escaping thermospheres dominated by H and H\(^+\) that drag heavier species up along with the escaping hydrogen (e.g., Yelle et al., 2004; García-Muñoz, 2007; Koskinen et al., 2013; Shaikhislamov et al., 2018)

Ultra-hot Jupiters will have metal atoms and ions throughout atmosphere (e.g., Lothringer et al., 2020)
Giant Planets: thermochemical equilibrium in IR “photosphere”

Giant planets are likely H$_2$-He rich

Thermochemical equilibrium predictions will depend on the relative abundance of the different elements, including metallicity (Fe/H).

Forward model grids are a useful tool and can provide a sanity check to supplement retrievals

Lower-mass giant planets may have higher-metallicity atmospheres (e.g., Fortney et al. 2013)

at 100 mbar, solar C/O ratio

modified from Moses et al. (2013b)
The composition can quench in the horizontal direction, as well as the vertical direction, if horizontal winds are faster than chemical conversion between different species (e.g., Cooper & Showman, 2006; Agúndez et al., 2012, 2014; Venot et al., 2020; Moses et al., 2021; Baeyens et al., 2021; Roth et al., 2021); see also 3D models (next slide). **Horizontal quenching can particularly affect phase curve observations**

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3D-GCMs with chemical kinetics and/or quenching included via relaxation methods exhibit complicated behavior but typically show more homogenized atmospheres that would be predicted by thermochemical equilibrium. Horizontal quenching is very important for transiting giant exoplanets (e.g., Drummond et al., 2018a,b, 2020; Mendonça et al., 2018; Steinrueck et al. 2019; Zamyatina et al. 2023; Lee et al. 2023).

Evolving towards the ultimate goal of handling realistic chemistry in GCMs! ... but photochemistry still missing, and if vertical quenching occurs deep, the deep adiabat must be prescribed realistically (see also Carone et al. 2020).
Giant Exoplanets: IR “photospheres” photochemistry

Figures and/or models from Tsai et al. (2023)

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Intermediate-sized Planets

Sub-Neptunes transition into Super Earths due to the escape of H/He from “photoevaporation” or core-powered mass loss (or both)? e.g., Owen & Wu, 2013; Lopez & Fortney, 2014; Gupta & Schlichting, 2019; Mordasini, 2020
Neptune-class exoplanets, sub-Neptunes, and super-Earths are likely to have diverse atmospheric compositions. Even if different planets formed in a similar location or similar ways, their evolutionary history could differ (impacts, escape, outgassing, etc.).

Thermochemical equilibrium can help define the possible parameter space.

from Moses et al. (2013); see also Guzmán-Mesa et al. (2022)
As H is lost from intermediate-sized planets, CO$_2$ and N$_2$ become more prominent and species such as CH$_4$ and NH$_3$ become less prominent, but H$_2$O is still important until atmosphere is severely depleted in hydrogen. There are probably lots of Venus-like super-Earths in known exoplanet population.
Thermochemical Equilibrium: Intermediate-sized Planets

Radius valley: Neptunes and sub-Neptunes are likely to have higher-metallicity atmospheres than hot Jupiters, assuming accretion of H/He occurs at all. If the H/He escapes, they can become super-Earths. While super-Earths don’t have “primordial” H/He atmospheres, outgassing and retention of species is possible.

To estimate bulk atmospheric content, consider the planet in context with its radius, mass, interior models (e.g., Malsky & Rogers, 2020; Kite et al., 2021; Schlichting & Young 2022), evolutionary history (including EUV instellation, e.g., Owen & Wu; Lopez & Fortney; Mordasini; and dissolution/outgassing, e.g., Kite et al., Schaefer et al., Misener & Schlichting).
The presence of a surface can affect atmospheric chemistry, even if the atmosphere and surface do not interact, simply because the atmosphere may not reach high-enough temperatures at depth to recycle photochemical products (e.g., Yu et al., 2021; Tsai et al., 2021).

Of course, the surface may not be “inert” and surface-atmosphere exchange can also occur, altering the atmospheric composition, e.g., magma oceans, water oceans, active geology, biology, etc. (see Kite et al. papers, Schlichting & Young, 2021; Krissansen-Totton et al., 2021; Hu et al., 2021).
Also, observations of CH$_3$OH and C$_2$H$_6$ might provide good indicators of the presence of a surface (Tsai et al., 2021; Madhusudhan et al., 2023).

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Atmospheric composition as a function of $T$ for planet with $g = 36.2$, from Schaefer et al. (2009)

BSE composition, 100 bar

Outgassed atmospheric composition at 100 bar from rocky planet with assumed CI chondrite composition, from Schaefer et al. (2010)

Secondary atmosphere affected by “geochemistry”

Hot rocky super-Earth atmosphere, from Ito et al. (2015)
For rocky terrestrial planets, boundary conditions and assumptions about background atmospheric composition control almost everything!

- Outgassing flux matters
- Effect of ocean (magma & water)
- Potential biosignatures
- Effect of stellar type
- Different catalytic cycles
- Pre-biotic chemistry

Is $O_2$ a biosignature on $CO_2$-dominant planets? e.g., James & Hu (2018), Hu et al. (2020), Harman et al. (2015, 2018), Ranjan et al. (2023) → atmospheric top boundary location matters

*from James & Hu (2018)*

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Photochemically produced hazes

from Gao et al. (2017), sulfur haze on a young Jupiter; see also Lavvas et al. (2017, 2019, 2021)

from He et al. (2020), laboratory simulations super Earth / sub-Neptune atmospheres

from Kawashima & Ikoma (2019), organic haze on warm sub-Neptunes
Conclusions

- Thermochemical equilibrium is a good starting point for predicting atmospheric composition, but disequilibrium processes like transport-induced quenching and photochemistry are likely affecting exoplanet atmospheres.

- Quenching is important if the planet has thermal gradients crossing from above to below ~1000 K. *Practical tip:* assume thermochemical equilibrium to some quench point (treat as free parameter) and then assume vertically constant mixing ratio above that point. Quenching likely affects observations on transiting planets.

- Photochemistry is more important for cooler planets. On hot ones, kinetics can drive composition back to equilibrium. Photochemically produced species have non-constant profiles (greater mixing ratio in peak production region). *Practical tip:* take a vertical profile from a chemical model and scale it, using the scaling factor as a free parameter. Key photochemical products on a variety of exoplanets include $C_xH_y$ hydrocarbons, HCN, $O_2$, $O_3$, sometimes $CO_2$, depending on situation, and hazes.

- Super-Earths/sub-Neptune atmospheres are probably widely diverse, potentially exotic, and chemically interesting; *don’t presume anything.* Same with terrestrial exoplanets. “Free” retrievals may be better.

- 3D effects matter for the chemistry of tidally locked planets. Practical tip may be to consider vertically quenched dayside atmospheric composition as representative everywhere... situation dependent.

- Use chemical models as a sanity check for retrievals, to help break degeneracies in posterior distributions, and to better understand exactly what you’re seeing and what that’s telling you about big-picture things.
Back-up slides
Thermochemical Equilibrium: Giant Planets

Appendix, Burrows & Sharp (1999)  
CO, CH₄, AND H₂O ABUNDANCES  
For H₂ dominant, T < 2500 K, O > C + Si

Given the equilibrium, CO + 3H₂ ⇄ H₂O + CH₄, the equilibrium constant is

\[ K_1(T) = \frac{P_{CO}}{P_{CH4}} \frac{P_{H2}^3}{P_{H2O}} = \exp \left( -\frac{\Delta G_1(T)}{RT} \right), \]  

(A1)

where \( \Delta G_1(T) \) is the Gibbs free-energy change in calories per mole associated with the equilibrium, and \( R \) is the gas constant in cal mol⁻¹ K⁻¹. Assuming that all the carbon is in CO and CH₄ and that all the oxygen is in CO and H₂O, equation (A1) can be solved analytically, yielding the results

\[ B_{CO} = A_C + A_O + \frac{P_{H2}^2}{2K_1(T)} - \sqrt{\left[ A_C + A_O + \frac{P_{H2}^2}{2K_1(T)} \right]^2 - 4A_C A_O}, \]  

(A2)

\[ B_{CH4} = 2A_C - B_{CO}, \]

and

\[ B_{H2O} = 2A_O - B_{CO}, \]  

(A3)

where

\[ K_1(T) = \exp \left[ (a_1/T + b_1 + c_1 T + d_1 T^2 + e_1 T^3)/RT \right], \]  

(A5)

and \( a_1, b_1, c_1, d_1, \) and \( e_1 \) are equal to 1.106131 × 10⁶, -5.6895 × 10⁴, 62.565, -5.81396 × 10⁻⁴, and 2.346515 × 10⁻⁸, respectively.

Similar procedure for NH₃·N₂. Heng et al. (2016) add C₂H₂; see also Woitke et al. (2021) for H₂O, N₂, CO₂, CH₄

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Thermochemical equilibrium predictions will depend on the relative abundance of the different elements, including metallicity (Fe/H) and C/O ratio (see also Hu & Seager (2014), Woitke et al. (2021)).

Giant Planets: thermochemical equilibrium in IR “photosphere”

at 100 mbar, 300x solar metallicity

modified from Moses et al. (2013b)

from Oberg et al. (2011)
Transport-Induced Quenching

Quench point depends on internal heat flux and dynamics

Quenching happens when $\tau_{\text{dyn}} \leq \tau_{\text{chem}}$ (e.g., Prinn and Barshay, 1977)

So, you just need to figure out what pressure that occurs at, and quenched abundances equal equilibrium abundances at that point.

BUT… both $\tau_{\text{dyn}}$ and $\tau_{\text{chem}}$ are model-dependent

Practical tips for predicting quench points: Visscher & Moses, 2011; Venot et al., 2012; Moses, 2014; Zahnle & Marley, 2014; Tsai et al., 2018).

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Transport-Induced Quenching

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So, you just need to figure out what pressure that occurs at, and quenched abundances equal equilibrium abundances at that point.

BUT... both $\tau_{\text{dyn}}$ and $\tau_{\text{chem}}$ are model-dependent, so quench points can be complicated to predict in practice (e.g., Visscher & Moses, 2011; Venot et al., 2012; Moses, 2014; Zahnle & Marley, 2014; Tsai et al., 2018). The method in the Z&M is probably the easiest to use, but it still depends on an uncertain reaction mechanism and $K_{zz}$ profile.
The predicted quenched abundances depend on the assumed chemistry as well as the assumed transport rates. Different modelers use different reaction mechanisms.
Transport-Induced Quenching: What should you do?

Lots of uncertainties revolving around quenching, so how should you handle it for your own application?

1. Just pick someone’s method (e.g., Visscher & Moses, 2011; Zahnle & Marley; 2015; Tsai et al., 2018) and consider a range of possible parameter space, especially in $K_{zz}$

2. Run your own kinetics-transport model to more accurately predict things yourself

3. Most practical solution: Consider the CH$_4$-CO-H$_2$O and NH$_3$-N$_2$ quench points as (separate) free parameters in your retrievals/forward spectra models... following equilibrium at depth and using (1) to define a reasonable range of possible quench points. Assume constant mixing ratio above quench point
Photochemistry: What to do about $K_{zz}$

**Radiative region:** $K_{zz} \propto P^{-0.5}$, dominated by waves, e.g., gravity wave breaking; Lindzen, 1981

**Convective region:** Use free-convection, mixing-length theory, e.g., Gierasch & Conrath (1985), or get fancier with rotation rate & latitude dependence (Visscher et al. 2010, Wang et al. 2015)

$K_{zz} \approx wH \approx \left(\frac{Fk_B}{\rho m c_p}\right)^{1/3} H$
The magnitude of $K_{zz}$ in the radiative region depends on various properties of the planet and its atmosphere, such as $T_{eq}$, $H$, $a$, $g$ (Zhang & Showman, 2018a,b; Komacek et al., 2019). I tried their exact scaling expressions, and they didn't quite work for all the solar-system planets, so I've used this simple scaling:

$$K_{zz} = 5 \times 10^8 \left[ P(\text{bar}) \right]^{-0.5} \left( \frac{H_{1\text{mbar}}}{620 \text{ km}} \right) \left( \frac{T_{\text{eff}}}{1450 \text{ K}} \right)^4,$$

where $K_{zz}$ is in units of cm$^2$ s$^{-1}$, $P$ is the atmospheric pressure (in bar), $T_{\text{eff}}$ is the effective temperature, $H_{1\text{mbar}}$ is the scale height at 1 mbar, and $a$ is the semi-major axis of the planet.

(From Moses et al. 2021)
Both transport-induced quenching and photochemistry affect composition of cool-to-warm giant exoplanets, whereas thermochemical equilibrium dominates on the hotter exoplanets.

Reactions should be fully reversed for close-in exoplanets.

From Moses (2014)
Solve the continuity equations: (Conservation of mass)

\[
\frac{\partial n_i}{\partial t} + \vec{\nabla} \cdot (n_i \vec{v}_i) = P_i - L_i
\]

In 1D, \( n_i \vec{v}_i = n_i \vec{w}_i = \) vertical flux \( \phi_i \):

\[
\Phi_i = -n_i D_i \left( \frac{1}{n_i} \frac{dn_i}{dz} + \frac{1}{H_i} + \frac{(1 + \alpha_i)}{T} \frac{dT}{dz} \right) - n_i K \left( \frac{1}{n_i} \frac{dn_i}{dz} + \frac{1}{H} + \frac{1}{T} \frac{dT}{dz} \right)
\]

Non-linear system of coupled partial differential equations. Solve using finite-difference techniques.
Photochemistry

- Reactions, branching ratios, rate coefficients
- Model atmosphere $(T, P, z, n_\alpha, n_i)$
- "Astronomical" inputs (stellar flux, planetary parameters, orbital parameters)
- Species UV photoabsorption, photodissociation, & photoionization cross sections and branching ratios
- Collision and other interaction cross sections for electrons and high-energy charged particles
- Species thermodynamic parameters
- Spectroscopic parameters for predictions of observational consequences

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Photolysis reaction: \( AB + h\nu \rightarrow A + B \) \( J_1 \) (s\(^{-1}\))

Unimolecular reaction: \( AB \rightarrow A + B \) \( k_2 \) (s\(^{-1}\))

Bimolecular reaction: \( AB + C \rightarrow AC + B \) \( k_3 \) (cm\(^3\) s\(^{-1}\))

Termolecular reaction: \( A + B + M \rightarrow AB + M \) \( k_4 \) (cm\(^6\) s\(^{-1}\))

Production rate \( P \) (cm\(^{-3}\) s\(^{-1}\)) for species AB: \( k_4[A][B][M] \)

Loss rate \( L \) (cm\(^{-3}\) s\(^{-1}\)) for species AB: \( J_1[AB] + k_2[AB] + k_3[AB][C] \)

where square brackets mean number density (cm\(^{-3}\))

In photochemical equilibrium \( \frac{d[AB]}{dt} = P - L = 0 \), so

\( k_4[A][B][M] = J_1[AB] + k_2[AB] + k_3[AB][C] \)

Rearrange algebraically to get

\( [AB] = k_4[A][B][M]/(J_1 + k_2 + k_3[C]) \)

M stands for any third body (constituent) in the atmosphere.

Photolysis rate: depends on molecular cross sections and local UV flux.

The k's are reaction rate coefficients.
Thermochemical Equilibrium: Intermediate-sized Planets

Sub-Neptunes and Super-Earths: Need to consider atmosphere-interior interactions, core formation, magma dissolution and outgassing, and other "geochemical" considerations.

Dissolution of H in magma ocean and allows H to survive longer (Kite et al. 2020).

Core formation and mantle chemistry matter for subsequent outgassed atmosphere

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<table>
<thead>
<tr>
<th>Sub-Neptune Formation Hypotheses (p ~ 10 d)</th>
<th>Sub-Neptune Si in Fe-Core</th>
<th>Volatile-free Core Redox</th>
<th>Volatile Origin &amp; Partitioning</th>
</tr>
</thead>
<tbody>
<tr>
<td>In-Situ Accretion, Formation Inside Ice-line, or Pebble Migration: + Nebular Gas</td>
<td>Less Si in Fe-metal core</td>
<td>Non-Reactive Impermeable Magma</td>
<td>Mis-states H₂ Needed For A Given Radius</td>
</tr>
<tr>
<td>In-Situ Accretion, Formation Inside Ice Line, or Pebble Migration: + Solid-Derived Volatiles</td>
<td>More Si in Fe-metal core</td>
<td>Relatively Reduced Magma</td>
<td>Low - ( \mu_{\text{atm}} ) atmosphere. Some gas dissolved (Chachan &amp; Stevenson 2018)</td>
</tr>
<tr>
<td>Planetesimal Migration or Whole-Planet Migration from beyond ice line: + Nebula Gas</td>
<td></td>
<td>Relatively Oxidized Magma</td>
<td>( \mu_{\text{atm}} ) atmosphere. Some gas dissolved (Chachan &amp; Stevenson 2018)</td>
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<td></td>
<td>More-Oxidized Magma</td>
<td>Intermediate ( \mu_{\text{atm}} ) (e.g. Rogers et al. 2011)</td>
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from Kite et al. (2020)