METHANE, CARBON MONOXIDE, AND AMMONIA IN BROWN DWARFS AND SELF-LUMINOUS GIANT PLANETS

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ABSTRACT

We address disequilibrium abundances of some simple molecules in the atmospheres of solar composition brown dwarfs and self-luminous giant planets using a kinetics-based one-dimensional atmospheric chemistry model. Our approach is to use the full kinetics model to survey the parameter space with effective temperatures between 500 K and 1100 K. In all of these worlds, equilibrium chemistry favors CH4 over CO in the parts of the atmosphere that can be seen from Earth, but in most disequilibrium favors CO. The small surface gravity of a planet strongly discriminates against CH4 when compared to an otherwise comparable brown dwarf. If vertical mixing is like Jupiter’s, the transition from methane to CO occurs at 500 K in a planet. Sluggish vertical mixing can raise this to 600 K, but clouds or more vigorous vertical mixing could lower this to 400 K. The comparable thresholds in brown dwarfs are 1100 ± 100 K. Ammonia is also sensitive to gravity, but, unlike CH4/CO, the NH3/N2 ratio is insensitive to mixing, which makes NH3 a potential proxy for gravity. HCN may become interesting in high-gravity brown dwarfs with very strong vertical mixing. Detailed analysis of the CO–CH4 reaction network reveals that the bottleneck to CO hydrogenation goes through methanol, in partial agreement with previous work. Simple, easy to use quenching relations are derived by fitting to the complete chemistry of the full ensemble of models. These relations are valid for determining CO, CH4, NH3, HCN, and CO2 abundances in the range of self-luminous worlds we have studied, but may not apply if atmospheres are strongly heated at high altitudes by processes not considered here (e.g., wave breaking).

Key words: astrochemistry – brown dwarfs – planets and satellites; gaseous planets

Online-only material: color figures

1. INTRODUCTION

Disequilibrium chemistry has been known in Jupiter’s atmosphere for several decades (Prinn & Barshay 1977; Bézard et al. 2002) and has been expected and suspected in brown dwarf atmospheres from the time of their discovery (Fegley & Lodders 1996; Noll et al. 1997; Saumon et al. 2000). The most famous disequilibrium is an overabundance of CO relative to CH4. This occurs in Jupiter and brown dwarfs when CO is dredged up from deep, hot layers of the atmosphere more quickly than chemical reactions with ambient hydrogen can convert it to CH4. It is to be expected that similar processes take place in young, self-luminous extrasolar giant planets. However, the apparent paucity of methane in the atmospheres of planets with effective temperatures comparable to those of methanenrich, T-type brown dwarfs was underpredicted and has been met with surprise.

Among field brown dwarfs methane appears—by definition—at the L- to T-type transition where their near-infrared colors turn toward the blue at effective temperatures near 1200 K (Kirkpatrick 2005). The first directly imaged planets, however, were found to have effective temperatures below 1200 K and yet their near-infrared spectra were devoid of signs of methane in the K band (e.g., Barman et al. 2011a). The best example is HR8799c: despite an effective temperature near 1100 K, in both low- and high-resolution spectra—particularly the high-resolution spectrum taken by Konopacky et al. (2013)—methane has gone missing.

Surface gravity is the defining difference between extrasolar giant planets and brown dwarfs and to date is the only proven difference, although there are great hopes for metallicity. Field brown dwarfs (hereafter BDs) have high surface gravities (g of the order of 10^5 cm s^-2) and therefore very compressed scale heights. Extrasolar giant planets (EGPs) have modest surface gravities (g of the order of 10^3 cm s^-2) and extended scale heights (e.g., Burrows et al. 1997; Saumon & Marley 2008). A BD and a self-luminous EGP of the same composition and the same effective temperature will have similar optical depths as a function of temperature, at least in the absence of clouds, i.e., the function T(τ) is roughly the same. However, because p ∝ τg, the BD has a much higher pressure at a given optical depth than does the EGP, and a BD is much cooler than the EGP at a given pressure. Because lower temperatures and higher pressure favor CH4 in its struggle with CO, it has been pointed out that CH4 will be seen more easily and CO seen less easily at lower gravity in BDs (Hubeny & Burrows 2007). Hence Barman et al. (2011a) suggested that the even lower gravity of HR8799b might be why no methane is seen in it. We agree. We will verify that the dependence on g is strong and leads to qualitatively different outcomes for BDs and self-luminous EGPs, a result implicit in previous work but far from fully appreciated.

Previous studies of carbon speciation in BDs and EGPs have mostly focused on a few particular objects (Saumon et al. 2006; Geballe et al. 2009; Barman et al. 2011a, 2011b; Moses et al. 2011; Line et al. 2011), or on hot highly irradiated EGPs (Moses et al. 2011; Visscher 2012), or used one of several quench approximations culled from the literature (Fegley & Lodders 1996; Saumon et al. 2000; Lodders & Fegley 2002; Hubeny & Burrows 2007), or various combinations of the above (Cooper & Showman 2006; Visscher & Moses 2011; Moses et al. 2013a, 2013b). The basic idea is that CH4 and CO will

1. We do not intend to wade into the nomenclature battles here. For our purposes, companion objects below ∼13 Mj are planets.
often be seen in disequilibrium because the chemical reactions that would enforce equilibrium do not have time enough to take place while the gas is cool (Prinn & Barshay 1977). The disequilibrium composition that results is described as “frozen-in” or “quenched.”

Quenching has been widely used to quantify discussions of CO–CH₄ and N₂–NH₃ disequilibria in a wide range of astrophysical problems, dating at least back to Prinn & Barshay’s (1977) study of CO in Jupiter. Earlier discussions of quenching can be found with respect to the N₂–O₂–NO system that is important in thunderbolts (Chameides et al. 1979), meteor entry and rocket reentry (Park & Menees 1978), and explosions in Earth’s atmosphere (Zel’dovich & Raizer 1967). In the quench approximation, the disequilibrium composition that one can observe is approximated by the equilibrium composition when the relevant chemical reaction timescale $t_{\text{chem}}$ equals the relevant cooling timescale, which, if due to mixing, can be written $t_{\text{mix}}$ (Prinn & Barshay 1977). There are many different prescriptions for defining $t_{\text{chem}}$ and $t_{\text{mix}}$ that we will discuss below. The history of quench schemes for jovian planets, exoplanets, and brown dwarfs has been comprehensively recounted in a series of recent papers by Moses and colleagues (Moses et al. 2010, 2011; Visscher & Moses 2011; Visscher et al. 2010).

Here we do something different. We use a one-dimensional (1D) chemical kinetics code coupled to $p$-$T$ profiles from a detailed 1D atmospheric structure code to compute a galaxy of chemical compositions in a wide range of possible brown dwarfs and cooling EGPs. The code explicitly includes reverses of all reactions so that in the absence of atmospheric physics the chemical composition would relax to equilibrium at every height. Our strategy is to find the apparent quench points in all models and analyze these for their systematic properties. We then fine tune our results by using them in quench approximations. Our objective is to describe the emergent properties of the chemical network as a whole. Our strategy differs from previous work that seeks to determine the one key rate-limiting step in a network of reactions, which is then treated as the effective reaction rate for the network as a whole.

We limit the study to self-luminous cooling worlds for which insolation is not (yet) thermally important. This includes brown dwarfs, free-floating planets, and young directly imaged planets. This category includes most of the exoplanets for which good data can be obtained in the present or in the near future. What this limitation means for carbon speciation is that we are concerned only with the conversion of CO to CH₄. Unlike Line et al. (2011), Visscher & Moses (2011), and Visscher (2012), we do not address the kinetic inhibition against oxidizing CH₄ to CO. The latter is an issue in strongly irradiated planets that are warm at high altitudes where, if vertical mixing is fast and the temperature not too hot, CH₄ and its photochemical products will be overabundant (Line et al. 2010; Miller-Ricci Kempton et al. 2011; Morley et al. 2013). Methane oxidation could be an issue for BDs and cooling EGPs if the higher parts of their atmospheres are strongly heated by wave-breaking processes not taken into account in our radiative-convective model, but we do not further address this possibility here.

Quenching in the nitrogen system has also been the subject of many studies over the years (Abelson 1966; Chameides & Walker 1981; Prinn & Fegley 1987; Fegley & Lodders 1994, 1996; Saumon et al. 2006; Moses et al. 2010, 2011; Line et al. 2011). As with methane, the underabundance of ammonia in brown dwarfs cold enough to favor it has been attributed to disequilibrium chemistry (Saumon et al. 2006). The visibility of ammonia has been made the distinguishing characteristic of the Y dwarf, the newest, coldest, and possibly last member of the stellar spectral sequence (Cushing et al. 2011). The NH₃–N₂–HCN system differs from CO and CH₄ in interesting ways that lead to significantly different behavior.

Finally, for completeness, we address quenching of CO₂, a gas that can be relatively easy to observe from a space-based observatory and, because its abundance is sensitive to metallicity, can be relatively telling. CO₂ is not always thought of as a species subject to quenching (but see Prinn & Fegley (1987)). In the H₂-rich, UV-poor worlds that are the subject of this study, CO₂ quenching does take place.

2. OVERVIEW OF CO AND CH₄

Figure 1 illustrates the most important chemical pathways between CO and CH₄ in a warm H₂-rich atmosphere. The path from CO to CH₄ climbs over three energy barriers, the first between CO and formaldehyde (H₂CO), the second between formaldehyde and methanol (CH₃OH), and the third between methanol and methane. The three barriers can be thought of as reducing the C≡O triple bond to a double bond, reducing the C=O double bond to a single bond, and splitting C from O entirely.

In photochemistry the first barrier is unimportant because atomic hydrogen is generated in abundances that vastly exceed equilibrium (Liang et al. 2003). Kinetic barriers to adding H to CO to make HCO or adding H to HCO to make H₂CO are insignificant. The third barrier is unimportant in photochemistry because incident UV radiation readily splits CH₃OH into CH₃ and OH, which is quickly followed by adding photochemical H to CH₃ to make CH₄. In photochemistry, the energy to overcome the first and third barriers comes from UV photons.

By contrast, the middle barrier is not easily overcome by photochemistry. Formaldehyde is readily photolyzed but the products are either CO or HCO, i.e., regress that leaves the C≡O bond unbroken. Meanwhile successive three-body additions of photochemical H to H₂CO to make CH₃OH face considerable kinetic barriers, except at high temperatures where CH₄ is

![Figure 1. Major chemical pathways linking CO and CH₄ in an H₂-rich atmosphere.](Image 321x614 to 567x736)
not favored. The historic focus of the planetary literature was therefore on reactions that go from formaldehyde to methanol. Prinn & Barshay (1977) suggested \(H_2 + H_2CO \rightarrow CH_3 + OH\), an ambitious reaction that jumps two hurdles at once, as the rate-limiting step, while Yung et al. (1988) suggested that \(H + H_2CO + M \rightarrow CH_3O + M\) (where M represents a third body) would be the bottleneck. Both schemes have been widely used for Jupiter (Bézard et al. 2002), EGPs (Cooper & Showman 2006; Line et al. 2011), and BDs (Hubeny & Burrows 2007; Barman et al. 2011a).

Without the photochemical assist, any of the three barriers could potentially block the reaction. Recently, Moses et al. (2011) concluded that the rate-limiting reaction is the one that breaks the C–O single bond. They report that the bottleneck is between methanol and methane, \(CH_3OH + M \rightarrow CH_3 + OH + M\) when methane is abundant, or goes through a free radical \(H + H_2COH \rightarrow CH_3 + OH\) when methane is scarce. We will concur with the former but not the latter.

3. The Photochemical Model

Standard 1D codes simulate atmospheric chemistry by computing the gains and losses of chemical species at different altitudes while accounting for vertical transport. Vertical transport is parameterized as a diffusive process with an “eddy diffusion coefficient,” denoted \(K_{zz}\) \([cm^2 s^{-1}]\). Volume-mixing ratios \(f_i\) of species \(i\) are obtained by solving continuity

\[
N \frac{\partial f_i}{\partial t} = P_i - L_i N f_i - \frac{\partial \phi_i}{\partial z} \tag{1}
\]

and force (flux)

\[
\phi_i = b_{ia} f_i \left( \frac{m_ag}{kT} - \frac{m_ig}{kT} \right) - (b_{ia} + K_{zz}N) \frac{\partial f_i}{\partial z} \tag{2}
\]

equations. In these equations, \(N\) is the total number density \([cm^{-3}]\), \(P_i - L_i N f_i\) represent chemical production and loss terms, respectively, \(\phi_i\) is the upward flux, \(b_{ia}\), the binary diffusion coefficient between \(i\) and the background atmosphere \(a\), describes true molecular diffusion, and \(m_a\) and \(m_i\) are the molecular masses of \(a\) and \(i\). We implement molecular diffusion of a heavier gas through \(H_2\) by setting \(b_{ia} = 6 \times 10^{19} (T/1400)^{0.75} \text{ cm}^{-1} \text{ s}^{-1}\)—appropriate for CO—for all the heavy species. This is a reasonable approximation for present purposes, as our concern is with quenching at altitudes well below the homopause. The physical meaning of \(b_{ia}\) is the ratio of the relative thermal velocities of the two species to their mutual collision cross section. In the present circumstances, the relative thermal velocity is effectively that of \(H_2\), so the only important source of variation in \(b_{ia}\) stems from the different diameters of the molecules. The code has been used by Zahnle et al. (2009) to address hot Jupiters and by Miller-Ricci Kempton et al. (2011) and Morley et al. (2013) to address \(H_2\)-rich hot Neptunes and super-Earths.

Temperature and pressure profiles are imported from the output of detailed radiative-convective models that are described elsewhere (Saumon & Marley 2008). The models are cloudless and of solar metallicity. Adding cloud opacity would make the \(p-T\) profiles hotter and less favorable to \(CH_3\). The cloudless model is something of a best case for methane.

Treating vertical transport as diffusion is a necessary evil in a 1D code. We will regard \(K_{zz}\) as a mildly constrained free parameter. In free convection, \(K_{zz}\) has been estimated from mixing length theory (Gierasch & Conrath 1985),

\[
K_{zz} = \frac{1}{3} H \left( \frac{\rho C_p}{\mu R_{\text{gas}}} \right)^{1/3}, \tag{3}
\]

where \(R_{\text{gas}}\) is the universal gas constant, \(F_{\text{conv}}\) the convective heat flux, \(\mu\) the mean molecular weight (dimensionless), \(\rho\) the density, and \(C_p\) the heat capacity of the gas. The mixing length is approximated by the scale height. An upper bound is obtained from Equation (3) by equating \(F_{\text{conv}}\) with \(\sigma T_{\text{eff}}^4\),

\[
K_{zz} < 2.5 \times 10^{10} \left( \frac{T_{\text{eff}}}{600} \right)^{8/3} \left( \frac{1000}{g} \right) \text{ cm}^2 \text{s}^{-1}. \tag{4}
\]

These large values of \(K_{zz}\) might be regarded with some skepticism. If applied to Earth’s troposphere, Equation (3) predicts \(K_{zz} > 10^7 \text{ cm}^2 \text{s}^{-1}\), which is two orders of magnitude too high. Even in the present context, \(F_{\text{conv}}\) can be much smaller than \(\sigma T_{\text{eff}}^4\) (or even fall to zero in places), because a considerable fraction of energy transport is by radiation. Depending on how well one tolerates theory, one might expect \(K_{zz}\) to be of the order of \(10^9-10^{11} \text{ cm}^2 \text{s}^{-1}\) in the convecting zones of self-luminous EGPs, and 100 times smaller for BDs with \(g = 10^4 \text{ cm} \text{s}^{-2}\).

It is likely that \(K_{zz}\) would be much smaller in stratified gas above the convecting regions. On Earth, \(K_{zz}\) drops by two orders of magnitude at the tropopause. Hubeny & Burrows (2007) reduce \(K_{zz}\) by several orders of magnitude in the stratosphere. Simulations by Freytag et al. (2010) support this expectation. The tradeoff is between simplicity (constant \(K_{zz}\)) and realism (a vertical discontinuity in \(K_{zz}\)). The latter choice would introduce two more free parameters, the value of \(K_{zz}\) in the stratosphere (ill-constrained) and the altitude of the discontinuity (reasonably well constrained, but results could be sensitive to this). A two-layer model also makes interpreting the numerical results in terms of a quench approximation less straightforward because there can be more than one quench point. For this study, we choose to treat \(K_{zz}\) as constant with height, but vary it over a range wide enough to encompass all likely values.

The chemical system used here comprises 366 forward chemical reactions and 32 photolysis reactions of 64 chemical species made of H, C, N, O, and S. The most important missing species is probably methylamine, \(CH_3NH_2\). Reaction rates, when known, are selected from the publicly available NIST database. Although many of the important reactions have been measured in both directions in the lab (e.g., both \(CH_4 + H \rightarrow CH_3 + H_2\) and \(CH_3 + H_2 \rightarrow CH_4 + H\) have been heavily studied), in general one direction is much better characterized than the other. Thermodynamic data (enthalpies and entropies) are usually better known over a wider range of temperatures. Thus, it is better to complement each specific reaction with its exact reverse, with the forward and reverse rates linked self-consistently by the thermodynamic data (enthalpies and entropies) are usually better known over a wider range of temperatures. Thus, it is better to complement each specific reaction with its exact reverse, with the forward and reverse rates linked self-consistently by the thermodynamic data of the species involved. This way the transition from equilibrium to kinetically controlled abundances is automatic. Equilibrium is reached when all the important forward and reverse reactions are fast compared to changes in the state variables.

How this is done is fully explained by Visscher & Moses (2011). What follows is a telegraphic summary. For reactions of the form \(A + B \rightarrow C + D\) with forward reaction rate \(k_f\), the reverse rate (i.e., the rate for \(C + D \rightarrow A + B\)) is \(k_r = k_f \exp(-\Delta G/RT)\), where \(\Delta G\), the Gibbs free energy, is obtained from enthalpies and entropies of the reactants and products, respectively.

\[
\Delta G = \Delta H - T \Delta S.
\]
products, $\Delta G = H_A + H_B - H_C - H_D - T(S_A + S_B - S_C - S_D)$. For associative reactions of the form $A + B \rightarrow AB$, the rate for the reverse reaction (dissociation of $AB$) is $k_r = k_r \left( \frac{kT}{P_c} \right) \exp(-\Delta G/RT)$, where $P_c = 10^6$ dynes cm$^{-2}$ is one atmosphere. Similarly, the associative reverse of a dissociative reaction is given by $k_r = k_r \left( \frac{P_c}{RT} \right) \exp(-\Delta G/RT)$.

Thermodynamic data as a function of temperature are available for atoms and most small molecules from NIST in the form of empirical Shomate equation fits for enthalpy and entropy.

Zero point data for HS are corrected by Lodders (2004). For CH$_3$OH and C$_2$H$_6$, we use heat capacities as a function of temperature to derive Shomate equation fits for enthalpy and entropy. Unfortunately, many of the more exotic free radicals are not listed in the publicly available NIST databases. For many of these, we use estimates given in Burcat & Ruscic’s (2005) widely available gray literature compilation. For NNH, we follow Haworth et al. (2003), and for N$_2$H$_2$ and N$_2$H$_3$ we follow Matus et al. (2006). Inaccurate thermodynamic data for free radicals are not a problem for equilibrium calculations of well-characterized abundant species because poorly characterized free radicals are never abundant. On the other hand, poorly characterized species do pose a problem in disequilibrium kinetics.

The lower boundary is set deep enough that all species are in thermodynamic equilibrium. We find that pressures above 300 bars and temperatures above 2000 K usually suffice, with the limiting species being N$_2$. The upper boundary condition is zero flux for all species. We place the upper boundary at ~$10^{-6}$ bars, as higher altitudes require additional physics and chemistry (ion chemistry, thermospheric heating) that go beyond the scope of this work. Steady state solutions are found by integrating the time-dependent chemical and transport equations through time using an overcorrected fully implicit backward-difference method. Most models take a few minutes to run to steady state from arbitrary initial conditions on a vintage laptop computer, although some particular cases can be more challenging.

Photolysis significantly affects the composition of atmospheres at very high altitudes even when the incident UV flux is small. In our models we have set the incident UV flux to 0.1% that at Earth. Photolysis plays almost no part at the higher pressures germane to quenching and is not further discussed here. We have not included the reverses of photolysis reactions (radiative attachment, e.g., OH + H $\rightarrow$ H$_2$O + hv) in detailed balancing. Recent work has shown that radiative attachment can be important in hydrocarbon growth in planetary atmospheres when the resulting molecule is complex enough that radiative relaxation can be effective (Vuitton et al. 2012).

3.1. Two Examples

Figure 2 shows how $K_{zz}$ affects chemistry on a tepid ($T_{\text{eff}} = 600$ K), cloud-free, relatively low-mass ($g = 10^3$ cm s$^{-2}$) extrasolar planet of solar composition. Insolation is insignificant. Three different $K_{zz}$ are compared. (1) Strong vertical mixing—$K_{zz} = 10^{10}$ cm$^2$ s$^{-2}$—suppresses CH$_4$ and maintains f$_{CO} > f_{CH_4}$ to very high altitudes. CO and CH$_4$ are in chemical equilibrium below the quench point at ~4 bars and 1450 K. (2) A more Jupiter-like $K_{zz} = 10^7$ cm$^2$ s$^{-1}$ raises the quench point to 1.5 bars and 1280 K, which is better for CH$_4$. (3) Weak mixing, $K_{zz} = 10^4$ cm$^2$ s$^{-1}$, raises the quench point to 0.6 bars and 1000 K, which is cool enough, barely, to fall into the CH$_4$ field, so that $f_{CH_4} > f_{CO}$ in this planet’s photosphere. The effect of molecular diffusion (in which heavy molecules sink through H$_2$) is apparent above $3 \times 10^{-6}$ bars at $K_{zz} = 10^{10}$ cm$^2$ s$^{-1}$ and obvious above $3 \times 10^{-3}$ bars at $K_{zz} = 10^4$ cm$^2$ s$^{-1}$.

At a given effective temperature, surface gravity determines whether the atmosphere is CO- or CH$_4$-dominated. Figure 3 shows CO and CH$_4$ abundances in three worlds that differ only in their surface gravities. The atmospheres are cloud-free and of elementally solar composition. The models shown here have effective radiating temperatures of 600 K and a Jupiter-like $K_{zz} = 10^{10}$ cm$^2$ s$^{-1}$. Surface gravities range from a Saturn-like $g = 10^3$ cm s$^{-2}$ to a brown-dwarf-like $g = 10^5$ cm s$^{-2}$. The computed CO/CH$_4$ ratio is sensitive to surface gravity. This is because the $p$-$T$ profile is displaced to higher pressures and lower temperatures when gravity is higher. Quenching at higher pressures and lower temperatures favors CH$_4$ over CO. The result is that the 600 K planet ($g = 10^3$ cm s$^{-2}$) has abundant CO and relatively little CH$_4$, while the 600 K brown dwarf is methane-rich with only a trace of CO.

3.2. The Ensemble of Models

We use the 1D chemical kinetics models to explore the phase space defined by $500 < T_{\text{eff}} < 1100$ K, $10^4 < K_{zz} < 10^{11}$ cm$^2$ s$^{-1}$, and $10^3 < g < 10^5$ cm s$^{-2}$. Models are run to steady state. Ensembles were computed at solar ($m = 1$) and thrice solar ($m = 3$) metallicities, but $p$-$T$ profiles were not adjusted to take into account the altered chemical composition. The CO and CH$_4$ abundances of all the models are summarized.

Figure 2. Methane and CO in an exemplary lukewarm EGP. The planet is cloud-free, has an effective radiating temperature of 600 K, $g = 10^3$ cm s$^{-2}$, and receives insignificant insolation. The $p$-$T$ profile of the atmosphere is compared to the $p$-$T$ curve (gold dot–dash) corresponding to equilibrium $f_{CH_4} = f_{CO}$. Methane is thermodynamically favored when $T$ is to the left of the $f_{CH_4} = f_{CO}$ curve, CO is favored to the right. Computed CO and CH$_4$ mixing ratios are shown from three 1D kinetics models that differ only in vertical eddy mixing: $K_{zz} = 10^{10}$ cm$^2$ s$^{-1}$ (solid), $K_{zz} = 10^7$ cm$^2$ s$^{-1}$ (dashed), and $K_{zz} = 10^4$ cm$^2$ s$^{-1}$ (dots). Deep in the atmospheres, CO and CH$_4$ are in equilibrium. High in the atmospheres, CO and CH$_4$ are unreactive and $f_{CO}$ and $f_{CH_4}$ would be constant but for molecular diffusion. The quench points are obvious and well-defined in all three models. (A color version of this figure is available in the online journal.)
Figure 3. Three models with three different surface gravities. The plot shows $p$–$T$ profiles and CO and CH$_4$ abundances. The planets are 600 K, self-luminous, cloudless, of solar composition, with $K_{zz} = 10^7$ cm$^2$ s$^{-1}$. Surface gravities are $g = 10^3$ cm s$^{-2}$ (solid), $g = 10^4$ cm s$^{-2}$ (dashed), and $g = 10^5$ cm s$^{-2}$ (dots). Higher gravity models are colder at a given pressure and are more favorable to CH$_4$.

(A color version of this figure is available in the online journal.)

Figure 4. Overview of the ensemble of models. There are six panels for six different combinations of gravity and metallicity. Relative CO and CH$_4$ abundances above the quench point are indicated by the areas of the semicircles, CO black and following, CH$_4$ green and preceding. In general, higher gravities, cooler temperatures, and lower metallicity favor CH$_4$ vs. CO. Different metallicities can give the same CO/CH$_4$ ratio at the same $T_{eff}$ and $g$ with modest and probably unmeasurable differences in $K_{zz}$. Blue squares denote the specific cases in Figures 2 and 3. Red circles denote the 16 cases used in Figure 7 to illustrate quenching. Orange diamonds denote the two models used in Figure 8 to compare reaction rates. The red star is the guide to Figure 1. In all cases, equilibrium $f_{CH_4} > f_{CO}$.

(A color version of this figure is available in the online journal.)

in Figure 4. Low-$K_{zz}$ models can be numerically challenging when the gas is very hot. We include two models that did not reach a true steady state in Figure 4: $T_{eff} = 600$ K, $g = 10^3$ cm s$^{-2}$, $m=1$, and $K_{zz} = 10^4$ and $10^5$ cm$^2$ s$^{-1}$. These models reached persistent near steady states, but were held back by undiagnosed features in the sulfur chemistry. They are included here as part of our exploration of conditions that can produce CH$_4$ at low gravity.

4. DETERMINING THE QUENCH POINT FOR CO AND CH$_4$

Here we want to determine the quench conditions that correspond to the asymptotic CO and CH$_4$ abundances in the complete kinetics models shown in Figure 4. Our purpose in doing so is to quantify the emergent quench behavior of the kinetics models, and, if possible, describe this behavior with a simple equation or set of equations. That it is possible to do this is the subject of Figure 5.

First, we determine the CO–CH$_4$ quench point in each atmosphere in Figure 4 by finding the lowest altitude in each atmosphere where the CO and CH$_4$ mixing ratios depart measurably from equilibrium. Deep in the atmosphere, CH$_4$ and CO are in chemical equilibrium with H$_2$ and H$_2$O. Thus, the product

$$K_{test} = \frac{p_{CH_4} \cdot p_{H_2O}}{p_{CO} \cdot (p_{H_2})^3}$$

equals the corresponding equilibrium constant

$$K_{CH_4, CO} = 5.24 \times 10^{-14} \exp\left(\frac{27285}{T}\right).$$
In Equations (5) and (6) (and all succeeding expressions of similar form), pressures are in atmospheres and temperatures in Kelvins.

In the regions of a convective atmosphere relevant to the present investigation, equilibrium contours of constant CH4/CO are always shallower than the adiabat, hence the equilibrium CH4 mixing ratio always decreases with increasing depth. To show this (and its limits), use the adiabatic relation $T^\gamma \propto p^{\gamma - 1}$, where $\gamma = C_p/C_v$ has its usual meaning as the ratio of heat capacities. The temperature gradient along the adiabat (constant entropy $S$) is

$$
\left( \frac{\partial T}{\partial p} \right)_S = \frac{\gamma - 1}{\gamma} \frac{T}{p} = \frac{R}{C_p} \frac{T}{p}.
$$

(7)

For a temperate cosmic mix of H2 (84%) and He (16%), we can expect H2 to have $C_p \approx 3.5R$ and He to have $C_v \approx 2.5R$, and hence $R/C_p \approx 0.30$. Warmer temperatures excite hydrogen’s vibrational modes, for which $C_p \approx 4.5R$ and $R/C_p \approx 0.24$. Detailed calculations show that $R/C_p$ decreases monotonically from 0.29 at 1000 K to 0.25 at 2100 K to 0.20 at 3000 K as dissociation (another energy sink) becomes important.

Equation 7 needs to be compared to contours of equilibrium chemistry. Defining $\xi \equiv CH_4/CO$, we can write the equilibrium (Equations (5) and (6)) in the form

$$
\xi \cdot \left( f_0 - \frac{f_C}{1 + \xi} \right) = p^2 f_{H_2} A e^{B/T},
$$

(8)

where $f_{H_2} \approx 0.84$ is the H2 mixing ratio, $f_0 \approx f_{H_2} + f_{CO}$ is the total oxygen mixing ratio, and $f_C \approx f_{CH_4} + f_{CO}$ is the total carbon mixing ratio. These are generally very good approximations for $T < 2500$ K. The quantity in parentheses is $f_{H_2}$. For contours of constant $\xi$, the left-hand side of Equation (8) is constant. Taking derivatives, the temperature gradient is

$$
\left( \frac{\partial T}{\partial p} \right)_\xi = \frac{2T}{B} \frac{T}{p} \approx 0.11 \frac{T}{1500} \frac{T}{p}.
$$

(9)

Thus, $(\partial T/\partial p)_\xi < (\partial T/\partial p)_S$ for temperatures lower than about 2900 K, by which point several of the assumptions made in deriving this relation have begun to break down. Even with $K_{zz}$ as high as $10^{11}$ cm$^2$ s$^{-1}$, quenching in the CO–CH4 system takes place at temperatures less than 2200 K. Hence, we can always presume that CO is most abundant and CH4 least abundant at the lower boundary of our model. It follows that we can determine the quench conditions (temperature $T_q$, pressure $p_q$) by working up from the lower boundary and finding the lowest altitude at which the product $K_{zz}$ is appreciably smaller than the equilibrium constant $K_{CH_4/CO}$. In practice, we searched for the lowest altitude where $K_{zz} < 0.9 K_{CH_4/CO}$.

We also wish to determine a quench timescale $t_q$. In principle, the right way to do this is to determine the true chemical reaction timescale from the sum of all relevant reaction rates at the quench point. In general this information is surprisingly hard to extract from a model, because the breakdown of equilibrium appears as small differences between much larger forward and reverse reaction rates in many reactions. This approach is practical only if one already knows exactly which species and reactions are key. Once known, for $t_q$ to be useful in a quench approximation, one then needs a comparably fine-grained description of the cooling time implicit in $K_{zz}$, and the particular chemical reactions that establish $t_q$.

Much easier, and more useful, is to define a quench timescale for the system as a whole in terms of a relevant mixing time.
$t_q = t_{\text{mix}} = L^2/K_{zz}$, where $L$ is a characteristic length scale. The simple choice is to set $L = H_q$, the scale height at $T_q$. This definition is arbitrary to within a multiplicative factor because the true mixing length $L$ is not in general equal to $H_q$. However, this definition of $t_q$ is precisely what is needed for constructing a new quench approximation that assumes $t_{\text{mix}} = H_q^2/K_{zz}$ and, as seen in Figure 5, it leads to a very simple description of the overall behavior of the full network of chemical reactions.

Smith (1998) demonstrated that $L$ is often considerably shorter than $H$, mostly because the key reactions determining $t_q$ are much more sensitive to temperature than to pressure. Smith (1998) developed a five-step iterative algorithm for determining $L$ and presented it in the form of a “recipe” to be used in quenching calculations, which is especially useful when the system is controlled by a single reaction whose rate is known. Several workers have employed Smith’s recipe. Unfortunately, the range of mixing times that results can be very great. For example, Visscher & Moses (2011) list values for $L$ between 0.1 $H$ and 0.7 $H$ for the CO–CH$_4$ system, the equivalent of a factor of 50 in $t_{\text{mix}}$ and therefore equivalent to a factor of 50 in the inferred value of $K_{zz}$, itself a parameter of easy virtue. The resulting uncertainty frustrates intercomparison between models. Our position is that the most useful approximations are simple approximations. We therefore stick with the old rule $L = H$ to define $t_{\text{mix}}$, rather than iterate between $L$ and $T_q$. This is defined is important for comparing to previous work regardless of how $L$ is defined, we find that we can fit the quench time $t_q$ to a simple functional form that spans all our models. We start from the expectation that CO → CH$_4$ will depend on temperature and pressure, perhaps the C/O ratio, and possibly on metallicity. It is reasonable to hope that the net reaction has an Arrhenius-like rate

$$t_q = Ap^{-b}m^{-c} \exp\left(B/T\right)$$  \hspace{1cm} (10)  

where possible pressure and metallicity dependencies are written as power laws.

Our hope is nicely borne out by Figure 5, which plots $t_q$ for the CO–CH$_4$ reaction for our complete roster of solar metallicity models. All but the coldest quench points are described by a rather well-defined Arrhenius expression with $b = 1$. The Arrhenius fit (for $m = 1$) is

$$t'_{q1} = 3.0 \times 10^{-6} p^{-1} \exp\left(42000/T\right) \text{s},$$ \hspace{1cm} (11)  

where $p$ is in bars. The timescale for models with $m = 3$ (not shown) is roughly half of this.

The prime is placed on $t'_{q1}$ because, by using $K_{\text{test}} < 0.9 K_{\text{eq}}$ rather than $K_{\text{test}} < K_{\text{eq}}$, we have overestimated the quench time. To correct for this—and to verify that a quench scheme works—we compare the predictions of the quench scheme with the predictions of the ensemble of models. Fits are shown in Figure 6. These use

$$t_{q1} = 1.5 \times 10^{-6} p^{-1} m^{-0.7} \exp\left(42000/T\right) \text{s}$$ \hspace{1cm} (12)  

The methods of Figures 6 and 5 are complementary. A satisfactory fit in Figure 6 is more sensitive to the A factor (overall rate) and the metallicity (Equation (10)), while the fit in Figure 5 is more sensitive to the B factor (temperature dependence) and pressure.

The half-dozen models that are ill fit by Equation (11) are fit instead by a second Arrhenius relation

$$t_{q2} = 40 p^{-2} \exp\left(25,000/T\right) \text{s},$$ \hspace{1cm} (13)  

where we have given the iterated rate. The models fit by Equation (13) are those with very low quench temperatures $T_q$ and very little CO. We have no such models with $m = 3$. The high- and low-temperature fits combine harmonically to give a general description of reaction times in the CO–CH$_4$
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10⁻⁶

10⁻⁵

10⁻⁴

600 800 1000 1200

K = pH₂CO / pH₂ / pCO

Temperature

equilibrium

CO + H₂ ↔ H₂CO

(a)

10⁻⁶

10⁻⁵

10⁻⁴

10⁻³

10⁻²

10⁻¹

10⁰

10¹

10²

500 1000 1500 2000

K = pCH₃OH * pH₂ / pCH₄ / pH₂O

Temperature K

equilibrium

CH₃OH + H₂ ↔ CH₄ + H₂O

(c)

10⁻⁸

10⁻⁶

10⁻⁴

10⁻₂

10⁰

10²

10⁴

800 1000 1200 1400 1600 1800 2000

K = pCH₄ * pH₂O / pCO / pH₂³

Temperature K

equilibrium

CO + 3H₂ ↔ CH₄ + H₂O

(d)

Figure 7. Quenching behavior of the three intermediate reactions (a), (b), and (c) and of the CO ↔ CH₄ system as a whole (d). Results are shown from 16 models chosen to provide a representative sample of the ensemble (marked by red circles in Figure 4). Panels (a) and (b) show that CO ↔ H₂CO and H₂CO ↔ CH₃OH appear to be equilibrated in all models at T > 900 K. Panel (c) shows that equilibration of CH₃OH and CH₄ is more difficult. In detail, the quench points for CH₃OH ↔ CH₄ appear to be the same as the quench points for CO ↔ CH₄, as shown in panel (d) for the same 16 models. Evidently the bottleneck is between CH₃OH and CH₄, in accord with conclusions reached by Moses et al. (2011).

Equation (14) when used with the timescale $t_{mix} = H²/τ_{zz}$ works for all of our models for CO and CH₄ and we expect it should work generally for compositions not too far from solar.

4.1. Analysis

We examine the ensemble of models for quench points pertinent to the reaction intermediates to determine where in the CO–CH₄ reaction network quenching first takes place. We consider the CO–H₂CO, H₂CO–CH₃OH, and CH₃OH–CH₄ equilibria. We analyzed 16 models taken arbitrarily from the ensemble. The chosen ones are marked on Figure 4 with scarlet circles. We find, to within our ability to determine this, that the CH₃OH–CH₄ reaction quenches at the same temperature as the CO–CH₄ reaction as a whole. This is shown by panels (c) and (d) of Figure 7. By contrast, the CO–H₂CO and H₂CO–CH₃OH reactions stay near equilibrium for temperatures above 900 K (Figures 7(a) and 7(b)). Hence, as a parcel cools, equilibrium first breaks down between CH₃OH and CH₄. This is in accord with conclusions reached by Moses et al. (2011) and Visscher & Moses (2011).

Figure 8 examines in detail the key reactions that break the CO–CH₄ equilibrium. The important reactions form the methyl radical CH₃ from species such as CH₃OH in which
Figure 8. Four most important reactions for quenching in our model CO–CH₄ system. All four reactions yield CH₃ + OH as products. Solid curves show rates of the forward reaction that creates CH₃, dashed curves show the reverse reaction that destroys CH₃, and wide dots show the difference (the net production of CH₃), which is equivalent to net loss of CO. Black dot-dashed lines are the altitudes where CH₄ and CO reach their final quenched values. Left: a warm, strongly mixed (Teff, Kzz, g = 1100, 10⁰, 1⁰) model dominated by CO. Disequilibrium reactions are fastest at 210 km (at 1700 K), but full quenching is delayed until 270 km (at 1560 K); the distance corresponds to a bit more than a pressure scale height. Right: a cool, moderately mixed (Teff, Kzz, g = 500, 10⁵, 1⁰) BD-dominated by CH₄. Disequilibrium reactions are fastest at 7 km, but quenching is at 9 km (the scale height is 5 km).

(A color version of this figure is available in the online journal.)

the C–O bond is still intact. Figure 8 illustrates two cases, one a cool (Teff = 500 K) brown dwarf with a preference for CH₄ (fCO = 1.4 × 10⁻⁵, fCH₄ = 4.7 × 10⁻⁴), and the other a warmer (Teff = 1100 K), smaller world that favors CO (fCO = 4.8 × 10⁻⁴, fCH₄ = 1.0 × 10⁻⁵). Both models assume solar metallicity (m = 1). In both cases the most important reaction is simple thermal decomposition of methanol, CH₃OH + M → CH₃ + OH + M, although the reaction of methanol with atomic hydrogen is nearly as fast in the colder, higher-gravity case. The reaction H₂COH + H, which Moses et al. (2011) report as the most important in their CO–methanol, CH₃OH + M → CH₃ + OH + M, although the reacction rates of furtive species like H₂COH are highly uncertain.

4.2. Comparisons with Previous Work

To put our results in perspective, we compare them to some quench approximations seen in the literature. Published quench approximations begin by identifying a particular forward reaction as the bottleneck and then calculate CO loss timescales from the chosen reaction’s rate; variety lies in the reactions that are chosen and the reaction rates adopted.

We begin with the classic Prinn & Barshay (1977) prescription, used by Hubeny & Burrows (2007) as their “slow” case. Prinn & Barshay (1977) suggested

H₂ + H₂CO → CH₃ + OH \quad (15)

as a rate-limiting reaction, with reaction rate \( k_f = 2.3 \times 10^{-10} e^{-36200/ T} \) cm³ s⁻¹. R15 is a reaction that jumps over two energy barriers in Figure 1, which makes it look like it should be relatively unlikely. Figure 8 shows that R15 is modestly important in our system, but we use a newer slower rate estimated by Jasper et al (2007). The time constant for CO loss by reaction R15 using Prinn & Barshay’s (1977) rate is approximated by the forward reaction

\[
\tau_{chem}^{-1} = \frac{1}{[\text{CO}]} \frac{\partial [\text{CO}]}{\partial t} = \frac{k_f [\text{H}_2][\text{H}_2\text{CO}]}{[\text{CO}]} \text{s}^{-1} \quad (16)
\]

where the notation [CO] refers to number density [cm⁻³]. To evaluate \( \tau_{chem} \) for R15, we put formaldehyde in equilibrium with CO and H₂,

\[
\frac{pH_2CO}{pH_2 \cdot pCO} = K_{H_2CO} = 3.3 \times 10^{-7} \exp(1420/T), \quad (17)
\]

to obtain

\[
\tau_{chem} = \frac{1.3 \times 10^{16} \exp(34,780/T)}{p N f_H^2} \text{s}. \quad (18)
\]

The number density \( N \) is related to the pressure \( p \) in bars by \( NkT = 10^7 p \). The predictions of Equation (18) are compared to results from our complete models in Figure 9. Equation (18) works quite well in a quench approximation to our full model, especially for cases where CH₄ is predicted to be abundant, despite its being based on the wrong reaction with the wrong rate. As the Prinn & Barshay (1977) approximation has been widely used for a very long time, it is valuable to see that it seems to work rather well. When compared to Equation (12), Equation (18) has a stronger pressure dependence (\( p^{-2} \) versus \( p^{-1} \)), a weaker temperature dependence (\( T \cdot e^{34780/T} \) versus \( e^{42000/T} \)), and no dependence on metallicity.
More recent discussions of the CO–CH4 quench approximation omit enough details that they can be challenging to reproduce. We attempt to do so here because the comparisons are illuminating. Yung et al. (1988) suggested that the rate-limiting step is the three-body reaction

$$H + H_2CO + M \rightarrow CH_3O + M.$$  \hspace{1cm} (19)

Hubeny & Burrows (2007) use R19 as their “fast” rate with $L = H$. Barman et al. (2011a) also use this rate, but, following Smith (1998), they set the mixing length $L$ to unspecified values between 10% and 20% of the scale height, which effectively slows the “fast” rate by a factor of 25–100 compared to $L = H$. Cooper & Showman (2006) implemented the CH$_3$O channel with a different reaction rate while following Smith’s “recipe.” We use the asymptotic high-pressure rate $k_{\infty} = 8.0 \times 10^{-10} \exp(-3160/T)$, a very fast rate which we obtained by reversing the first order rate for CH$_3$O $\rightarrow$ H + H$_2$CO given by Rauk et al. (2003). If we presume that H and H$_2$CO are both in equilibrium, we can use the hydrogen equilibrium constant $K_{H_2 CO H_2} = 1155 \cdot 10^{-29516/T} = pH \cdot pH_2^{-0.5}$ to obtain

$$t_{\text{chem}}^{-1} = k_{\infty} \frac{[H][H_2CO]}{[CO]} = k_{\infty} p^{1.5} f_{H_2}^{0.5} \left( \frac{10^6}{kT} \right) K_{H_2 CO H_2}.$$  \hspace{1cm} (20)

Evaluated,

$$t_{\text{chem}} = 4.5 \times 10^{-10} T p^{-1.5} f_{H_2}^{-1.5} \exp(28656/T).$$  \hspace{1cm} (21)

The results of using Equation (21) are shown as red diamonds in Figure 9 with $L = 0.14H$, which is comparable to what Barman et al. (2011a) use (the fit would look worse with $L = H$). These stand out with too much CH$_4$ and too little CO, because R19 is not a true bottleneck.

Line et al. (2011) moved the bottleneck to CH$_3$O $+ H_2 \rightarrow$ CH$_2$OH $+ H$. To compute a rate constant, we use $pCH_3O = K_{CH_3O \cdot pH_2 \cdot pH \cdot pCO}$, where $K_{CH_3O} = 3.0 \times 10^{-11} e^{16382/T}$ is the relevant equilibrium constant (the large number of significant digits in these equilibrium constants do not imply accuracy). To complete the equation, we also assume that H and H$_2$ are in equilibrium. We use the reaction rate given by Line et al. (2011), which results in

$$t_{\text{chem}} = 1.2 \times 10^2 \exp(45720/T) \frac{T^4 N_p f_{H_2}^{0.5}}.$$  \hspace{1cm} (22)

Results are shown as green squares in Figure 9 using $L = H$, as Line et al. (2011) do. Because it predicts too much CO and too little CH$_4$, $t_{\text{chem}}$ given by Equation (22) is too slow.

Based on detailed analysis of the reactions in a complete 1D model similar to our own, Moses et al. (2011) concluded that the bottleneck is associated with breaking the C–O bond. They propose several key channels. One channel is thermal decomposition of methanol,

$$CH_3OH + M \rightarrow CH_3 + OH + M.$$  \hspace{1cm} (23)

Visscher & Moses (2011) and Moses et al. (2011) state that this is more important when CH$_4$ is abundant. Another channel, which they state is more important when CO $\gg$ CH$_4$, is

$$CH_2OH + H \rightarrow CH_3 + OH.$$  \hspace{1cm} (24)

The rate of R24 depends on the uncertain thermodynamic properties of CH$_2$OH.

In the high-pressure limit, methanol decomposition R23 is a first order reaction,

$$\frac{\partial [CH_3OH]}{\partial t} = -k_{\infty} [CH_3OH].$$  \hspace{1cm} (25)
Jasper et al. (2007) estimate \( k_\infty \) from theory

\[
k_\infty = 6.251 \times 10^{16} \frac{(300/T)^{0.6148} \exp(-46573/T)}{s^{-1}}.
\]

The methanol equilibrium constant

\[
K_{\text{CH}_3\text{OH}} = \frac{p\text{CH}_3\text{OH}}{p\text{CO} \cdot p\text{H}_2} = 1.1 \times 10^{-13} e^{13000/T}
\]
relates \([\text{CH}_3\text{OH}]\) to \([\text{CO}]\). The reaction timescale is then

\[
\tau_{\text{chem}} = \left( k_\infty p\text{H}_2 K_{\text{CH}_3\text{OH}} \right)^{-1} = 4.4 \times 10^{-6} T^{0.6148} \exp(33573/T) p^{-2} f_{\text{H}_2^{-2}} \text{s}. \tag{26}
\]

Equation (26) has a weaker dependence on \( T \), a stronger dependence on \( p \) than we find for the ensemble, and no dependence on metallicity.

Figure 9 illustrates quenching using Equation (26) as black triangles. For comparison, we take \( L = 0.14 H \). This approximates what Moses et al. (2011) may be using. Equation (26) does well, especially in cases where \( CO \ll CH_4 \), at quenching, which is the regime for which Moses et al. (2011) report that Equation (26) applies. Equation (26) does better if \( L > 0.14 H \). The match is best for \( CO \) with \( L = 0.2 H \), and better for \( CH_4 \) with \( L \approx 0.5 H \).

To reconstruct a simple form for the \( H_2\text{COH} \) channel, we need to estimate the equilibrium abundance of \( H_2\text{COH} \). We use \( p\text{H}_2\text{COH} = K_{\text{H}_2\text{COH}} p\text{H}_2 p\text{H} p\text{CO} \) with \( K_{\text{H}_2\text{COH}} = 1.0 \times 10^{-12} e^{15843/T} \). We assume that \( H \) and \( H_2 \) are in equilibrium. Jasper et al. (2007) list a fast rate, \( k = 2.8 \times 10^{-10} \text{cm}^3 \text{s}^{-1} \), for the reaction of \( H \) and \( H_2\text{COH} \). Assembling the parts, we obtain

\[
\tau_{\text{chem}} = \frac{2.7 \times 10^{15} \exp(38000/T)}{Np_{\text{H}_2^{-2}}} \text{s}. \tag{27}
\]

Results are shown as blue circles in Figure 9. Equation (27) has a similar \( T \) dependence to what we find for the system as a whole, but the overall rate is about three orders of magnitude slower using \( L = 0.14 H \), or about 10 times slower using \( L = H \).

Disagreement between our model and Moses et al. over the \( H_2\text{COH} \) channel is also apparent in Figure 8. The \( H_2\text{COH} \) radical plays a much more modest role in our 1D code than it does in Moses et al.’s (2011). The same is true for \( CH_3O \). Why this should be so is likely related to differing guesses of \( H_2\text{COH} \)’s and \( CH_3O \)’s ill-known thermodynamic properties.

There are some more subtle differences between our model and previous quench models that should be noted. One is that we find \( \tau_{\text{chem}} \propto p^{-1} \) by fitting to the ensemble, while quench models that attempt to identify the one key forward reaction tend to get \( \tau_{\text{chem}} \propto p^{-2} \). This difference is the reason why quench prescriptions in Figure 9 that do well with \( f_{\text{CO}} \ll f_{\text{CH}_3\text{OH}} \) miss the mark somewhat with \( f_{\text{CH}_4} \ll f_{\text{CO}} \). Figure 6, which uses \( \tau_d \propto p^{-1} \), shows fine agreement at both ends of the scale.

Another difference is that we see a well-defined metallicity dependence when fitting to the ensemble. The metallicity dependence probably stems from the reverse reaction, which as noted is usually ignored. As equilibrium breaks down, the reaction slows in both directions, more quickly in the reverse direction than in the forward direction. This behavior is shown clearly in Figure 8, where forward, reverse, and net reaction rates are plotted. It is the net reaction, the difference between the forward and reverse reactions, which defines the retreat from equilibrium, not the forward reaction alone. For example, the timescale for the methanol decomposition channel is

\[
\tau_{\text{net}}^{-1} \approx -\frac{1}{[\text{CO}]} \frac{\partial [\text{CO}]}{\partial t} = k_f [\text{CH}_3\text{OH}] - k_r [\text{CH}_4][\text{OH}]. \tag{28}
\]

The reverse reaction is quadratic in metallicity, while \([\text{CO}]\) is quadratic in metallicity only for \( f_{\text{CO}} \ll f_{\text{CH}_4} \), which suggests that it is through the reverse reaction that metallicity enters \( t_{\text{CO}} \). The same consideration applies for all the important reactions in Figure 8, as the reverse reaction in every case is between \( CH_3 \) and \( OH \).

5. QUENCHING IN THE \( N_2–NH_3 \) SYSTEM

The approach we used to search for quenching of \( CO \) and \( CH_4 \) does not work well for \( N_2 \) and \( NH_3 \). Indeed, Figure 10—the analog to Figure 4 for \( N_2 \) and \( NH_3 \)—shows no sign that quenching plays any role in the \( N_2–NH_3 \) reaction, although doubtless quenching occurs.

Two things get in the way. Of less importance, a third species—\( HCN \)—becomes non-negligible at high temperatures. HCN also quenches at high temperature, which leaves the nitrogen system with three possibly distinct quench points: \( NH_3–N_2, \text{NH}_3–\text{HCN}, \text{and} N_2–\text{HCN} \). Although HCN is never very abundant in equilibrium, it is often abundant enough that its decomposition can increase the \( NH_3 \) abundance by more than 10% after the \( NH_3–N_2 \) reaction has quenched. When confused with the second, greater obstacle, HCN can make it difficult to pinpoint where quenching occurs.

The greater obstacle is that curves of constant \( NH_3/N_2 \) are nearly parallel to the adiabat at the pressures and temperatures where quenching occurs. This is illustrated in Figure 11. Consequently, the \( NH_3/N_2 \) ratio in a parcel remains close to equilibrium well after quenching has taken place, which makes the \( NH_3/N_2 \) ratio indifferent to quenching (Saumon et al. 2006).

To show this, write the \( N_2–NH_3 \) equilibrium in the form

\[
K_{\text{NH}_3, N_2} = 5.90 \times 10^{-13} \exp(13207/T) = \frac{p\text{NH}_3^2}{p_{N_2} \cdot p_{H_2}}. \tag{29}
\]

Define \( \xi \equiv NH_3/N_2 \). If we approximate the total mixing ratio of \( N \) by \( f_N \approx f_{\text{NH}_3} + 2f_{\text{N}_2} \) (including HCN makes this very complicated), we can write

\[
\xi^2 \left( \frac{f_N}{2 + \xi} \right) = p^2 f_{\text{N}_2}^3 A e^{B/T}. \tag{30}
\]

With context-obvious substitutions, the temperature gradient for contours of constant \( \xi \) is

\[
\left( \frac{dT}{dp} \right)_{\xi} = 2 \frac{T}{B} \frac{T}{p} \approx 0.23 \frac{T}{1500} \frac{T}{p}. \tag{31}
\]

The temperature gradient in Equation (31) is parallel to the adiabat (Equation (7)) at 1750 K, and nearly parallel for 1500 < \( T < 2000 \) K. For temperatures initially greater than 1750 K, the equilibrium ratio of \( NH_3/N_2 \) decreases as the parcel cools, reaching a minimum at \( \sim 1750 \) K, where \( (dT/dp)_\xi \approx (dT/dp)_S \). If the parcel remains in chemical equilibrium, \( NH_3/N_2 \) will increase again as it cools further. This then is how we explain the insensitivity of \( NH_3/N_2 \) to \( K_{\text{CO}} \) seen in Figure 10: the \( NH_3/N_2 \) ratio computed by the full kinetics model is near the equilibrium value at the temperature where the contours of \( NH_3/N_2 \) are parallel to the adiabat, which is
Figure 10. Nitrogen. The six panels are as in Figure 4. Relative abundances of NH$_3$ (red, east) and N$_2$ (blue, west) are indicated by area. HCN abundances are multiplied by five to make them visible at lower $g$ and superposed in gold on N$_2$. Higher gravities and cooler temperatures favor NH$_3$. The NH$_3$/N$_2$ ratio is insensitive to $K_{zz}$ and only weakly sensitive to $m$, which suggests that NH$_3$ can be a proxy for $g$. HCN fares best at high $g$ and high $K_{zz}$. The HCN/NH$_3$ ratio is sensitive to $K_{zz}$ and only weakly sensitive to metallicity. The two boxed models are illustrated in Figure 11.

(A color version of this figure is available in the online journal.)

Figure 11. Two examples of quenching in nitrogen. The particular models are indicated by boxes in Figure 10. Volume mixing ratios of N$_2$, NH$_3$, and HCN are shown for two different $K_{zz}$ pertinent to brown dwarfs. The relative insensitivity of NH$_3$ and N$_2$ to $K_{zz}$ is a consequence of contours of constant NH$_3$/N$_2$ being nearly parallel to the adiabat $p(T)$. This is illustrated here by showing three relevant contours of constant $\xi \equiv NH_3/N_2$. Both $\xi$ and $p(T)$ are plotted against the temperature axis (top). In the full models $\xi = 0.28$ and $\xi = 0.24$ for $K_{zz} = 10^{10}$ cm$^2$ s$^{-1}$ and $K_{zz} = 10^7$ cm$^2$ s$^{-1}$, respectively.

(A color version of this figure is available in the online journal.)

also the minimum equilibrium value in the atmosphere. For the kinds of atmospheres considered in this paper, it appears that the amount of ammonia in the visible parts of the atmosphere will be comparable to the minimum equilibrium abundance computed along the adiabat.

On the other hand, because our results are insensitive to quenching, it is not difficult to find a non-unique chemical reaction timescale for the nitrogen system that predicts $f_{NH_3}$ well. A chemical reaction timescale that works well in a quenching scheme that sets the reaction rate $t_{NH_3}$ equal to the mixing time $t_{mix} = H^2/K_{zz}$ is

$$t_{NH_3} = 1.0 \times 10^{-7} p^{-1} \exp(52,000/T) \text{s.}$$

(32)

This particular choice preserves the activation energy barrier is set by N$_2$ + H$_2$ -> NNH + H. This choice of $t_{NH_3}$ is not unique. Almost any plausible choice of Arrhenius parameters that gives roughly the same timescale as Equation (32) at 10 bars and 1750 K
will work just as well. We have no information to constrain dependence on \( p \) or \( m \).

Figure 12 shows how our expression compares to some expressions in the literature. The chemical reaction time recommended by Lodders & Fegley (2002) is equivalent to

\[
\tau_{\text{chem}} = 1.2 \times 10^8 \frac{\exp(81.515/T)}{p \cdot N \cdot f_H^2} \text{ s,} \tag{33}
\]

Equation (33) is based on the possible reaction \( \text{N}_2 + \text{H}_2 \rightarrow \text{NH}_2 + \text{N} \). Figure 12 shows that Equation (33) used with \( L = H \) gives as good a fit to our models as Equation (32). The extreme temperature dependence of Equation (33) appears justified.

Line et al. (2011) look for quenching in the reaction \( \text{H}_2 + \text{N}_2 \text{H}_2 \rightarrow 2\text{NH}_2 \). Using rates given by Line et al. (2011), and using \( \frac{p\text{N}_2\text{H}_2}{p\text{N}_2} = K_{\text{N}_2\text{H}_2} = 3.8 \times 10^{-6} e^{-25738/T} \), we get

\[
\tau_{\text{chem}} = 1.3 \times 10^{11} T^{-0.93} \frac{\exp(46,400/T)}{p \cdot f_H^2} \text{ s} \tag{34}
\]

as our best effort to reproduce their chemical timescale for \( \text{NH}_3 \) equilibration with \( \text{N}_2 \). Figure 12 shows that Equation (34) agrees well with the predictions of our kinetics model when \( m = 3 \), but sometimes predicts more \( \text{NH}_3 \) than we find for \( m = 1 \). Disagreement is limited to cases with \( K_{\text{zz}} < 10^7 \text{ cm}^2 \text{ s}^{-1} \), which means that Equation (34) is relatively fast at the lowest quench temperatures. It is possible that the temperature dependence of Equation (34) is not steep enough, or that the bottleneck involves \( \text{N}_2 \) rather than \( \text{N}_2\text{H}_2 \), or that the highly uncertain thermodynamic parameters of \( \text{NNH} \) are being treated differently between models.

### 5.1. \( \text{HCN}–\text{NH}_3–\text{N}_2 \)

The approach we used for \( \text{CO} \) and \( \text{CH}_4 \) works moderately well for \( \text{HCN} \) and \( \text{NH}_3 \) and less well for \( \text{HCN} \) and \( \text{N}_2 \).

The equilibrium between \( \text{HCN} \) and \( \text{CH}_4 \) and \( \text{NH}_3 \),

\[
K_{\text{HCN}–\text{CH}_4} = \frac{p\text{CH}_4 \cdot p\text{NH}_3}{p\text{HCN} \cdot p\text{H}_2} = 3.0 \times 10^{-14} \exp(33,460/T). \tag{35}
\]

closely resembles the parallel equilibrium Equation (6) between \( \text{CO} \) and \( \text{CH}_4 \). For the cool objects in which \( \text{CH}_4 \) is abundant at depth, the strong temperature dependence of \( K_{\text{HCN}–\text{CH}_4} \) means that \( \text{HCN} \) fares best with respect to \( \text{NH}_3 \) at high temperature when parcels move up or down along an adiabat.

For warmer worlds where \( \text{CO} \) and \( \text{N}_2 \) are dominant at depth, the most informative equilibrium is with \( \text{CO}, \text{N}_2, \text{H}_2, \) and \( \text{H}_2\text{O} \), all of which are nearly constant when nearly all the C is in \( \text{CO} \). The formal reaction is \( 2\text{CO} + \text{N}_2 + 3\text{H}_2 \leftrightarrow 2\text{HCN} + 3\text{H}_2\text{O} \), and the corresponding equilibrium constant is

\[
K_{\text{HCN}–\text{NH}_3} = \frac{p\text{CO}^2 \cdot p\text{N}_2 \cdot p\text{H}_2}{p\text{HCN}^2 \cdot p\text{H}_2\text{O}^2} = 4.278 \times 10^{11} \exp(-528/T), \tag{36}
\]

for which the temperature dependence is weak at quenching where \( T_q \approx 2000 \text{ K} \). Equation (36) indicates that \( f_{\text{HCN}} \propto p \). Hence, in both the cool and the warm limits HCN increases with depth in deep atmospheres. Thus, to identify HCN quenching, it suffices to start from the bottom and find the altitude where the HCN abundance stops decreasing.

We looked for quench points defined against Equation (35), Equation (36), and a third equilibrium with \( \text{CO} \) and \( \text{NH}_3 \),

\[
K_{\text{HCN}–\text{CO}} = \frac{p\text{CO} \cdot p\text{NH}_3}{p\text{HCN} \cdot p\text{H}_2\text{O}} = 0.5025 \exp(6339/T). \tag{37}
\]

Quenching with \( \text{N}_2 \) \( (K_{\text{HCN}–\text{N}_2}) \) gives an indifferent fit to an Arrhenius relation, as might be expected given the insensitivity of Equation (36) to \( f_{\text{HCN}} \) and the high thermal stability of \( \text{N}_2 \). The other two equilibria both give plausible Arrhenius-like fits, although far from perfect (Figure 13).
A direct fit to the chemical timescale derived from the equilibrium \( K_{\text{HCN} \cdot \text{CH}_4} \) for the full ensemble of models is

\[
t_q' = 1.6 \times 10^{-4} p^{-1} m^{-0.7} \exp(37,000/T) \text{s},
\]

while the corresponding fit to \( K_{\text{HCN} \cdot \text{CO}} \) is

\[
t_q' = 1.3 \times 10^{-4} p^{-1} m^{-1} \exp(34,500/T) \text{s}.
\]

At quench temperatures greater than 1600 K, the pressure dependence is better described by \( t_q \propto p^{-0.5} \) and the \( T \) dependence is stronger with an Arrhenius \( B \)-factor of the order of 46,000 K. The stronger temperature dependence for high \( T_q \) suggests that reactions with \( \text{N}_2 \) with its high activation energy are becoming important. The higher \( T_q \) cases correspond to higher \( K_{\text{HCN} \cdot \text{CO}} \).

As noted above, the quench approximation is not very sensitive to the details of \( t_q \), and that is the case here as well. Computed quenched abundances using \( t_q = t_{\text{mix}} = H^2/K_{zz} \) provide a good approximation to the HCN mixing ratios computed by the full model with

\[
t_{\text{HCN}} = 1.5 \times 10^{-4} p^{-1} m^{-0.7} \exp(36,000/T) \text{s}.
\]

This expression seems to work well for all cases we have considered (Figure 14).

Fegley & Lodders (1996) treat HCN destruction as controlled by direct reaction of HCN with \( \text{H}_2 \) to make \( \text{NH} \) and \( \text{CH}_2 \). The corresponding chemical timescale is

\[
t_{\text{chem}} = \frac{9.3 \times 10^7 \exp(70,456/T)}{N_f_{\text{H}_2}^{1.5}} \text{s}.
\]

This has a very steep temperature dependence. Quench approximations using Equation (41) with \( L = H \) are shown in Figure 14. This approximation predicts much more HCN (a higher quench temperature) than we find in our 1D models, a result consistent with the steep temperature dependence of Equation (41).

Moses et al. (2010) presume that HCN destruction is controlled by reaction of \( \text{H}_2 \) with the \( \text{H}_2\text{CN} \) radical. This is a much faster reaction. To convert their discussion into a reaction time requires defining the \( \text{H}_2\text{CN} \) equilibrium abundance. We write \( p_{\text{H}_2\text{CN}} = K_{\text{H}_2\text{CN} \cdot \text{HCN} \cdot \text{H}} \) with \( K_{\text{H}_2\text{CN}} = 1.0 \times 10^{-6} e^{14240/T} \). This is likely not the same as what Moses et al. (2010) use. Atomic and molecular hydrogen are also assumed to be in equilibrium. Other pertinent information is given in Moses et al. (2010). The reaction timescale that results is

\[
t_{\text{chem}} = \frac{8.3 \times 10^{20} \exp(23,358/T)}{T^{1.941} N_p^{0.5} f_{\text{H}_2}^{1.5}} \text{s}.
\]

Figure 14 shows that Equation (42) used in a quench approximation predicts much less HCN than we compute in our 1D models. This means that reactions destroying HCN are occurring at relatively low temperatures. This fits with the relatively weak temperature dependence of \( t_{\text{chem}} \) in Equation (42).

The comparison of models may be frustrated in part by a hole in our model. We did not include methyamine (\( \text{CH}_3\text{NH}_2 \)), which Moses et al. (2010) argue plays the same role in hydrogenation of HCN at low temperatures and high pressures that methanol plays for CO. Their scheme is plausible but almost entirely hypothetical because it passes through several free radicals that must exist but about which little else is known. Our omission of a \( \text{CH}_3\text{NH}_2 \) channel implies that Equation (40) overestimates HCN, especially in cool worlds. Another issue undermining comparison between models is that we have not implemented Moses et al.’s (2010) full quench scheme: Moses et al. (2010) require that HCN quench with respect to already quenched abundances of \( \text{CH}_4 \) and \( \text{NH}_3 \). However, at the temperatures at which HCN might actually be abundant enough to be detectable in EGPs and BDs, our prescription should work and is easy to use.
6. CO₂

In principle, CO₂ is also subject to quenching (Prinn & Fegley 1987), with caveats. First, because CO₂ quenches at a lower temperature than CO, it quenches with respect to the disequilibrium (quenched) abundance of CO. Second, in practice, CO₂ can be much enhanced by photochemistry if the world in question is subject to significant stellar irradiation. Under such conditions, quenching is a poor guide. However, for solitary brown dwarfs and planets in wide orbits it should do fine.

The approach is similar to that used for CO and CH₄ above. Equilibrium between CO₂, CO, H₂, and H₂O can be approximated by

\[ K_{\text{CO₂}} = \frac{p_{\text{CO₂}} \cdot p_{\text{H₂O}}}{p_{\text{CO₂}} \cdot p_{\text{H₂}}} = 18.3 \exp\left(-2376/T - (932/T)^2\right). \]

(43)

The equilibrium product Equation (43) is evaluated using the quenched values of pCO and pH₂O, beginning at the altitude where CO and CH₄ quench, and then extending to all higher altitudes. CO₂ quenching is pinned at the altitude where the equilibrium defined by Equation (43) breaks down. Figure 15 shows the results of doing so for the ensemble of models. Figure 15 is noisy because the deviations from equilibrium are modest and can go in either direction. It is interesting that the quenching timescale \( t_q \) varies inversely with the square root of the quench pressure \( p_q \), and that unlike the CO–CH₄ system there is no discernible dependence on metallicity. The temperature dependence in the Arrhenius-like relation \( t_q \cdot p_q^{0.5} \propto \exp(38,000/T) \) is similar to the other cases we have looked at involving CO, which is also notable.

Figure 15 shows that CO₂ abundances in the ensemble of models are well approximated by a quench model provided that the appropriate disequilibrium CO and H₂O mixing ratios are used. A chemical reaction timescale that works well for CO₂ quenching is

\[ t_{\text{CO₂}} = 1.0 \times 10^{-10} p^{-0.5} \exp(38,000/T) \text{ s} \]

(44)

where \( p \) is in bars. The results shown in Figure 15 are rather insensitive to the Arrhenius A factor in \( t_{\text{CO₂}} \), which perhaps is to be expected given the weak temperature dependence of the equilibrium constant Equation (43) compared to the very strong temperature dependence of Equation (44).

7. DETECTABILITY

Whether or not a molecule can be detected depends on the abundance and opacity of the species in question and on the opacities of other molecules and clouds. For reference, Figure 16 shows absorption cross sections at 650 K and 1 bar pressure for H₂O, NH₃, CH₄, HCN, and CO. These can be compared to illustrative column densities shown in Figure 17. The latter are integrated upward from the 1, 0.1, and 0.01 bar pressure level, typical near-IR photospheric pressures for planets or brown dwarfs with gravities of 10⁵, 10⁴, and 10³ cm s⁻², respectively. For CO, CH₄, CO₂, and HCN, we plot column densities for only one value of \( K_{zz} \) for each \((g, T_{\text{eff}})\) pair. We arbitrarily select \( K_{zz} = 10^{13}/\text{g} \), a high value of \( K_{zz} \) but consistent with Equation (3), for illustration. For N₂ and NH₃, we plot column densities for all \( K_{zz} \) to emphasize how little these depend on mixing.

While only a complete model spectrum can definitively predict the visibility of each molecule given a set of assumptions, we can use Figure 16 together with Figure 17 to make some generalizations. We defer the task of properly including our new chemical network into a complete model atmosphere to the future.

The absorption cross section per molecule for the CO band head at 2.3 μm is about \( 10^{-21} \text{ cm}^² \) per molecule. We know from model comparisons to data (e.g., Cushing et al. 2008) that by
\[ T_{\text{eff}} = 1100 \, \text{K} \text{ at } g = 10^5 \text{ this band head produces only a slight spectral feature. Consulting Figure 17 and scaling appropriately, we expect, all else being equal, that CO would remain detectable down to } T_{\text{eff}} \sim 900 \, \text{K} \text{ at } g = 10^4 \text{ and } 500 \, \text{K} \text{ at } g = 10^3. \text{ This temperature is considerably cooler than expected by the conventional wisdom.}

We likewise can consider the appearance of the 2.2 \, \mu \text{m methane band, which, by definition, first appears at the T0 spectral type at } T_{\text{eff}} \sim 1200 \, \text{K. Figure 17 suggests that a comparable gravity-adjusted column abundance of methane will not appear in a Saturn-like } g = 10^5 \text{ planet until } T_{\text{eff}} \sim 650 \, \text{K. The directly imaged companion GJ 504 b (Kuzuhara et al. 2013; Janson et al. 2013) provides a test of this reasoning. The mass}

and effective temperature of GJ 504 b have been estimated at \sim 5 \, \text{M}_J \text{ and 600 K. Its gravity should be } \sim 6000 \, \text{cm} \, \text{s}^{-2}. \text{ By the reasoning above, methane would be expected and indeed has been detected (Janson et al. 2013).}

Methane is far more detectable in the 3.3 \, \mu \text{m fundamental band where the absorption cross section is over an order of magnitude larger. CH}_4 \text{ has been detected here as early as spectral type L5 (Noll et al. 2000) in field dwarfs. Likewise, spectra over this wavelength range would better help to constrain the arrival of methane at low gravity in the directly imaged planets. Indeed, Skemer et al. (2013) report a possible detection of this same feature in HR 8799 c, suggesting a trace abundance in the upper atmosphere.
Another test of these ideas may be provided by field T or Y dwarfs with unusual colors not predicted by models. Faint, red objects, in particular, would be good candidates for the low-gravity, methane-poor objects we predict. For example, the cool Y dwarf WISE 1828+2650 (Cushing et al. 2011) is both faint and unusually red in J−H color (Beichman et al. 2014). While Cushing et al. did detect methane in this object, chemical equilibrium models do a very poor job fitting the available photometry (Beichman et al. 2014). Near-IR spectra should be obtained of all such color outliers to search for methane spectral features.

We note that some searches for planetary companions to young stars (e.g., Liu et al. 2010) as well as surveys for “planetary-mass” T-dwarfs in young stellar clusters (e.g., Parker & Tinney 2013) have employed differential-methane band imaging. In this technique (Tinney et al. 2005), two images of a target are taken, one in a filter that matches the 1.7 μm CH4 band and one which probes the entire H band. When the two images are differenced, methane-bearing objects stand out as they are dark in the CH4 filter. Our conclusions here suggest that such techniques must be used with caution as methane may simply not yet be present in planetary-mass objects even at effective temperatures below 1000 K.

Similar arguments can be made for the appearance of other spectral features of interest. We expect that NH3 will appear at temperatures below 1000 K. Not yet be present in planetary-mass objects even at effective temperatures higher than 1000 K, while Cushing et al. did detect methane in this object, chemical equilibrium models do a very poor job fitting the available photometry (Beichman et al. 2014). Near-IR spectra should be obtained of all such color outliers to search for methane spectral features.

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Similar arguments can be made for the appearance of other spectral features of interest. We expect that NH3 will appear at temperatures below 1000 K, but with solar abundances its column (1–2 × 10^21 cm^-2) is 1000 times what HCN can reach at its best. Carbon dioxide has an absorption cross section of 10^−12 cm^2 per molecule at 2.3 μm, and, with abundances approaching 10^18 cm^-2, we expect it to be detectable at around 900 to 1100 K in field brown dwarfs. Indeed, the AKARI space telescope discovered CO2 features in several late L and early T dwarfs (Yamamura et al. 2010). Judging by Figure 17, we would predict CO2 to be detectable to 500 K and cooler in the lowest-mass planets.

8. CONCLUSIONS

We use a reasonably complete 1D chemical kinetics code to survey the parameter space that encompasses atmospheres of cool brown dwarfs and warm young extrasolar giant planets. Our model contains only gas phase chemistry of small molecules containing H, C, N, O, and S. We use realistic p-T profiles for cloudless atmospheres with effective temperatures between 500 and 1100 K and surface gravities between 10^5 cm s^-2 to 10^7 cm s^-2. Vertical transport is described by an eddy diffusivity Kzz that we vary over a wide range. Our objective is to describe carbon and nitrogen speciation, especially at lower (planetary) surface gravities. Reviews of what we found are presented in Figure 4 for carbon and Figure 10 for nitrogen.

We find that carbon in cloudless brown dwarfs is predominantly in the form of methane at 900 K for g = 10^5 cm s^-2. The small surface gravity of planets strongly discriminates against CH4 when compared to an otherwise comparable brown dwarf. If vertical mixing is comparable to Jupiter’s, methane first predominates over CO in planets cooler than 500 K. Sluggish vertical mixing can raise the transition to 600 K; clouds or more vigorous vertical mixing could lower it to 400 K.

The detectability of specific molecular features in a spectrum depends on the strength of the molecular absorption cross sections as well as the gaseous abundance. Nevertheless, a natural prediction of our model is that there will be cool planets with no methane observed in the H or K spectral bands. The refractory behavior of CO in low-gravity objects is likely at least partially responsible for the lack of cool planets found by the NICI survey, which relied upon methane absorption in the H band to identify planets (Liu et al. 2010).

Ammonia is also sensitive to gravity, but, unlike methane and CO, ammonia is insensitive to mixing, which makes it a proxy for gravity. We did not explore temperatures low enough...
to determine the transition from N\textsubscript{2} to ammonia in planets, but it is nearly as abundant as N\textsubscript{2} at 500 K in brown dwarfs, which is broadly consistent with the observed properties of the Y dwarfs (Cushing et al. 2011) for which NH\textsubscript{3} is seen in the H band. On the other hand, ammonia persists as an abundant minor species to rather high temperatures and this is consistent with it being readily detected in mid-IR spectra of T-dwarfs (Cushing et al. 2006). HCN might become interesting in high-gravity brown dwarfs if vertical mixing is very vigorous.

When expressed in terms of quenching parameters, nearly all our results for CO and CH\textsubscript{4} can be reduced to a simple equation in Arrhenius form that is easy to use but not easy to interpret. From a strictly practical perspective, what we find is close to what one gets using Prinn & Barshay’s (1977) algorithm in its original form (a fortuitous accident of using too high a rate for the wrong reaction). The apparent simplicity is somewhat surprising given the complexity of the chemistry involved and the many different ways the system has been described in the literature, nor is our result quite what we expected. First, we find that the timescale \(t_{CO}\) for hydrogenation of CO is shorter for higher metallicity. Because the forward reactions that destroy CO have no metallicity dependence, we infer that metallicity dependence enters through the reverse reaction (oxidation of CH\textsubscript{4}). By definition, the reverse reaction is as fast as the forward reaction while in equilibrium, but it falls off more quickly than the forward reaction as the temperature drops. The important forward reactions are linear in metallicity while the important reverse reactions are quadratic in metallicity.

Second, we find that \(t_{CO}\) is inversely proportional to pressure. Analyses based on isolating a limiting reaction predict a stronger dependence on pressure, typically \(p^{-2}\). The weaker \(p^{-1}\) pressure dependence is expected for a reaction involving CO itself, such as

\[
H\textsubscript{2} + CO \rightarrow HCO + H. \tag{45}
\]

It is interesting that R45 actually does have the highest \(\Delta G\) value in the CO hydrogenation sequence, and therefore the highest energy barrier, and that the magnitude of \(\Delta G\) of R45 is what we infer in Equation (14). However, it is also quite clear from Figure 7 that equilibrium breaks down between CH\textsubscript{3}OH and CH\textsubscript{4} well before it breaks down between CO and CH\textsubscript{3}OH, as was found by Moses et al. (2011). Reactions involving CH\textsubscript{3}OH imply a \(p^{-2}\) pressure dependence, because the equilibrium abundance of CH\textsubscript{3}OH with respect to CO goes as the square of the H\textsubscript{2} pressure. The system behaves—both in the 40,000 K energy adiabat to a scale height, rather than as the complex function of many variables that it probably is (Smith 1998).

For nitrogen and ammonia we were unable to recover an emergent Arrhenius-like behavior from the full system. On the other hand, it was easy to devise a good quench approximation, and we also found that some published quench approximations (e.g., Fegley & Lodders 1994) work very well. For HCN, we met with mixed success. We did find emergent Arrhenius-like behaviors, and we developed a new quench approximation that works quite well for our models. On the other hand, there does not yet appear to be a consensus on what the quench chemistry of HCN actually is. We found a wide scatter of different outcomes when comparing different published quench schemes. We believe our quench approximation should work well for warm objects where HCN is predicted to be relatively abundant but, because we did not consider hypothetical hydrogenation channels through methylamine (Moses et al. 2010), our models may overestimate \(f_{HCN}\), especially in cooler objects.

There are many effects that our models do not address. None of these effects have much sway over our quench approximations, but they have much to do with what might actually be present in a real atmosphere.

Clouds are likely the most important. Adding infrared opacity to an atmosphere is effectively equivalent to reducing the gravity. This is because opacity raises the \(p-T\) profile (i.e., the adiabat) to a lower pressure for a given effective temperature. A cloudy atmosphere favors CO and N\textsubscript{2} over CH\textsubscript{4} and NH\textsubscript{3}, other things equal. Increasing metallicity also increases opacity to the detriment of methane and ammonia.

Another issue for real worlds is that \(K_{zz}\) may be much smaller in higher altitude radiative regions of the atmosphere than it is in the convecting region. The radiative stratosphere is the part of the atmosphere where \(K_{zz}\) the modeling parameter is most suspect. For N\textsubscript{2} and NH\textsubscript{3}, pronounced vertical structure in \(K_{zz}\) will not matter much. For CO and CH\textsubscript{4}, sharply lower values of \(K_{zz}\) in the stratosphere might be important, because if \(K_{zz}\) is low enough, the atmosphere can have a second quench point in the stratosphere. Such behavior poses no problem to a full kinetics model, but it can make implementing quench approximations more complicated.

Photochemistry induced by irradiation from a nearby star can deplete NH\textsubscript{3} and increase CO\textsubscript{2} and HCN. Lightning and/or impact shocks in cool NH\textsubscript{3}- and CH\textsubscript{4}-rich atmospheres can generate CO and HCN (Chameides & Walker 1981). In warmer objects, catalysts that may be present in metallic clouds (here we mean real metals) will lower the quench point and thus will favor NH\textsubscript{3}, CH\textsubscript{4}, and CO\textsubscript{2} (Prinn & Fegley 1987).

All of these ideas will be put to the test by the directly imaged planets that are expected to be discovered in the coming months and years. Constraining the composition of their atmospheres will no doubt be a rewarding endeavor.

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