

Atmospheric Disequilibrium Chemistry

Planetary Atmospheres 4/14/20

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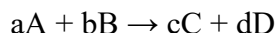
Part 1: The Thermodynamics of Chemical Equilibrium

- Chemical equilibrium is probably the most important/essential application of thermodynamics to chemistry
- But before we talk about the thermo stuff, let's do a quick crash course on gen chem equilibrium constants and kinetics...

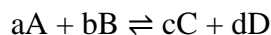
Part 1a: Reaction Equilibria and Kinetics

Equilibrium Constant

- Reactions often written as:



- But most chemical reactions, especially in atmospheres, are actually like:



- Equilibrium constant K is:

$$K_{eq} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

- Where [X] is the concentration of X.
- K can also be expressed in terms of partial pressure for gas-phase rxns (more relevant for atmospheres):

$$K_P = \frac{P_A^a P_B^b}{P_C^c P_D^d}$$

- Relationship between K_P and K_{eq} is:

$$K_P = K_{eq} \cdot (RT)^{\Delta n}$$

- If $\Delta n = 0$, $K_P = K_{eq}$
- Solids and liquids are **excluded** from K calculations – only dissolved and gaseous species are accounted for.
- For example (heterogeneous equilibrium):

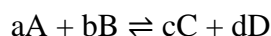


$$K_{eq} = [\text{CO}_2]$$

- K_{eq} is dependent on certain parameters like temperature and solvent, but NOT catalysts.
- A few examples asking about equilibrium shift given changing concentrations or conditions.

Reaction Rates

- Rate of reaction is defined as:

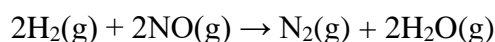


$$v = k[A]^n[B]^m$$

- Where v is the reaction rate and k is the rate constant, and $n+m$ is the order of the reaction rate, which is dependent on the mechanism of the reaction. In single-step mechanisms, n and m are the stoichiometric ratios.
- v in a closed, isochoric system without build-up of intermediates is:

$$v = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt}$$

- For example, for the following reaction:



- Has the following mechanism:

1. $2\text{NO} \rightleftharpoons \text{N}_2\text{O}_2$ fast
2. $\text{N}_2\text{O}_2 + \text{H}_2 \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O}$ slow
3. $\text{N}_2\text{O} + \text{H}_2 \rightarrow \text{N}_2 + \text{H}_2\text{O}$ fast

- The step 2 is the slowest, so it is the **rate determining step**.

$$v = k_2 [\text{H}_2] [\text{N}_2\text{O}_2]$$

- Since step 1 is in equilibrium, $[\text{N}_2\text{O}_2]$ can be found in terms of initial reactant concentration:

$$[\text{N}_2\text{O}_2] = K_1 [\text{NO}]^2$$

- Substitution gives:

$$v = k_2 K_1 [\text{H}_2] [\text{NO}]^2$$

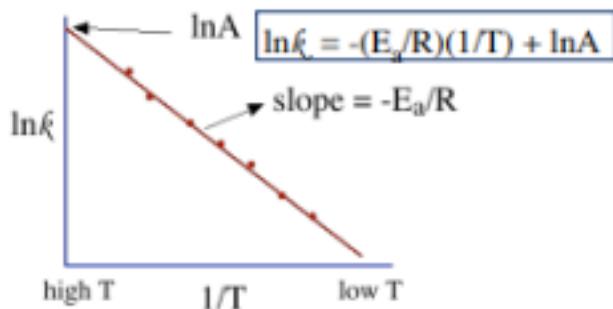
- Meaning the reaction is third order with a rate constant $k = k_2 K_1$.
- K and k of the forward and backward rxn are related via:

$$K = \frac{k_f}{k_r}$$

- If intermediate reactions are rate-limiting, this complicates things.

Temperature Dependence

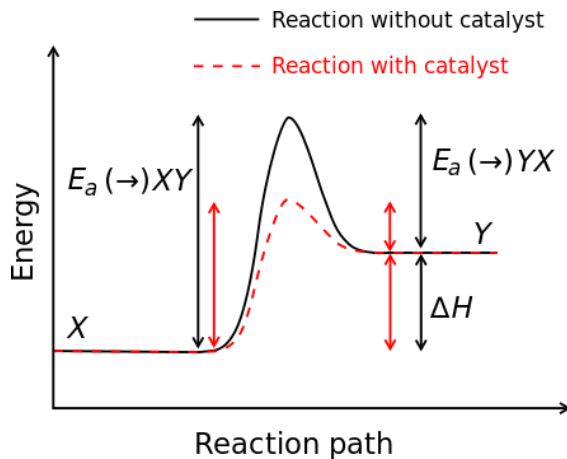
- For most reactions, rates increase with increase in temperature, and, if $\ln k$ is plotted against $1/T$, the plot is a straight line with a negative slope.



- In these cases, k is given by the empirical Arrhenius equation:

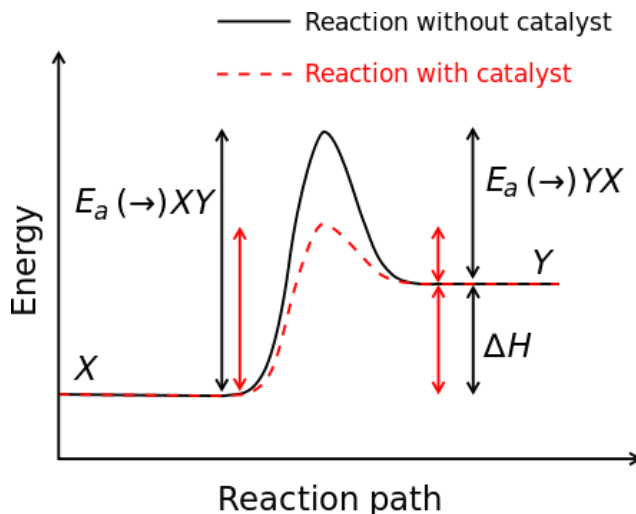
$$k = A e^{\frac{-E_a}{RT}}$$

- Where A is the pre-exponential factor, a constant for every chemical reaction, and represents the frequency of collisions in the correct orientation for a reaction, E_a is the activation energy, and T is temperature.
- So, rates of reaction are affected by parameters like temperature and solvent, which affect collision frequency and the likelihood of each molecule having sufficient energy to cross E_a .
- A **catalyst** will also affect the rate due to the lowering of the activation energy. It will **NOT** change the equilibrium or outcome of the reaction.



Part 1b: Link Between Thermodynamics and Equilibrium

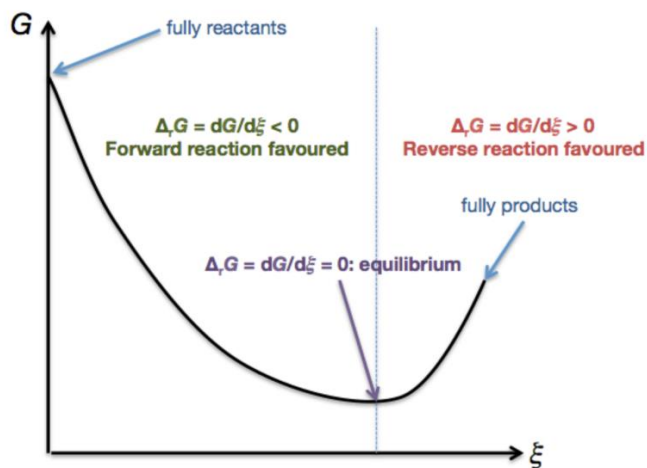
- Equilibrium equations given at this point have been empirical – but can we describe a system in chemical equilibrium from a more **fundamental, physical** perspective?
- Let's take another look at this plot...



- “Energy” can be represented by enthalpy (H) or Gibbs free energy (G) (related)

	+	-
ΔH	Endothermic	Exothermic
ΔG	Endergonic	Exergonic

- What do people know about Gibbs free energy in terms of chemical applications?
- Gibbs free energy is particularly important it defines if a reaction is **spontaneous** and is closely related to equilibrium
- Gibbs free energy represents reversible work that can be done by the system (minus work done by pressure forces)
- Thus, once Gibbs free energy reaches a minimum, the system cannot do any more work – another way to think of this: the reaction reaches **equilibrium**



$$\Delta G = \left(\frac{\partial G}{\partial \xi} \right)_{T,p} = 0 \text{ at equilibrium}$$

- G and K are related via:

$$\Delta G = -RT \ln K$$

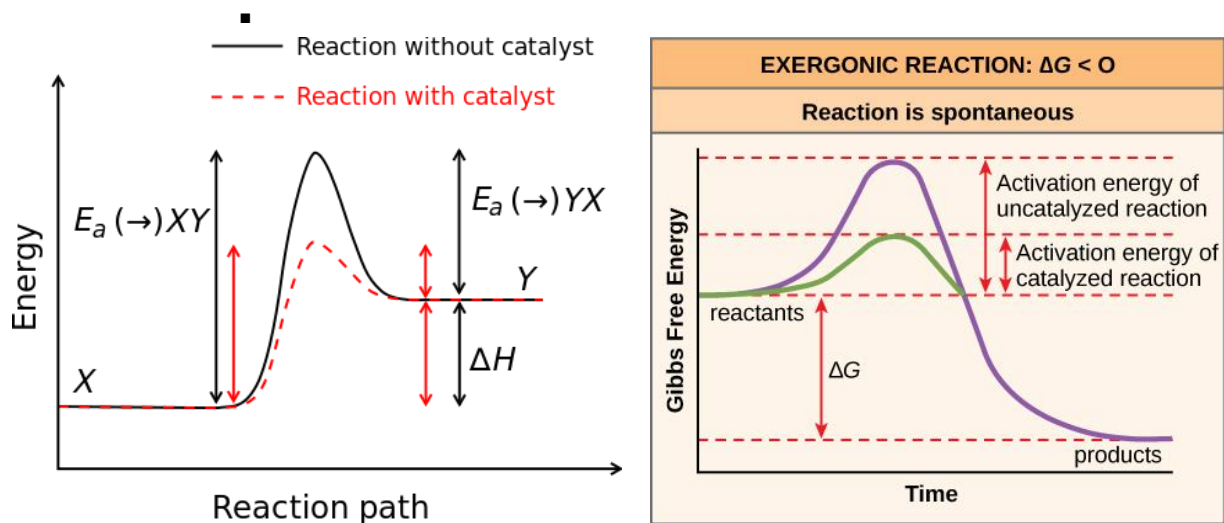
- When $\Delta G < 0$, rxn is **spontaneous** and can proceed
- There are a couple more important ways to calculate and think about Gibbs free energy:
 - Balance between the chemical potentials of reactants and products

$$\Delta G = \sum \Delta G_{prod} - \sum \Delta G_{react}$$

- Remember Hess's Law for calculating reaction enthalpy in PPP? This is the same thing but with G (because G is also a state function!)
- Balance between entropy of the system and surroundings

$$\Delta G = \Delta H - T\Delta S$$

- When ΔH is sufficiently negative, it can overcome a negative ΔS due to distribution of heat into surroundings leading to an overall increase of entropy in the system + surroundings



Part 1c: Disequilibrium

- Should be pretty easy to figure out what disequilibrium means at this point
 - Reaction does not reach (or goes past) equilibrium point K
 - $\Delta G \neq 0$
 - Requires some external force/work
- Disequilibrium chemistry is ubiquitous on Earth, in the Solar System, and outside of it (exoplanets!)
- Life depends on disequilibrium. Equilibrium = death
 - How come life exists despite so many endergonic processes?
 - Endergonic processes can occur when coupled to exergonic processes (e.g. powering the endergonic polymerization of amino acids to make proteins with the exergonic and exothermic dephosphorylation of ATP to ADP)

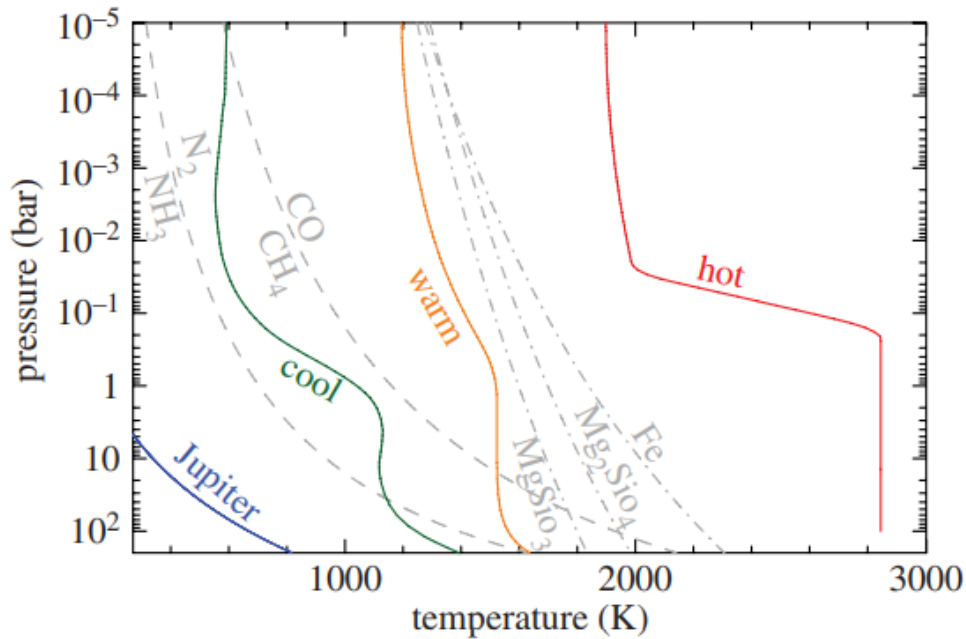
Part 1 Main Takeaways

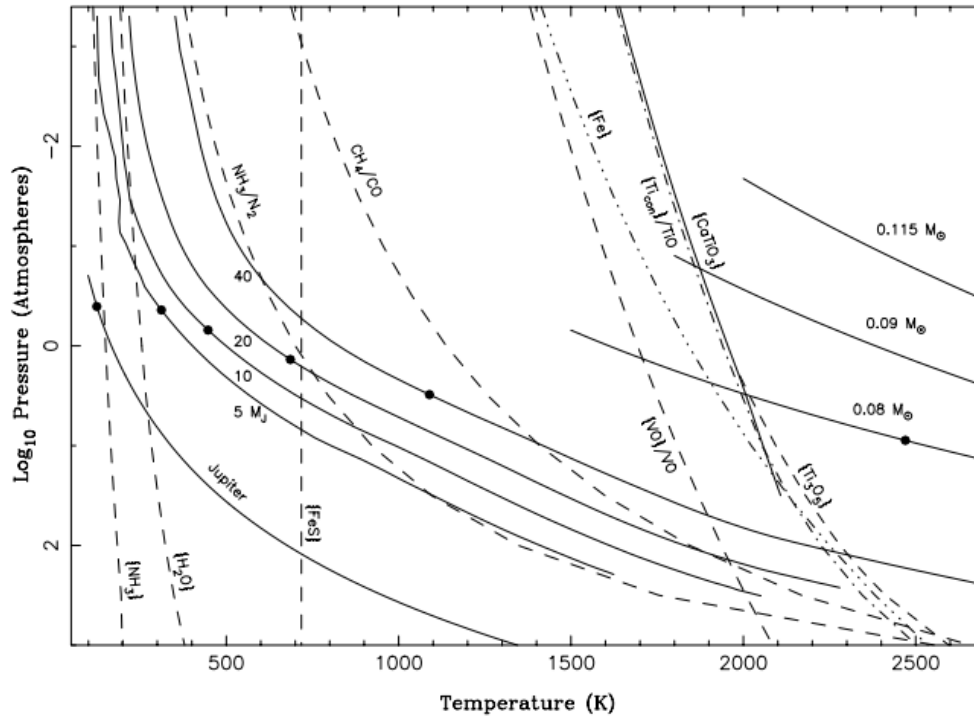
- Thermodynamics and equilibrium are closely related

- Equilibrium is achieved when Gibbs free energy is minimized, so “disequilibrium” indicates some sort of disruptive force
- Temperature has a very important effect on equilibrium, both on the equilibrium state itself and the speed with which it is reached

Part 2: Disequilibrium Processes in Atmospheres

- To the first order, atmospheric composition can be predicted by assuming thermochemical equilibrium – the only effects on atmosphere are composition, temperature, and pressure
- As seen above, temperature makes it easier to reach equilibrium – so very hot planets (>2000K) often stay at equilibrium, except at high altitudes
- Also works best for atmospheres which have thermal profiles that do not cross stability thresholds for certain molecules



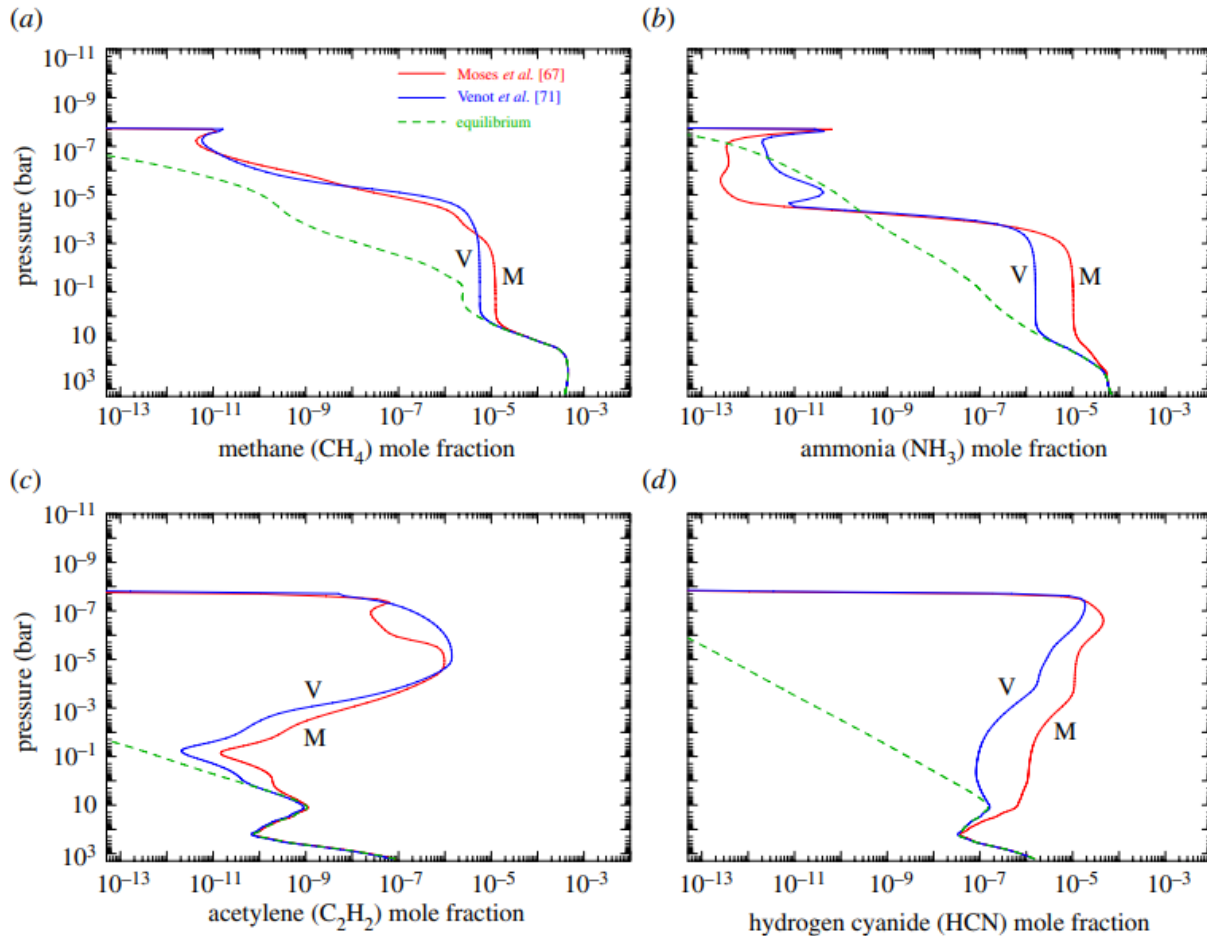


- For example, in this plot, a model planet with a mass of 40 Jupiter masses crosses the CH_4/CO threshold around 10 atm, indicating that, if at equilibrium, this is the point at which the atmosphere contains more CH_4 than CO
- CO , N_2 , and H_2O dominate atmospheres hotter than 1600K in 0.1-1000 mbar region
- CH_4 and NH_3 dominate in cooler atmospheres (more photochemically interesting)
- The closer to this threshold the atmosphere, the greater the disequilibrium effects
- Disequilibrium considered “second-order effects” but can have huge impact on compositions, radiative properties, and thermal profiles of atmospheres

Part 2a: Transport-Induced Quenching

- Disruption from equilibrium via transport of molecules through atmosphere at more rapid time scales than kinetic time scales
- Transport can occur via:
 - Convection
 - Eddy diffusion (vertical)
 - Zonal and longitudinal winds
- A given molecule has τ_{chem} , the time scale of the fastest reaction producing and destroying it, and τ_{mix} , the time it takes to transport the molecule to cooler regions

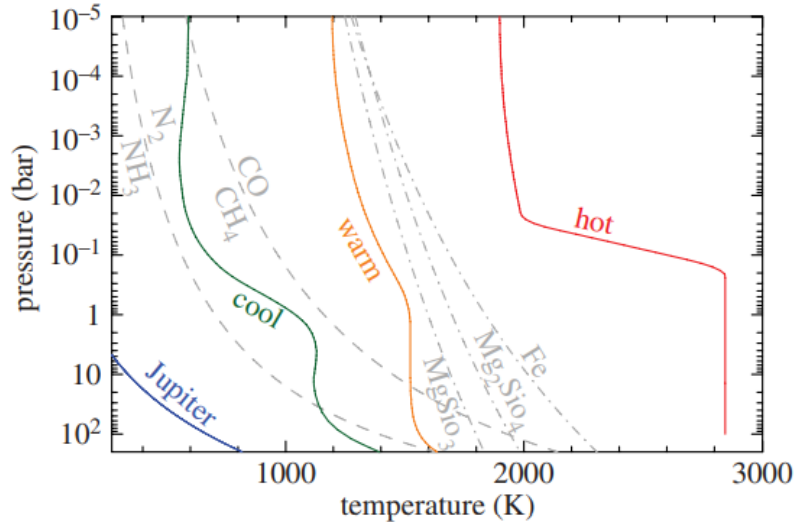
- In cooler regions, reactions creating and destroying the molecule will be kinetically inhibited
- At altitude where $\tau_{\text{chem}} = \tau_{\text{mix}}$, abundance of molecule starts to be “quenched” due to transport carrying away molecules before they can react
- Quenching occurs when $\tau_{\text{chem}} > \tau_{\text{mix}}$
- Quenching level different for each species



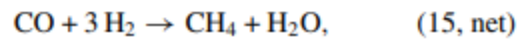
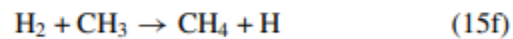
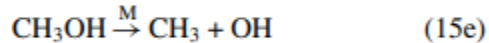
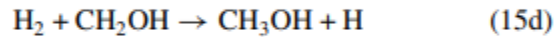
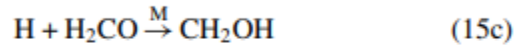
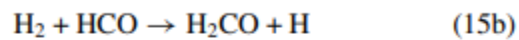
- Chemical models of HD 189733b, the closest transiting Hot Jupiter to Earth
 - Green line is thermochemical equilibrium, red and blue lines include disequilibrium processes
- Occurs when rxns proceed slowly in both directions:
 - Temps are low, so less molecules can overcome E_a
 - Pressure is low, so collision frequencies are lower
- Contribution often calculated using a mass continuity equation, where mass flow due to created and destroyed species as well as eddy diffusion are balanced

Solar System Example: CO Enrichment on Jupiter

- 1 ppb abundance of CO seen in Jupiter's upper troposphere despite Jupiter's profile being to the far left of the CH₄/CO line



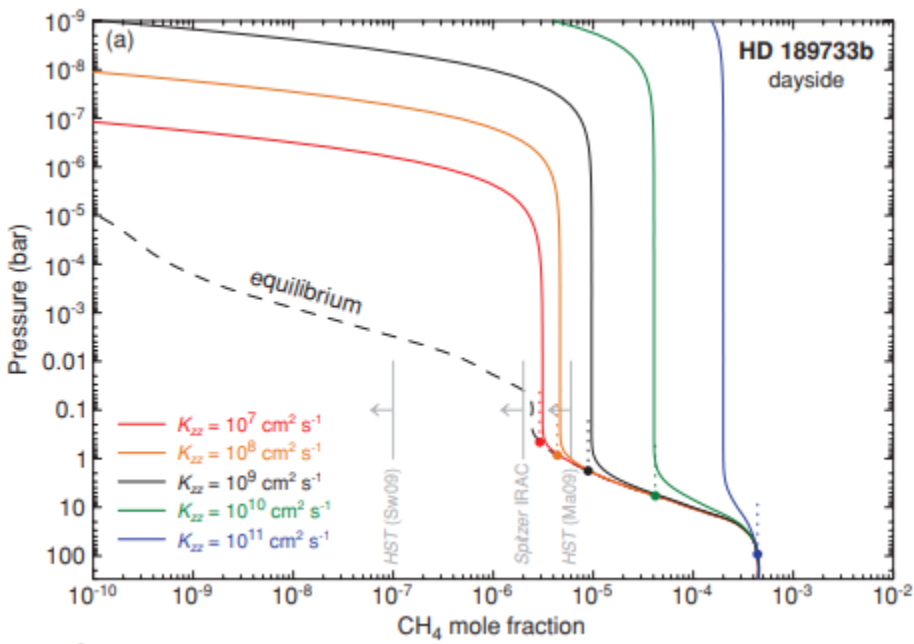
- Exact mechanism and rate determining step of interconversion between CH₄ and CO in Jovian atmosphere has not been established



- This overabundance is caused by very rapid upward mixing 3-4 orders of magnitude faster than vertical mixing on Earth
- Implies an internal heat source in Jupiter is driving very rapid convection in its atmosphere
- Significant amount of CO was also produced during the Shoemaker-Levy impact, indicated by high-temperature lines and uneven amounts on north and south hemispheres

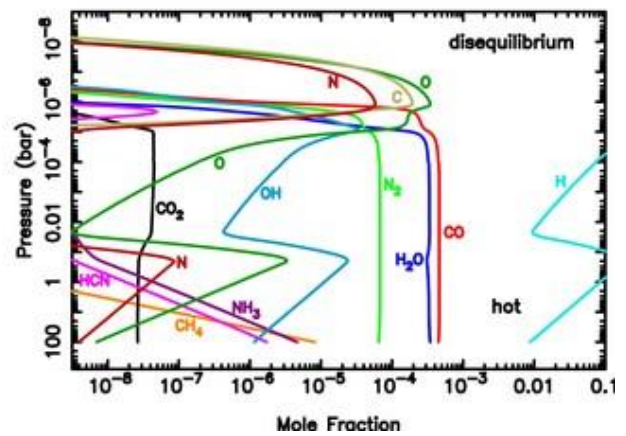
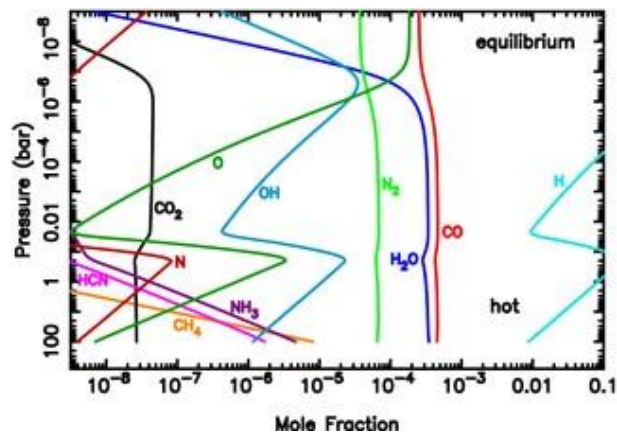
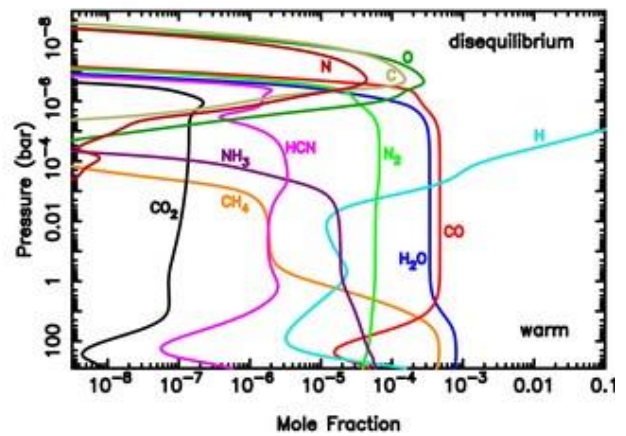
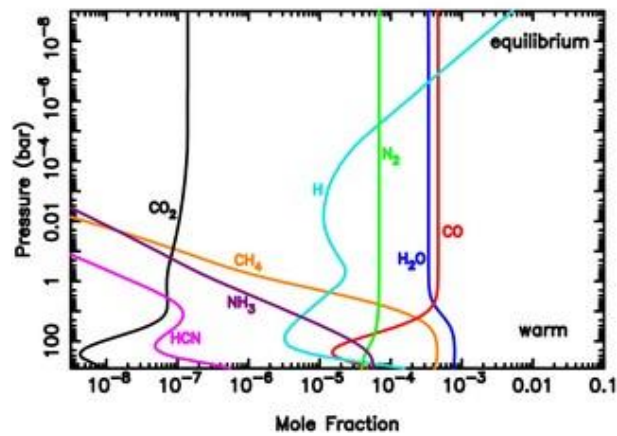
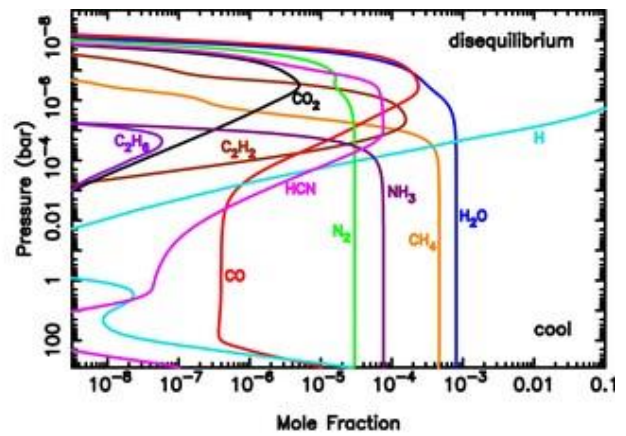
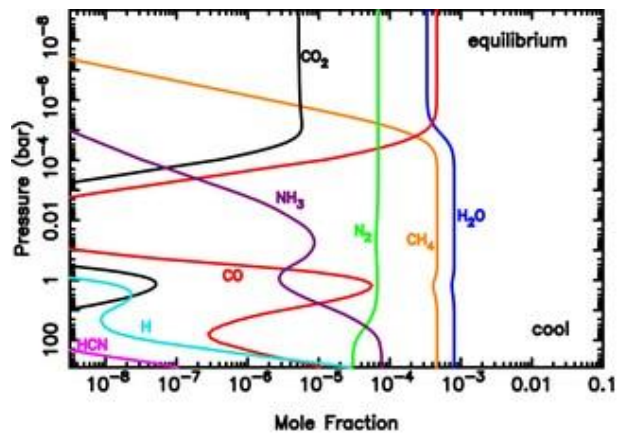
Exoplanet Example: CH₄ Mole Fraction on HD 189733b

- Much hotter and bigger than Jupiter

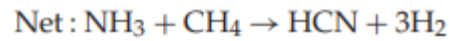
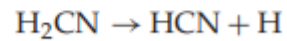
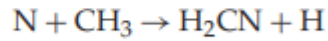
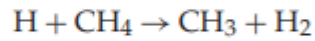
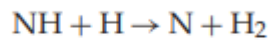
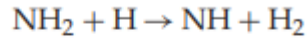
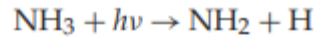
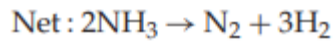
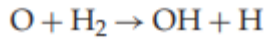
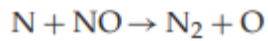
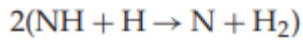
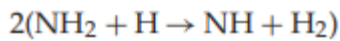
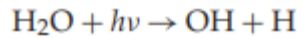
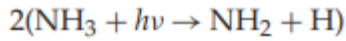


Part 2b: Photochemistry

- Stellar UV photons primary instigators but also affected by Vis and NIR
- Radiation will photolyze weaker bonds
 - CH₄ and NH₃ weaker than CO and N₂
 - So cooler atmospheres will be affected more by photochem



- Huge H production due to H₂ photolysis, thermal decomposition, and H₂O photolysis
- In cooler atmospheres, quench points for CH₄-CO and N₂-NH₃ are deeper in the atmosphere, and, once mixed to higher regions, they can be photochemically destroyed
- Ammonia is very easily photolyzed:



- HCN one of most prominent products of photolysis in C and N containing atms
- Formation of more complex hydrocarbons and nitriles in upper atmosphere and eventual settling of these refractories into a haze layer

Solar System Example: Haze Layer on Titan

- Haze layer of tholins on Titan

Exoplanet Example: Effects of Photochemistry on Hot Jupiters

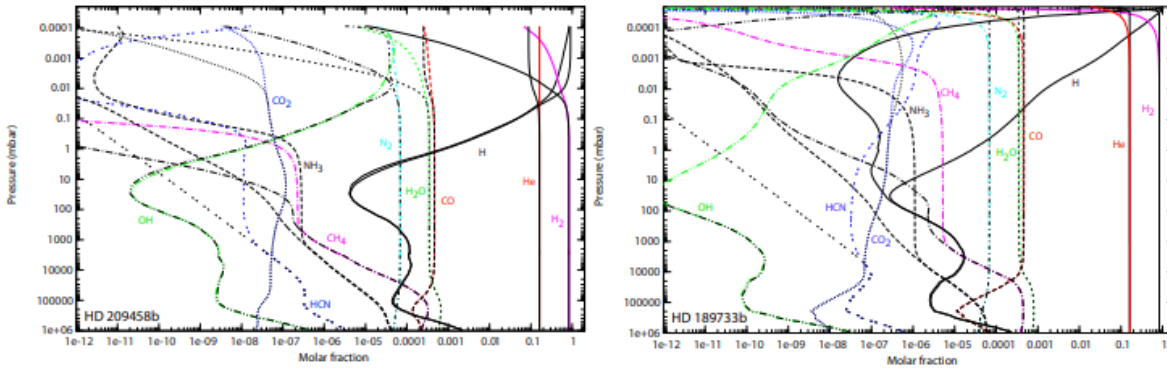


Fig. 5. Steady-state composition of HD 209458b (*left*) and HD 189733b (*right*) calculated with our nominal model (color lines), compared to the thermodynamic equilibrium (thin black lines).

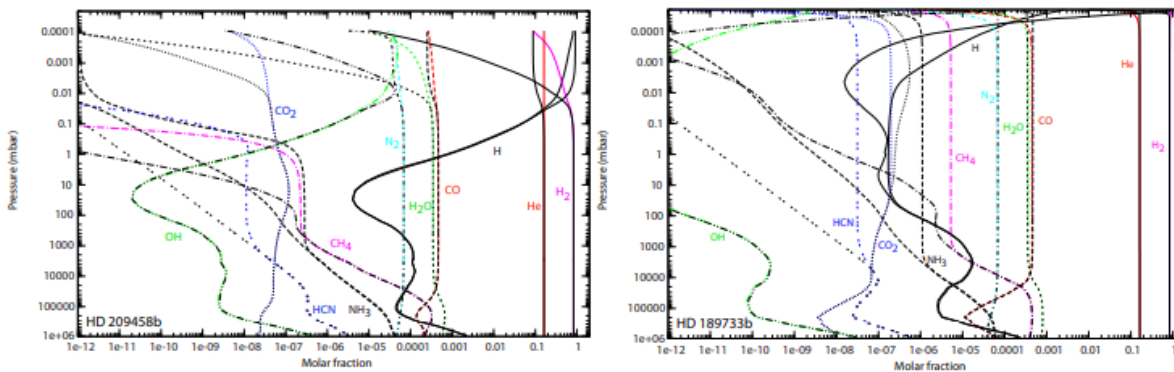


Fig. 6. Steady-state composition of HD 209458b (*left*) and HD 189733b (*right*) calculated with our nominal model without photodissociation (color lines), compared to the thermodynamic equilibrium (thin black lines).

Part 2 Main Takeaways

- Cool and low-pressure atmospheres are most affected by disequilibrium processes due to temperature-dependence on rate constant
- Transport-induced quenching moves molecules throughout atmosphere to disrupt equilibrium
- Photochemistry can create haze layers on atmospheres that are not too hot