Nitrogen as a Tracer of Giant Planet Formation. I. A Universal Deep Adiabatic Profile and Semianalytical Predictions of Disequilibrium Ammonia Abundances in Warm Exoplanetary Atmospheres

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Abstract

A major motivation of spectroscopic observations of giant exoplanets is to unveil planet formation processes from atmospheric compositions. Several recent studies suggested that atmospheric nitrogen, like carbon and oxygen, can provide important constraints on planetary formation environments. Since nitrogen chemistry can be far from thermochemical equilibrium in warm atmospheres, we extensively investigate under what conditions, and with what assumptions, the observable NH$_3$ abundances can diagnose an atmosphere’s bulk nitrogen abundance. In the first paper of this series, we investigate atmospheric $T$–$P$ profiles across equilibrium temperature, surface gravity, intrinsic temperature, atmospheric metallicity, and C/O ratio using a 1D radiative-convective equilibrium model. Models with the same intrinsic temperature and surface gravity coincide with a shared “universal” adiabat in the deep atmosphere, across a wide equilibrium temperature range (250–1200 K), which is not seen in hotter or cooler models. We explain this behavior in terms of the classic “radiative zero solution” and then establish a semianalytical $T$–$P$ profile of the deep atmospheres of warm exoplanets. This profile is then used to predict vertically quenched NH$_3$ abundances. At solar metallicity, our results show that the quenched NH$_3$ abundance only coincides with the bulk nitrogen abundance (within 10%) at low intrinsic temperature, corresponding to a planet with a sub-Jupiter mass ($\lesssim 1 M_J$) and old age ($\gtrsim 1$ Gyr). If a planet has a high-metallicity ($\gtrsim 10 \times$ solar) atmosphere, the quenched NH$_3$ abundance significantly underestimates the bulk nitrogen abundance at almost all planetary masses and ages. We suggest modeling and observational strategies to improve the assessment of bulk nitrogen from NH$_3$.

Unified Astronomy Thesaurus concepts: Exoplanet atmospheres (487); Exoplanet atmospheric structure (2310); Exoplanet atmospheric composition (2021); Chemical abundances (224)

1. Introduction

Planetary atmospheric compositions offer valuable clues to the planet formation and evolution process, especially for giant planets with primordial atmospheres. Over the past decade a number of studies have suggested that atmospheric elemental ratios, such as the carbon-to-oxygen ratio (C/O), can diagnose the orbital distance where a planet initially forms (e.g., Öberg et al. 2011; Ali-Dib et al. 2014; Helling et al. 2014; Madhusudhan et al. 2014, 2017; Piso et al. 2015, 2016; Thibaudeau et al. 2015; Cridland et al. 2016, 2017, 2019; Eistrup et al. 2016, 2018, 2022; Öberg & Bergin 2016; Booth et al. 2017; Espinoza et al. 2017; Booth & Ilee 2019; Öberg & Wordsworth 2019; Schneider & Bitsch 2021a; Ohno & Ueda 2021; Turrini et al. 2021; Bitsch et al. 2022; Eistrup 2023; Mollière et al. 2022; Notsu et al. 2022; Pacetti et al. 2022). Many previous studies focused on the atmospheric C/O ratio, as it has significant impacts on atmospheric chemistry and likely leaves observable fingerprints (e.g., Madhusudhan 2012; Moses et al. 2013a, 2013b; Mollière et al. 2015; Drummond et al. 2019; Notsu et al. 2020; Dash et al. 2022). Beyond the C/O ratio, several recent studies also have also discussed the potential importance of other elements, such as nitrogen (Piso et al. 2016; Cridland et al. 2020; Ohno & Ueda 2021; Notsu et al. 2022), sulfur (Turrini et al. 2021; Pacetti et al. 2022), and refractory metals (Schneider & Bitsch 2021b; Lothringer et al. 2021; Chachan et al. 2023; Hands & Helled 2022).

Nitrogen is the third most abundant volatile element in solar composition and may provide important constraints on the planetary formation environments. Nitrogen has particular advantages for probing the formation locations. Piso et al. (2016) first pointed out that the N/O ratio of disk gas is always higher than stellar N/O by a factor of $>2$ and monotonically increases with radial distance, which provides additional clues to constrain planetary formation location from a planet’s atmospheric N/O ratio. Cridland et al. (2020) studied the atmospheric compositions of warm Jupiters using a population synthesis model and suggested that combining C/O and N/O helps to probe the formation history, such as whether the planet acquired its atmosphere outside of the refractory carbon erosion front. Ohno & Ueda (2021) also stressed that the atmospheric N/O is expected to be sensitive to formation location if disk solids, such as pebbles and planetesimals, determine the atmospheric composition. This is because the solid N/O ratio has an order-of-magnitude variation as a function of a radial distance (see also Notsu et al. 2022 for the discussion based on a disk chemistry model). Turrini et al. (2021) and Pacetti et al. (2022) suggested that C/N, N/O, and S/N ratios help to constrain the formation and migration pathways of giant planets.

To clarify the usefulness of the N/O ratio for example, Figure 1 shows the nitrogen-to-oxygen ratio (N/O) of solids
and gas in a protoplanetary disk computed by the phase equilibrium model of Ohno & Ueda (2021) for the protosolar disk model of Öberg & Wordsworth (2019). The gas-phase N/O monotonicly increases with orbital distance, as the O-bearing molecules (e.g., H₂O, CO₂) are gradually removed from the gas phase via condensation while most N remains as a highly volatile N₂ gas within the N₂ snowline. The solid-phase N/O shows an order-of-magnitude orbital variation because of large abundance difference between NH₃ and N₂ (e.g., Öberg & Bergin 2021). The latter indicates the strong dependence of atmospheric N/O on formation location if solid (e.g., planetesimal) accretion predominantly determines the atmospheric composition.

It is also worth noting that several recent studies have discussed formation scenarios for Jupiter in our solar system. Motivated by the abundance of nitrogen being comparable to that of other heavy elements in the Jovian atmosphere (for recent review, see Atreya et al. 2022; Guillot et al. 2022), Öberg & Wordsworth (2019) and Bosman et al. (2019) proposed that Jupiter might have initially formed outward of the N₂ snowline beyond 30 au where solid elemental ratios coincide with solar values (see also Owen et al. 1999). Ohno & Ueda (2021) suggested that the Jovian atmospheric composition could also be explained if Jupiter formed in a locally cold disk region caused by the shadow cast by a disk substructure, such as a dust pileup at the H₂O snowline, which is not nearly as far away from the central star.

In substellar atmospheres, in the absence of ionizing flux, N₂ and NH₃ are the main nitrogen reservoirs (Lodders & Fegley 2002). HCN can also be abundant if photochemical processes are at work (Moses et al. 2013a). NH₃ and HCN would be likely detectable in the near future by infrared observations by JWST and Ariel (MacDonald & Madhusudhan 2017), while N₂ is in general not observable due to the negligibly low visible and infrared opacity for the temperature regime of exoplanets. Hobbs et al. (2019) used a photochemical kinetic model to show that the abundances of C- and O-bearing species, such as H₂O and CO, are insensitive to N/H ratio in hot Jupiters like HD 209458b. Ramírez et al. (2020) also investigated the impact of N/H ratio on TiO abundances in ultrahot Jupiters and found that the TiO abundance is nearly independent of N/H. Since the abundances of C- and O-bearing species are insensitive to bulk nitrogen abundance in substellar atmospheres, it appears that the only route to diagnose the bulk nitrogen abundance of a giant planet is from NH₃ and/or HCN.

However, constraining the bulk nitrogen abundance from NH₃ and HCN is a complex task. The NH₃ and HCN abundances in the observable atmosphere readily deviate from thermochemical equilibrium abundances because of disequilibrium effects, such as vertical mixing and photochemistry (e.g., Line et al. 2011; Moses et al. 2011; Venot et al. 2013). For warm planets of $T_{eq} \lesssim 1000$ K, Fortney et al. (2020) investigated disequilibrium NH₃ abundances on Saturn-like planets with various $T_{eq}$ and found that NH₃ abundance depends on a number of factors, such as planetary mass, age, and metallicity. They also suggested that N₂ will actually dominate over NH₃ over a very wide range of temperatures and ages, making the observable NH₃ abundance only a lower limit to the bulk nitrogen abundance. Hu (2021) also investigated photochemistry on temperate/cold H₂-rich planets and found that NH₃ tends to be depleted due to photodissociation, especially on planets around G/K stars.

In this study, we expand the work of Fortney et al. (2020) with a particular focus on nitrogen chemistry. Here in Paper I we systematically investigate the thermal structure of planetary deep atmospheres, which significantly affects the disequilibrium abundance of NH₃, as demonstrated by Fortney et al. (2020). While Fortney et al. (2020) investigated the effects of planetary deep atmospheres using numerical models, this study advances the field by establishing a semianalytical model that explicitly links planetary gravity, intrinsic temperature, metallicity, bulk nitrogen abundance, and disequilibrium NH₃ abundance. The model is readily applicable to arbitrary planets and will be useful for interpreting the retrieved NH₃ abundance in future observations.

The organization of this paper is as follows. In Section 2, we introduce a basic background of nitrogen equilibrium and disequilibrium chemistry. In Section 3, we investigate atmospheric pressure–temperature ($P$–$T$) profiles for a wide range of planetary parameters. We derive a semianalytical fit to understand why giant planets typically have a universal deep adiabat, irrespective of incident flux, which has a major impact on NH₃ abundances from disequilibrium chemistry from vertical mixing. In Section 4, we identify the relation between NH₃ and bulk nitrogen abundances as a function of planetary parameters from semianalytical arguments. In Section 5, we describe caveats of this study. In Section 6, we summarize our findings. In Paper II of this series (Ohno & Fortney 2023), we verify our semianalytical predictions using a photochemical kinetics model and discuss the observational implications of atmospheric nitrogen species on transmission and emission spectra.

\section{2. Nitrogen Chemistry: The Importance of the Structure of the Deep Atmosphere}

One of the important factors in controlling the observable NH₃ abundance is vertical mixing within an atmosphere. Atmospheric compositions follow thermochemical equilibrium in the deep hot atmospheres, while the abundances at lower
pressure, where it is colder, tend to be out of equilibrium and vertically constant, and to reflect the equilibrium compositions of the deep atmosphere (though see Section 5.2 for a caveat on this picture). This phenomenon is often called “quenching” (e.g., Fegley & Prinn 1985; Fegley & Lodders 1994; Zahnle & Marley 2014; Tsai et al. 2018) and was originally identified for CO/CH$_4$ in the Jovian atmosphere, where detected CO abundances are many orders of magnitude higher than thermochemical equilibrium calculations (Prinn & Barshay 1977). This quenching is caused by the slow thermochemical conversion compared to relatively fast vertical mixing (e.g., Moses et al. 2011). Several recent studies have attempted to constrain the strength of vertical mixing in brown dwarf and giant planet atmospheres from quenched molecular abundances (Miles et al. 2020; Kawashima & Min 2021; Mukherjee et al. 2022).

Since the upper atmospheric composition is related to the composition of the deep hot atmosphere, it is necessary to understand the planetary deep atmosphere and interior to relate the observable NH$_3$ abundance to bulk nitrogen abundance (Fortney et al. 2020). To this end, we first introduce the nitrogen chemistry in deep atmospheres where thermochemical equilibrium is expected.

### 2.1. Thermochemical Equilibrium and Vertical Quenching of NH$_3$

The quenching behavior of NH$_3$ has an interesting characteristic: the quenched NH$_3$ abundance is insensitive to the strength of vertical mixing (Saumon et al. 2006; Zahnle & Marley 2014; Fortney et al. 2020). As discussed in Zahnle & Marley (2014), this is caused by the abundance ratio contours of NH$_3$/N$_2$ being nearly parallel to the adiabatic profiles of substellar atmospheres (see also Figure 2). The vertically quenched abundance is determined, to a good approximation, by the equilibrium abundance at a certain depth where thermochemical interconversion timescale becomes equal to the vertical mixing timescale. However, since the deep adiabat is nearly along the contour of constant NH$_3$/N$_2$ ratio, the quenched NH$_3$ abundance is nearly the same wherever the quenching takes place. This characteristic has an advantage in interpreting the quenched NH$_3$: one does not need to worry too much about the uncertainty of vertical mixing strength, parameterized by $K_{zz}$.

To further clarify the quenching behavior of NH$_3$, the right panel of Figure 2 shows the vertical distribution of NH$_3$ in an atmosphere of solar composition computed by the chemical kinetics code VULCAN (Tsai et al. 2017, 2021) for various planetary equilibrium temperatures and eddy diffusion coefficients. While the NH$_3$ distribution in the upper atmosphere depends on the eddy diffusion coefficient for hot ($T_{eq} \simeq 1000$ K) planets where the quenching occurs in shallower radiative parts of the atmosphere, the abundances are nearly independent of the eddy diffusion for warm ($T_{eq} < 1000$ K) planets where the quenching occurs in deep adiabatic atmospheres.

Since the quenched abundance is determined by the composition at a point deep in the atmosphere where thermochemical equilibrium is valid, it is worth first examining the equilibrium abundance of nitrogen species. The law of mass action provides the relation between N$_2$ and NH$_3$ that should be

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**Figure 2.** Left: $P$–$T$ profiles of atmospheres of solar composition computed in radiative–convective equilibrium (see Section 3.2 for details). Different colored lines show the $P$–$T$ profiles for different equilibrium temperatures. We assume a surface gravity of $g = 10$ m s$^{-2}$ and planetary intrinsic temperature of $T_{int} = 100$ K. The gray dashed lines show the abundance ratio contours of NH$_3$/N$_2$ = 0.01, 0.1, 1, 10, and 100 from top to bottom, computed by Equation (3). Right: vertical distribution of NH$_3$ volume mixing ratio for the $P$–$T$ profiles in the left panel. The solid and dashed–dotted lines show the distributions for eddy diffusion coefficients of $10^8$ and $10^{10}$ cm$^2$ s$^{-1}$, respectively. Note that the distributions of different eddy diffusion coefficients are almost superimposed on each other at $T_{eq} < 1000$ K. We have turned off photochemistry for the sake of simplicity.
satisfied in thermochemical equilibrium, which is given by

\[ \frac{p_{\text{NH}}^2}{p_{\text{N}_2}p_{\text{H}_2}} = K_{\text{N}_2=\text{NH}_3} = A e^{\beta/T}, \]  

where \( P_{\text{H}_2}, P_{\text{N}_2}, \) and \( P_{\text{NH}_3} \) are the partial pressure of \( \text{H}_2, \text{N}_2, \) and \( \text{NH}_3, \) respectively, \( K_{\text{N}_2=\text{NH}_3} \) is the equilibrium constant of \( \text{N}_2-\text{NH}_3 \) interconversion, \( \lambda = 5.90 \times 10^{-13} \text{ bar}^{-2}, \) and \( B = 13,207 \text{ K} \) (Zahnle & Marley 2014). Assuming that \( \text{N}_2 \) and \( \text{NH}_3 \) accommodate most of the nitrogen, we can approximate the nitrogen conservation as \( f_N \approx f_{\text{NH}_3} + 2f_{\text{N}_2}, \) where \( f_N, f_{\text{NH}_3}, \) and \( f_{\text{N}_2} \) are volume mixing ratios of total nitrogen, \( \text{N}_2, \) and \( \text{NH}_3. \) Then, one can obtain the pressure–temperature relation of \( \text{NH}_3/\text{N}_2 = \xi \) contour as (Zahnle & Marley 2014)

\[ f_N \left( \frac{\xi^2}{2 + \xi} \right) = p_{\text{H}_2}^2 A e^{\beta/T}, \]  

where \( f_{\text{H}_2} = \text{H}_2/(\text{H}_2 + \text{He}) = 0.859 \) and \( f_N = 1.16 \times 10^{-4} \) in the solar elemental abundances of Asplund et al. (2021). We note that \( f_N \) is not identical to the \( N/\text{H} \) ratio, as it is given by

\[ f_N = \frac{N}{\text{H}_2 + \text{He}} = \frac{2N/\text{H}}{1 + 2\text{He}/(\text{H} + \text{He})} = 2f_{\text{H}_2}N/\text{H}, \]  

where \( N/\text{H} = 6.76 \times 10^{-5} \) is the value for solar composition (Asplund et al. 2021). Equation (2) is inconvenient from an observational perspective, as both \( f_N \) and \( \xi \) are unknown. Instead, eliminating \( f_{\text{N}_2} \) in Equation (1) using \( f_N \approx f_{\text{NH}_3} + 2f_{\text{N}_2}, \) we obtain

\[ N/\text{H} = \frac{f_{\text{NH}_3}}{2f_{\text{H}_2}} \left[ 1 + \frac{2f_{\text{NH}_3} e^{\beta/T}}{A(f_{\text{H}_2}^2 P)^{2}} \right], \]  

where we use Equation (3). Under chemical equilibrium, Equation (4) can straightforwardly constrain the bulk nitrogen abundance from the \( \text{NH}_3 \) abundance. In addition, as introduced above, the equilibrium \( \text{NH}_3 \) abundance is approximately constant along the deep adiabatic profile. Thus, it is expected that the quenched \( \text{NH}_3 \) abundance is mostly determined by the deep adiabatic profile alone.

3. Constraining Thermal Structures of Deep Atmospheres

3.1. Radiative Zero Solution of Irradiated Exoplanets

The preceding argument highlights the importance of identifying the thermal structures of deep atmospheres (below the photosphere) to relate the quenched \( \text{NH}_3 \) abundance with bulk nitrogen abundance. Here, we point out an interesting trend of deep atmospheres: many planets with different equilibrium temperatures\(^3\) (\( T_{\text{eq}} = 250–1200 \text{ K} \)) have nearly the same deep adiabatic profile as seen in Figure 2. Fortney et al. (2007) first reported such a universal deep adiabat in their radiative–convective models. Motivated by simplified calculations with dual-band radiative transfer (Guillot 2010), Fortney et al. (2020) speculated that the universal deep adiabat may emerge owing to the steep change in visible-to-infrared opacity ratio caused by the loss of gas-phase alkali metals, although the actual cause still remains unclear. The universality of the deep adiabat has a crucial impact on the disequilibrium abundance of \( \text{NH}_3; \) the quenched \( \text{NH}_3 \) abundance is nearly independent of the equilibrium temperature for temperate to warm exoplanets, as seen in the right panel of Figure 2.

Here, we elaborate why many planets have nearly the same deep adiabatic profile for a wide range of equilibrium temperatures. The common thermal structure independent of upper boundary conditions is reminiscent of the “radiative zero solution” discussed in the context of stellar and protoplanetary envelope structures (e.g., Hayashi et al. 1962; Mizuno 1980; Stevenson 1982; Kippenhahn & Weigert 1994). In purely radiative atmospheres without convection, the atmospheric temperature structure follows

\[ \left( \frac{d \ln T}{d \ln P} \right)_{\text{rad}} = \frac{3k L_{\text{int}}}{64\pi GM T^4} = \frac{3k_0 P^{1+\alpha} T^3}{16g T^4}, \]  

where \( L_{\text{int}} = 4\pi R^2 \sigma T^4 \) is the planetary intrinsic luminosity, \( T_{\text{int}} \) is the planetary intrinsic temperature, \( \sigma \) is the Stefan–Boltzmann constant, \( g = GM/R^2 \) is the planetary gravity, and \( k_0 = \kappa_0 P^{\alpha} T^{-\beta} \) is the atmospheric Rosseland mean opacity. Assuming constant gravity, \( \alpha, \) and \( \beta, \) Equation (5) yields an analytical solution of

\[ T = T_0 + \left[ \frac{3k_0 T_0^4 (4 - \beta)}{16g (1 + \alpha)} \right]^{1/(4 - \beta)} \times \left( P^{(1+\alpha)/(4-\beta)} - P_0^{(1+\alpha)/(4-\beta)} \right), \]  

where \( P_0 \) and \( T_0 \) are the pressure and temperature of the upper boundary. For \( (4 - \beta)/(1 + \alpha) > 0, \) since \( P \gg P_0 \) and \( T \gg T_0 \) in the limit of a deep atmosphere, the temperature structure asymptotically approaches the same temperature structure relation with \( P_0 = 0 \) and \( T_0 = 0 \) in Equation (6) regardless of the upper boundary condition, which is called the radiative zero solution (e.g., Hayashi et al. 1962; Mizuno 1980; Stevenson 1982; Kippenhahn & Weigert 1994).

The radiative zero solution does not necessarily apply for atmospheric structures, because convection sets in to force the temperature gradient to the adiabatic temperature gradient \( \nabla_{\text{ad}}. \) In the convective region, from the definition of the adiabatic gradient \( (d \ln T / d \ln P) = \nabla_{\text{ad}}, \) the temperature structure follows

\[ T = T_{\text{rcb}} \left( \frac{P}{P_{\text{rcb}}} \right)^{\nabla_{\text{ad}}}, \]  

where \( P_{\text{rcb}} \) and \( T_{\text{rcb}} \) are pressure and temperature of radiative–convective boundary (RCB), and we assume a constant adiabatic gradient for the sake of simplicity. Inserting Equation (6) into this equation with \( P = P_{\text{rcb}} \gg P_0, \) the deep

\[^4\text{For} (4 - \beta)/(1 + \alpha) < 0, \text{the temperature structure converges to the following isothermal profile in the limit of} P \gg P_0:} \]

\[ T \approx T_0 - \left[ \frac{3k_0 T_0^4 P_0^{1+\alpha}(4 - \beta)}{16g (1 + \alpha)} \right]^{1/(4-\beta)}. \]  

In this case, the upper boundary conditions controls the temperature structure of the deep atmosphere.
adiabatic temperature can be expressed as

\[
T = \left[ T_0 + \left( \frac{3k_gT_{\text{int}}^4r_{\text{rcb}}^{1-\alpha} (4 - \beta)}{16g(1 + \alpha)} \right)^{1/(4 - \beta)} \left( \frac{P}{P_{\text{rcb}}} \right)^{\nabla_{\text{ad}}^2} \right], \tag{9}
\]

This equation could strongly depend on the upper boundary condition if the first term in the prefactor (i.e., \( T_0 \)) dominates over the second term. In other words, the deep adiabatic profile does depend on the upper boundary condition (i.e., stellar insolation) if the atmospheric \( P-T \) profile converges to the RCB before it converges to the radiative zero solution.

Based on the preceding argument, we suggest that planets have a common deep adiabatic profile regardless of stellar insolation if the \( P-T \) profile converges to the radiative zero solution above the RCB pressure level. Equating Equation (5) and \( \nabla_{\text{ad}} \), the RCB pressure is given by

\[
P_{\text{rcb}} = \left( \frac{16gT_{\text{int}}^{4-\beta}P_{\text{rcb}}^{-\beta}}{3k_gT_{\text{int}}^4 \nabla_{\text{ad}}^{1/(1 + \alpha)}} \right). \tag{10}
\]

Inserting Equation (10) into Equation (6), we obtain the relation between the RCB temperature and upper boundary temperature \( T_0 \) as

\[
\frac{T_0}{T_{\text{rcb}}} \approx 1 - \phi^{1/(4 - \beta)}, \tag{11}
\]

where we have approximated \( P_0 = 0 \) because \( P_{\text{rcb}} \gg P_0 \). We have introduced a dimensionless parameter defined as

\[
\phi \equiv \frac{4 - \beta}{1 + \alpha} \nabla_{\text{ad}}. \tag{12}
\]

The \( \phi \) parameter is equivalent to the ratio of adiabatic temperature gradient to radiative temperature gradient in the limit of deep atmospheres. Equation (11) is invalid at \( \phi > 1 \) because one cannot define an RCB in the atmosphere with \( \phi > 1 \), where convection does not occur (see the Appendix). Meanwhile, solving the equality of the first and second terms in the prefactor of Equation (9) with respect to \( P_{\text{rcb}} \), we can evaluate a threshold RCB pressure above which the thermal structure converges to the radiative zero solution before it meets the RCB, as

\[
P_{\text{thr}} = \left[ \frac{16gT_0^{4-\beta}(1 + \alpha)}{3k_gT_{\text{int}}^4(4 - \beta)} \right]^{\frac{1}{1/(1+\alpha)}}, \tag{13}
\]

Taking the ratio of Equation (10) to Equation (13) and using Equation (11), we achieve the diagnostic metric, given by

\[
\frac{P_{\text{rcb}}}{P_{\text{thr}}} = \left[ \frac{4 - \beta}{1 + \alpha} \nabla_{\text{ad}}^{1/(1+\alpha)} \left( \frac{T_{\text{rcb}}}{T_0} \right)^{(4 - \beta)/(1 + \alpha)} \right]. \tag{14}
\]

If \( P_{\text{rcb}}/P_{\text{thr}} > 1 \), the \( P-T \) profile converges to the radiative zero solution before it meets the RCB, resulting in a deep adiabatic profile being independent of the upper boundary condition, i.e., the level of stellar insolation. Interestingly, Equation (14) indicates that whether or not stellar insolation affects the deep profile depends only on the adiabatic gradient and the pressure and temperature dependence of atmospheric opacity.

Next we investigate Equation (14) using the opacity of gas of solar composition, from Freedman et al. (2014). We numerically compute \( \alpha \) and \( \beta \) from the analytical fit of the Rosseland mean opacity obtained by Freedman et al. (2014) as a function of pressure and temperature, as shown in the upper two panels of Figure 3. While previous studies adopted single values of \( \alpha \) and \( \beta \) (e.g., Rogers & Seager 2010; Owen & Wu 2017; Ginzburg et al. 2018), these values differ for different pressure and temperature conditions. We also note that since the complex Freedman et al. (2014) analytic fitting formula changes at 800 K, which is necessary since the opacities change with \( T \), this leads to plots of that somewhat exaggerate the sharpness of this change in the opacities. The adiabatic gradient is taken from the equation of state for H/He mixtures (Chabrier et al. 2019), which has updated the widely used ScVH equation of state (Saumon et al. 1995). The lower left panel of Figure 3 shows \( \phi P_{\text{rcb}}/P_{\text{thr}} \) as a function of pressure and temperature. We find that the RCB pressure is much higher than the threshold pressure in the temperature range \( \sim 800-1400 \text{ K} \). Actually, the \( \phi \) parameter takes a value of \( \phi \gtrsim 1 \) in that temperature range, which prohibits the transition from a radiative atmosphere to a convective one. This indicates that the \( P-T \) profiles tend to converge to the radiative zero solution before reaching the RCB in that temperature range. In Figure 2, \( P-T \) profiles indeed converge to the same deep adiabatic profile when the temperature at the second (deeper) nearly isothermal region at \( P \sim 10-100 \text{ bar} \) falls to \( \sim 800-1500 \text{ K} \), consistent with the phase space of \( P_{\text{rcb}}/P_{\text{thr}} \) in Figure 3. Fortney et al. (2007, 2020) also obtained \( P-T \) profiles converging to the same deep adiabatic line when the same condition applies.

We note that the deep adiabatic profile might diverge even if the \( P-T \) profile converges to the radiative zero solution. This is because the temperature structure obeys \( T \sim P^{(1+\alpha)/(4-\beta)} \) in the radiative zero solution (Equation (6)), where a different power-law index of \( (1+\alpha)/(4-\beta) \) yields different lines of temperature structure. As shown in the bottom right panel of Figure 3, the index is roughly constant, \( (1+\alpha)/(4-\beta) \sim 0.25 \), in the temperature range \( \sim 800-1300 \text{ K} \). Thus, it might be expected that the \( P-T \) profiles tend to converge to the radiative zero solution of \( T \sim P^{0.25} \) in this temperature range where Equation (14) predicts \( P_{\text{rcb}} \gtrsim P_{\text{thr}} \).

3.2. Numerical Exploration of \( P-T \) Profiles

To further study the thermal structure of deep atmospheres, we explore the \( P-T \) profiles for a wide range of planetary properties using EGP, a version of the 1D radiative-convective equilibrium model of McKay et al. (1989) and Marley & McKay (1999). The model solves for radiative-convective equilibrium in a plane-parallel atmosphere based on the algorithm of Toon et al. (1989) with thermochemical equilibrium accounting for rain-out effects (Fegley & Lodders 1994; Lodders & Fegley 2002; Visscher et al. 2006, 2010). The model implements non-gray atmospheric opacity with the correlated-\( k \) approximation, where we adopt data sets with correlated \( k \)-coefficients calculated for 1060 pressure-temperature grid points (Lupu et al. 2021, see references

\footnote{A Python version of the adopted model has now been made publicly available (Mukherjee et al. 2023).}
radiative zero solution before it meets the RCB for
Freedman et al. P contour denotes solution at fi converge to the same radiative zero solution of
temperature, atmospheric metallicity, and C therein for the details of opacity sources). We note that our
calculations omit TiO/VO opacity, except for the C/O = 1.1
models. In convective layers, the model switches to use the
adiabatic temperature gradient extracted from the equation of
state for an H/He mixture with Y = 0.292 in Chabrier et al.
(2019). The model has been extensively applied for solar
system objects (McKay et al. 1989; Marley & McKay 1999;
Fortney et al. 2011), exoplanets (Fortney et al. 2005, 2007, 2008, 2020; Morley et al. 2013, 2015, 2017;
Thorngren et al. 2019; Gao et al. 2020; Mayorga et al. 2021),
and brown dwarfs (Marley et al. 1996, 2021; Saumon &
Marley 2008; Morley et al. 2012, 2014; Robinson &
Marley 2014; Karalidi et al. 2021; Tang et al. 2021; Mukherjee
et al. 2022). We refer readers to Marley & Robinson (2015)
and Marley et al. (2021) for further details of the radiative–
convective equilibrium model.

Figure 4 shows P–T profiles for various values of the
planetary equilibrium temperature, surface gravity, intrinsic
temperature, atmospheric metallicity, and C/O ratio. As found
in previous studies, cooler planets (Teq < 1000 K) tend to have
steeper temperature gradients, which yields hotter middle
atmospheres (P ∼ 0.1–1 bar) than the equilibrium temperature.
The cooler atmospheres (Teq < 250–600 K) also develop
detached convective layers at around P ∼ 0.1–10 bar. A
convective zone at these pressures is found in unirradiated
models at these Teff values, and is the “natural” outcome for
these atmospheres, given the high thermal infrared opacities
(Marley & Robinson 2015). Such convective zones are not
possible in the more highly irradiated objects given the high
temperatures at low pressure, which forces a shallower-than-
adiabatic temperature gradient throughout much of the
atmosphere.

The P–T profiles converge to the same deep adiabatic profile
in the equilibrium temperature range Teq ∼ 250–1200 K for a
given set of planetary intrinsic temperature, gravity, and
atmospheric compositions. For solar metallicity with g = 1,
10, and 100 m² s⁻¹ and Tin = 50, 100, and 200 K (top five
panels), planets with the equilibrium temperature of
Teq = 250–1200 K have nearly the same P–T profiles in deep
convective layers. These atmospheric models have tempera-
tures in the middle atmosphere (P ∼ 10–100 bar) between
~1000 and 1500 K, which is consistent with the criterion
argued in the previous section. $P-T$ profiles also tend to converge to the same adiabatic profile for high-metallicity models of $\text{[Fe/H]} = +1$ and $+2$, as well as a model with higher $\text{C/O} = 1.1$. At very high metallicities, the deep adiabatic profiles start to deviate from the same deep profile at a lower equilibrium temperature, for instance at $T_{\text{eq}} = 1000$ K for $\text{[Fe/H]} = 2$. This could be attributed to the middle atmosphere being hotter than for low-metallicity models, which acts to cause the RCB before the temperature structure converges to the radiative zero solution.

3.3. Semianalytical Model of the Deep Adiabat

We now derive a semianalytical fit to the universal thermal structure of deep atmospheres for $T_{\text{eq}} \sim 250$–1200 K. Since the deep adiabatic profile would be scaled by the
RCB, we infer the parameter dependence of $P \propto (\kappa_0 g)^{1/(1+\alpha)} T^{-4/3/(1+\alpha)} T^{-4/(1+\alpha)}$ from Equation (10). According to Figure 3, the opacity law approximately follows $\alpha \sim 0.5$ and $(4 - \beta)/(1 + \alpha) \sim 4$ in the temperature range of interest. In addition, the reference opacity $\kappa_0$ depends on the metallicity. We assume the metallicity dependence of $\kappa_0 \propto 10^{4[F_e/H]}$, where $c$ is a fitting constant.\footnote{This dependence is motivated by the analytic Rosseland mean opacity of Freedman et al. (2014), who also assumed the opacity to be proportional to $10^{4[F_e/H]}$. Freedman et al. (2014) considered different $c$ coefficients between high- and low-pressure limits and also considered a temperature dependence of $\kappa$ in the high-pressure limit. Here, we have assumed a constant value of $c$ for the sake of simplicity.} Inserting these values and determining the reference pressure to match numerical results, we achieve the following analytical form of the deep adiabatic $P-T$ profile, to which $P-T$ profiles converge at $T_{eq} \sim 250-1200$ K, as

$$P \approx 70 \times 10^{-0.4[F_e/H]} \text{bar} \left( \frac{T}{1000 \text{ K}} \right)^{4/3} (\frac{g}{10 \text{ m s}^{-2}})^{2/3} \left( \frac{T_{int}}{100 \text{ K}} \right)^{-8/3},$$

or equivalently

$$T \approx 1090 \times 10^{0.4[F_e/H]} \text{K} \left( \frac{P}{100 \text{ bar}} \right)^{1/4} (\frac{g}{10 \text{ m s}^{-2}})^{-1/6} \left( \frac{T_{int}}{100 \text{ K}} \right)^{2/3},$$

where we have inserted $c \approx 0.6$ to fit the metallicity dependence of the numerical results. Equation (15) indicates that the deep adiabat becomes hotter at higher intrinsic temperature and metallicity, and lower gravity. The black dotted lines in Figure 4 show the analytic deep adiabatic $P-T$ profile of Equation (15). As seen in the Figure, Equation (15) explains the common deep adiabatic profile for $T_{eq} \sim 250-1200$ K very well, including its dependence on surface gravity, intrinsic temperature, and atmospheric metallicity. Thus, for cool to warm exoplanets with $T_{eq} \sim 250-1200$ K, one can utilize Equation (15) to estimate the thermal structure of the deep atmosphere, such as for estimating the quenched abundance of disequilibrium chemical species.

4. Exploring the Relationship between NH$_3$ and Bulk Nitrogen Abundances

In the previous section we worked to derive a semianalytical theory of the temperature structure of the deep atmosphere as a step toward a semianalytical understanding of an atmosphere’s NH$_3$ abundance. We continue along this path here. In this section we explore the relationship between observable NH$_3$ and the bulk nitrogen abundance based on semianalytical arguments.

4.1. Semianalytical Predictions

We first estimate how the vertically quenched NH$_3$ abundance relates to the bulk nitrogen abundance based on the semianalytical argument established in previous sections. Since exoplanets with $T_{eq} \sim 250-1200$ K have nearly the same deep adiabatic profile (Section 3) and the NH$_3$/N$_2$ ratio is nearly constant along the deep adiabat (Section 2.1), the quenched NH$_3$ abundance would be nearly independent of the equilibrium temperature, as previously demonstrated in Fortney et al. (2020). For cool to warm exoplanets with $T_{eq} \sim 250-1200$ K, we solve Equation (4) with respect to $f_{N_{NH3}}$ and predict the quenched NH$_3$ abundance of

$$f_{N_{NH3}} \approx \sqrt{1 + 8 \kappa^{-1} - 1},$$

where

$$\kappa = P^{2/3} f_{N_{NH3}}^{-1} A e^{B/T} \approx 3.46 \times 10^{-0.8[F_e/H]} \left( \frac{f_N}{10^{-4}} \right)^{-1} (\frac{g}{10 \text{ m s}^{-2}})^{4/3} \left( \frac{T_{int}}{100 \text{ K}} \right)^{-16/3},$$

where we have inserted the semianalytical deep adiabat (Equation (15)) with $T = 2000$ K, where the temperature is chosen arbitrarily because the equilibrium NH$_3$ abundance is approximately constant along the deep adiabat. Qualitatively speaking, low intrinsic temperature, low atmospheric metallicity, and high surface gravity lead to colder deep atmospheres, which correspond to large $\kappa$. Thus, Equation (17) yields NH$_3$-rich deep atmospheres of $f_{N_{NH3}} = f_N$ in the limit of high $\kappa$ and vice versa for low $\kappa$. Meanwhile, substitution of Equation (15) into Equation (4) with $T = 2000$ K yields

$$f_{N_{NH3}} \approx 1 + 0.58 \times 10^{-0.8[F_e/H]} \left( \frac{f_{N_{NH3}}}{10^{-4}} \right)^{-1} (\frac{g}{10 \text{ m s}^{-2}})^{4/3} \left( \frac{T_{int}}{100 \text{ K}} \right)^{16/3}.$$

Equation (19) enables us to constrain the bulk nitrogen abundance for a given quenched NH$_3$ abundance, atmospheric metallicity, surface gravity, and intrinsic temperature. The former three values could be constrained by observations, while the intrinsic temperature could be constrained by either thermal evolution models (e.g., Guillot et al. 1996; Burrows et al. 1997; Guillot & Showman 2002; Baraffe et al. 2003; Fortney et al. 2007; Morley et al. 2017; Thorngren et al. 2016; Kubyshkina et al. 2020) and/or emission spectroscopy in the limit of very high $T_{int}$ (Morley et al. 2017).

Focusing on cool to warm exoplanets, we here predict the quenched NH$_3$ abundance and its fraction in relation to bulk nitrogen, $f_{N_{NH3}}/f_N$, over a wide range of planetary mass and age. We combine Equations (17) and (19) with the thermal evolutionary tracks of Fortney et al. (2007) to predict $g$ and $T_{int}$ for given planetary masses and ages, where we adopted the evolutionary track for the core mass of $10 M_{\oplus}$ and semimajor axis of 0.1 au.\footnote{Grids of the evolutionary tracks are available at https://www.ucolick.org/~jfornney/models.htm.} Figure 5 shows the predicted NH$_3$ abundance and its fraction in relation to the bulk nitrogen abundance. The quenched NH$_3$ abundance is in general higher for lower mass
and older planets, as these planets have cooler interiors and deep atmospheres that allow an NH$_3$-rich deep atmosphere. In many cases, the quenched NH$_3$ abundance exceeds what is a potentially detectable mixing ratio of $10^{-6}$ (see Fortney et al. 2020 for a discussion on the threshold), except for super-Jupiter-mass planets at very young ages of $\lesssim 0.01$ Myr. In terms of the NH$_3$ fraction in relation to the total nitrogen, for atmospheres of solar metallicity (left column of Figure 5), the quenched NH$_3$ abundance is almost identical to the bulk nitrogen abundance if the planet has a sub-Jupiter mass ($\lesssim 1 M_J$) and old ages ($\gtrsim 1$ Gyr). For more massive and younger planets, the quenched NH$_3$ abundance starts to deviate from the bulk nitrogen abundance. For example, the NH$_3$ abundance is approximately an order of magnitude lower than the bulk nitrogen abundance in Jupiter-mass planets at 0.1 Gyr. Thus, for massive and young planets, the observed NH$_3$ abundance would only constrain the lower limit of the bulk nitrogen abundance.

The discrepancy between the NH$_3$ and bulk nitrogen abundances becomes even larger if the planet has an atmosphere of higher metallicity. The right column of Figure 5 shows the quenched NH$_3$ abundance and $f_N/f_{\text{NH}_3}$...
for atmospheres of $10\times$ solar metallicity. Interestingly, the expected quenched NH$_3$ abundance is comparable to that expected for atmospheres of solar metallicity, as N$_2$ is favored for both higher N/H and hotter deep atmospheres due to higher metallicities. This can also be understood as follows. Assuming an atmosphere of high metallicity with $K \ll 8$ and $f_N \propto 10^{([\text{Fe}/\text{H}]_\odot)}$, Equation (17) approximately yields the NH$_3$ abundance of

$$f_{\text{NH}_3} \approx f_N \sqrt{\frac{K}{2}} \propto 10^{0.1(\text{Fe}/\text{H})_\odot}.$$  

(20)

Thus, the NH$_3$ abundance is insensitive to [Fe/H] for atmospheres of high metallicity. The weak metallicity dependence of $f_{\text{NH}_3}$ leads to the fraction of NH$_3$ in relation to the bulk nitrogen, i.e., $f_{\text{NH}_3}/f_N$, being lower in the atmospheres of higher metallicity for a given planetary mass and age. In other words, the fraction of observable nitrogen (i.e., NH$_3$) decreases with an increased atmospheric metallicity because of the conversion of NH$_3$ to N$_2$. Importantly then, it is necessary to assess the overall atmospheric metallicity from other spectral features to correctly infer the bulk nitrogen abundance from NH$_3$.

5. Discussion

5.1. Issues of the Strong Dependence on Metallicity

One of our main findings is the strong metallicity dependence of the ratio of the quenched NH$_3$ abundance to the bulk nitrogen abundance. Atmospheric metallicity could be constrained by the presence of chemical species sensitive to the metallicity, such as CO$_2$ (e.g., JWST Transiting Exoplanet Community Early Release Science Team et al. 2023; Alderson et al. 2023; Rustamkulov et al. 2023) and SO$_2$ (Tsai et al. 2022; Polman et al. 2023). Broad wavelength coverage and the unprecedented precision of JWST may also help to better constrain the metallicity. Thus, we anticipate that observers can use a planet’s observationally constrained metallicity for converting the retrieved NH$_3$ abundance to bulk nitrogen abundance through Equation (19). However, the inference would be further complicated if a planetary atmosphere has strongly nonsolar elemental ratios (e.g., C/O $\gg$ 1), as it may cause a distinct deep adiabatic profile from our semianalytical $P$–$T$ profile.

It is difficult to predict whether the quenched NH$_3$ abundance is comparable to the bulk nitrogen abundance before observations. There a few potential ways to coarsely aid such predictions, however. Interior structure models could set an upper limit on atmospheric metallicity assuming that the metals in the planetary interior are fully mixed with the atmosphere (Thorngren & Fortney 2019). The estimated upper limit may be used to predict the largest discrepancy between the quenched NH$_3$ and bulk nitrogen abundances. One might eventually also be able to utilize the relation between planetary mass and atmospheric metallicity suggested by the giant planets of the solar system (e.g., Kreidberg et al. 2014; Wakeford et al. 2017; Welbanks et al. 2019). However, exoplanets have not shown a clear mass–metallicity relation as of yet (Wakeford & Dalba 2020; Edwards et al. 2022; Guillot et al. 2022). We need better knowledge about the population-level metallicity trend of exoplanetary atmospheres to make a reliable prediction.

5.2. Caveats

We have assumed that the NH$_3$ abundance is vertically constant above the quench level. While several studies assumed the same approximation to model the transport-driven disequilibrium chemistry (e.g., Morley et al. 2017; Fortney et al. 2020; Mukherjee et al. 2022), the assumption is not always valid. For example, Moses et al. (2011) showed that NH$_3$ abundance gradually decreases with decreasing pressure above the quench level in the hot Jupiter HD189733b. Moses et al. (2021) also obtained similar NH$_3$ profiles in their pseudo-2D photochemical simulations for many planetary equilibrium temperatures. These vertically nonuniform profile could occur when the eddy diffusion timescale is not sufficiently short as compared to chemical interconversion timescale. We anticipate that the vertically constant abundance would be reasonable for warm to cool exoplanets where the chemical timescale quickly increases with altitude (see Tsai et al. 2018). However, one should always be encouraged to verify the assumption using a kinetic chemical model for a specific planet of interest.

We have assumed a nearly constant equilibrium abundance of NH$_3$ along the deep adiabat. While the assumption is reasonably valid for hydrogen-dominated substellar atmospheres, it would no longer be valid if an atmosphere had different a primary composition with different adiabatic index.

We have only considered the transport-induced disequilibrium chemistry, while other physical processes can also affect the NH$_3$ vertical profile. Molaverdikhani et al. (2019) provides an in-depth discussion about how the photochemistry and molecular diffusion could cause a discrepancy from a vertically constant profile. Hu (2021) showed that NH$_3$ tends to be depleted by photodissociation in temperate to cold exoplanets. We investigate the effect of photochemistry and how the observable NH$_3$ abundance relates to bulk nitrogen abundance in our Paper II.

5.3. Relevance for Cold and Directly Imaged Planets

Plants that lack strong radiative forcing from their parent star would in some ways be simpler to interpret, from an observational perspective. First, lacking external forcing, their interiors would cool off somewhat faster, into the NH$_3$-dominated chemical $T$–$P$ phase space. While their deep atmospheres would not share the radiative zero solution, they do have the real added benefit that their intrinsic temperature (the object’s effective temperature in this case) and the $T$–$P$ conditions of their deep atmosphere adiabat can be directly constrained by thermal infrared observations. Moreover, those isolated objects can avoid NH$_3$ depletion by photodissociation, which limits the observability of NH$_3$ for irradiated planets (Hu 2021). Nitrogen disequilibrium in the atmospheres of such isolated objects was recently modeled in Karalidi et al. (2021) and Mukherjee et al. (2022).

For the very coldest planets whether irradiated or not, one needs to further consider relevant condensation physics. In cold exoplanets where NH$_3$ clouds form, NH$_3$ must be depleted above the NH$_3$ cloud base, as in the giant planets of the solar system. The formation of H$_2$O clouds may also affect NH$_3$ abundances. Recent microwave observations of Jupiter by JUNO revealed that NH$_3$ is still partly depleted even below the NH$_3$ cloud base (Bolton et al. 2017; Li et al. 2017). Guillot et al. (2020a, 2020b) suggested that such NH$_3$ depletion could be explained by the formation of NH$_3$·H$_2$O condensate.
can also be depleted because of the dissolution into liquid H₂O clouds (Hu 2019). Thus, one needs to be cautious in interpreting the NH₃ abundances on very cool planets where NH₃ and/or H₂O clouds potentially form.

6. Summary

In this study, we have investigated how observable NH₃ abundances relate to bulk nitrogen abundances of exoplanetary atmospheres. We first identified that irradiated substellar atmospheres follow nearly the same deep adiabatic profile over a wide range of equilibrium temperatures ($T_{eq} \sim 250$–$1200\,K$). We have derived a semianalytical model of such a universal deep adiabat (Equation (15)) that readily explains the radiative–convective equilibrium model. Then, we established a semianalytical model that relates vertically quenched NH₃ abundances with the bulk nitrogen abundance of the atmosphere (Equation (19)). Based on the semianalytical model, we predict the relation between the quenched NH₃ and bulk nitrogen abundances as a function of planetary mass and age. We verify our semianalytical model using a photochemical kinetic model in Paper II. Our key findings are summarized as follows.

1. Irradiated giant planet atmospheres have nearly the same deep adiabatic profile for the equilibrium temperature of $T_{eq} \sim 250$–$1200\,K$ for a given set of planetary gravity and intrinsic temperature. This is caused by the fact that their atmospheric $P$–$T$ profiles tend to converge to the radiative zero solution that is independent of the upper boundary conditions before they meet the radiative–convective boundary (Section 3). Based on the series of radiative–convective equilibrium calculations, we have derived a semianalytical model of such universal deep adiabats applicable to planets with $T_{eq} \sim 250$–$1200\,K$ (Section 3.2, Equation (15) or (16)).

2. We have established a semianalytical model that relates the vertically quenched NH₃ abundance to the bulk nitrogen abundance (Equations (17) and (19)). Our model is applicable to warm irradiated giant exoplanets. We are able to readily assess discrepancies between the quenched NH₃ and bulk nitrogen abundances. This helps when attempting to infer the bulk nitrogen abundance from an observed NH₃ abundance.

3. At solar composition in a giant planet atmosphere, the vertically quenched NH₃ abundance nearly coincides with the bulk nitrogen abundance only when a planet has a sub-Jupiter mass ($\leq 1\,M_J$) and old age ($\geq 1\,Gyr$). For planets with super-Jupiter mass and/or age younger than 1 Gyr, in contrast, the quenched NH₃ abundance is considerably lower than the bulk nitrogen abundance, because the deep atmosphere is so hot that N₂ dominates over NH₃ (Section 4 and Figure 5).

4. As the atmospheric metallicity increases, while the predicted quenched NH₃ mixing ratio remains constant at a given mass and age, the ratio of NH₃ abundance to the bulk atmospheric nitrogen abundance decreases significantly. The issue of NH₃ only containing a fraction of the bulk nitrogen abundance then occurs across all giant planet phase space, for planets less massive than Jupiter and old ages. This “missing nitrogen” problem can be corrected with an assessment of the deep atmospheric $P$–$T$ profile (likely from structure or evolution models) and an overall assessment of atmospheric metallicity from other species, such C- and O-bearing molecules or alkali metals.

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Appendix

Physical Meaning of the $\phi$ Parameter

In this appendix, we elaborate on the physical meaning of $\phi$, which is introduced in Section 3 to quantify whether the $P$–$T$ profile converges to the radiative zero solution above the RCB pressure level. The radiative temperature gradient (Equation (5)) approaches zero in the limit of $P \rightarrow 0$ and increases with increasing pressure. However, the gradient does not increase indefinitely. It converges to a certain value controlled by the opacity law. Inserting the radiative zero solution (Equation (6) with $T_0 = 0$ and $P_0 = 0$) back into Equation (5), one can find an asymptotic gradient that the radiative gradient approaches:

$$\left(\frac{d \ln T}{d \ln P}\right)_{rad,\text{limit}} = \frac{1 + \alpha}{4 - \beta}. \quad (A1)$$

Thus, the definition of the $\phi$ parameter (Equation (12)) can be understood as the ratio of the adiabatic gradient $\nabla_{ad}$ to the above asymptotic radiative gradient:

$$\phi \equiv \frac{4 - \beta}{1 + \alpha} \nabla_{ad} = \frac{(d \ln T/d \ln P)_{ad}}{(d \ln T/d \ln P)_{rad,\text{limit}}}. \quad (A2)$$

If the asymptotic radiative gradient is much larger than the adiabatic gradient, i.e., $\phi \ll 1$, convection would quickly set in before the $P$–$T$ profile converges to the radiative zero solution with the asymptotic gradient. By contrast, $\phi > 1$ means that the radiative gradient never exceeds the adiabatic gradient even in the limit of deep atmospheres. Thus, convection does not occur for $\phi > 1$.

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