CHEMICAL EQUILIBRIUM ABUNDANCES IN BROWN DWARF AND EXTRASOLAR GIANT PLANET ATMOSPHERES

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ABSTRACT

We explore detailed chemical equilibrium abundance profiles for a variety of brown dwarf and extrasolar giant planet atmosphere models, focusing in particular on Gl 229B, and derive the systematics of the changes in the dominant reservoirs of the major elements with altitude and temperature. We assume an Anders & Grevesse solar composition of 27 chemical elements and track 330 gas-phase species, including the monatomic forms of the elements, as well as about 120 condensates. In our fiducial, limiting reference model, we do not assume that condensation sequesters elements at depth and present true chemical equilibrium calculations for the solar element mix. However, there is evidence in the atmosphere of Gliese 229B that it is depleted in heavy elements. To explore depletion and rainout, which are fundamentally nonequilibrium processes, we perform a series of rainout calculations in which refractory elements are withdrawn from the equilibrium in stoichiometric ratios via an ad hoc algorithm. Then we compare the true equilibrium results with the rainout results, with an eye to understanding the near-infrared spectrum of Gliese 229B, as well as the new “L dwarfs” with $T_{\text{eff}}$‘s above ~1500 K. We address the issue of the formation and composition of clouds in the cool atmospheres of substellar objects. We conclude that the opacity of clouds of low-temperature ($\leq 900$ K), small-radius condensables (specific chlorides and sulfides, not silicates), may in part be responsible for the steep spectrum of Gl 229B observed in the near-IR below 1 $\mu$m. We assemble a temperature sequence of chemical transitions in substellar atmospheres that may be used to anchor and define a sequence of spectral types for substellar objects with $T_{\text{eff}}$‘s from ~2200 to ~100 K.

Subject headings: stars: abundances — stars: low-mass, brown dwarfs

1. INTRODUCTION

After a decade of ambiguous detections, bona fide brown dwarfs and extrasolar giant planets (EGPs; Burrows et al. 1995) are now being discovered at an accelerating pace. Whether by radial velocity techniques (Mayor & Queloz 1995; Marcy & Butler 1996; Butler & Marcy 1996; Latham et al. 1989; Cochran et al. 1997), by direct detection in the field (Tinney, Delfosse, & Forveille 1997; Martin et al. 1997; Tinney et al. 1998 [DENIS]; Kirkpatrick, Beichman, & Skrutskie 1997; Kirkpatrick et al. 1998 [2MASS]), by direct detection in young stellar clusters (Zapatero-Osorio, Rebolo, & Martin 1997; Rebolo et al. 1996; Comerón et al. 1993), by direct detection around nearby stars (Nakajima et al. 1995; Oppenheimer et al. 1995, 1998 [Gl 229B]; Matthews et al. 1996), or from space (Terebey et al. 1998 [the near-IR camera and multiobject spectrometer]), the expanding census of objects beyond the solar system with masses between 0.5 and 80 $M_J$ is lending new urgency to theoretical efforts to understand their evolution, spectra, and compositions.² At the low temperatures ($100 \leq T \leq 2500$ K) achieved in the dense, high-gravity atmospheres of brown dwarfs and EGPs, chemical species not encountered in traditional stellar realms assume a new and central importance.

The molecular compositions of these exotic, low-ionization atmospheres can serve as diagnostics of temperature, mass, and elemental abundance and can help define a spectral sequence, just as the presence or absence of spectral features associated with various ionization states of dominant, or spectroscopically active, atoms and simple molecules does for M through O stars. However, the multiplicity of molecules that appear in their atmospheres lends an additional complexity to the study of substellar mass objects that is both helpfully diagnostic and confusing. Nowhere is the latter more apparent than in the appearance at low temperatures of refractory grains and clouds. These condensed species can contribute significant opacity and can alter an atmosphere’s temperature/pressure profile and its albedo. Grain and cloud droplet opacities depend on particle size and shape distribution, and these are intertwined with the meteorology (convection) in complex ways. Furthermore, condensed species probably rain out and deplete the upper atmosphere of heavy elements, thereby changing the composition and the observed spectrum. Hence, in brown dwarf and EGP atmospheres, abundance and temperature/pressure profiles, particle properties, spectra, and meteorology are inextricably linked.

One might naturally throw up one’s hands at the messiness of this problem were it not for two things: (1) there are chemical systematics that somewhat simplify the study of these atmospheres, and (2) further progress in understanding the edge of the main sequence, brown dwarfs, and EGPs hinges directly on its resolution. The goal of this paper is to explore and clarify the chemical condensation sequences, molecular abundance profiles, and molecular spectral diagnostics of brown dwarf and EGP atmospheres.

The formation of refractory silicate grains below 2500 K was already shown by Lunine et al. (1989) and Burrows, Hubbard, & Lunine (1989) to influence the evolution of late

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² $M_J$ is the mass of Jupiter and is equal to $9.55 \times 10^{-4} M_\odot$. 

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M dwarfs and young brown dwarfs through their Mie opacity. The blanketing effect they provide lowers the effective temperature ($T_{\text{eff}}$) and luminosity ($L$) of the main-sequence edge mass from about 2000 K and $10^{-4} L_\odot$ to about 1750 K and $6 \times 10^{-5} L_\odot$, an effect recently verified by Chabrier et al. (1998). In addition, grain opacity slightly delays the cooling of older brown dwarfs, imprinting a slight bump on their luminosity/age trajectories (see Fig. 7 of Burrows et al. 1997). The presence of grains in late M dwarf spectra was invoked to explain the weakening of the TiO bands and the shallowing of their troughs in the H$_2$O troughs in the near-IR (Tsuji et al. 1996; Jones & Tsuji 1997). Tsuji and collaborators concluded that titanium was being depleted into refractories, a conclusion with which we agree (see §3).

GI 229B (Nakajima et al. 1995; Oppenheimer et al. 1998) is a Rosetta stone for brown dwarf research. With a $T_{\text{eff}}$ of $\sim 950$ K, a luminosity below $10^{-5} L_\odot$, and spectra or photometry from the R band through 5 $\mu$m, GI 229B hints at or exemplifies all of the unique characteristics of the family (Marley et al. 1996; Allard et al. 1996): metal (Fe, Ti, V, Ca, Mg, Al, and Si) depletions, the dominance of H$_2$O vapor, the appearance of CH$_4$ and alkali metals, and the signatures of clouds. Clouds of low-temperature condensable species above the photosphere are a possible explanation, although not the only one, because of the drop below 1 $\mu$m in the Keck spectra between 0.83 and 1 $\mu$m (Oppenheimer et al. 1998). These clouds may not be made up of the classic silicate refractories formed at much higher temperatures, as these species have probably rained out (Marley et al. 1996). From simple Mie theory, their mean particle size must be small ($\sim 0.2 \mu$m) in order to influence the “optical” without much perturbing the near-IR. In addition, such a population of small droplets might help explain why GI 229B’s near-IR troughs at 1.8 and 3.0 $\mu$m are not as deep as theory would otherwise have predicted. Just as Tsuji and collaborators have shown that silicate grains at higher temperatures can shallow out the H$_2$O troughs, so too can species that condense at lower temperatures ($\lesssim 1000$ K?) explain the shallower than predicted GI 229B H$_2$O troughs. What those species might be can be illuminated by chemical abundance studies and is one of the subjects of this paper. Note that while a cloud grammage in these small-radius, low-temperature refractories of only $10^{-5}$ g cm$^{-2}$ might be adequate to explain the anomalies, this has yet to be demonstrated with full spectral synthesis calculations.

With GI 229B as a reference benchmark, we explore the composition profiles of low-temperature brown dwarfs and EGPs to derive the systematics of the changes in the dominant reservoirs of the major elements (Table 1). These equilibrium chemical sequences are predominantly a function of temperature and can help define a spectral sequence for substellar objects from the main-sequence edge near 2000 K to EGPs with $T_{\text{eff}}$s of a few hundred K. The appearance and disappearance of various molecules and refractories delineates an effective temperature sequence, and the new proposed “L” dwarf spectral classification (Kirkpatrick et al. 1998) may correspond to a subset of the compositional sequences we derive.

However, as was mentioned above, the full problem requires that the composition profiles, opacities, meteorology, temperature/pressure profiles, and spectra be handled self-consistently. At the present time, given the ambiguities in the grain/cloud properties and the paucity of optical constants, such a program is not realistic. In lieu of this, we employ the temperature/pressure profiles derived in Burrows et al. (1997). This allows us to define the overall trends while at the same time focusing on the essential chemistry. The models of Burrows et al. (1997) consistently incorporate the abundances of the major gas-phase species, with their opacities, but do not include the thermal effects of the low-temperature condensables. Burrows et al. (1997) do, however, assume that refractories are depleted from the atmospheres for $T_{\text{eff}}$’s less than $\sim 1300$ K. Such depletion is indeed indicated in the observed spectrum of GI 229B (Marley et al. 1996) and is discussed further in §4. However, we emphasize that fully consistent calculations of the true thermal profiles in the atmospheres of substellar objects have yet to be done and that our use of the Burrows et al. (1997) profiles is a stopgap measure.

The thermal profiles below the photospheres (at higher pressures) are always close to adiabatic, while the thermal profiles at lower depths are generally superadiabatic ($|dT/dr|$ small). Coolants in the atmosphere and non-gray effects generally lower the temperatures achieved at the lower pressures far below the Milne temperature ($\sim 0.81 T_{\text{eff}}$) to near $0.5 T_{\text{eff}}$. This has the consequence that species that would not otherwise condense in GI 229B-like atmospheres may in fact be present. The Burrows et al. (1997) models incorporate such cooling and non-Eddington effects. In §2 we describe the techniques and procedures we employ to perform the true equilibrium calculations with rainout. In §3 we present temperature profiles for representative model brown dwarf and EGP atmospheres. We also calculate various composition boundaries in temperature-pressure space between the major compounds of the abundant elements. In addition, element by element we describe the abundance profiles in equilibrium brown dwarf/EGP model atmospheres. These are benchmark, limiting, true equilibrium profiles against which to compare profiles for depleted atmospheres that may be more realistic but whose actual character, given the complications of meteorology, is as yet unknown. In §4 we explore the potential effects of rainout and depletions on the remaining mix of dominant chemical species. In §5 we summarize the list and order, as a function of temperature, of chemical indicators that can help to define a spectral classification scheme for substellar objects, and we review our general findings.

### Table 1

| Element | Abundance | Element | Abundance |
|---------|-----------|---------|-----------|
| H       | $9.10 \times 10^{-5}$ | Ni       | $1.61 \times 10^{-6}$ |
| He      | $8.87 \times 10^{-2}$ | Cr       | $4.40 \times 10^{-7}$ |
| O       | $7.76 \times 10^{-4}$ | P        | $3.39 \times 10^{-7}$ |
| C       | $3.29 \times 10^{-4}$ | Mn       | $3.11 \times 10^{-7}$ |
| Ne      | $1.12 \times 10^{-4}$ | Cl       | $1.71 \times 10^{-7}$ |
| N       | $1.02 \times 10^{-5}$ | K        | $1.23 \times 10^{-7}$ |
| Mg      | $3.49 \times 10^{-5}$ | Ti       | $7.83 \times 10^{-8}$ |
| Si      | $3.26 \times 10^{-5}$ | Co       | $7.34 \times 10^{-8}$ |
| Fe      | $2.94 \times 10^{-5}$ | F        | $2.75 \times 10^{-8}$ |
| S       | $1.68 \times 10^{-5}$ | V        | $9.56 \times 10^{-9}$ |
| Ar      | $3.29 \times 10^{-6}$ | Li       | $1.86 \times 10^{-9}$ |
| Al      | $2.77 \times 10^{-6}$ | Rb       | $2.31 \times 10^{-10}$ |
| Ca      | $1.99 \times 10^{-6}$ | Cs       | $1.21 \times 10^{-11}$ |
| Na      | $1.87 \times 10^{-6}$ |          |           |

* The elements are given as fractions by number in order of decreasing abundance.
2. TECHNIQUES, ALGORITHMS, AND PROCEDURES

Using the brown dwarf and giant planet model atmospheres of Burrows et al. (1997) and assuming an Anders & Grevesse (1989) solar composition of the 27 chemical elements H, He, Li, C, N, O, F, Ne, Na, Mg, Al, Si, P, S, Cl, Ar, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Rb and Cs, we calculate the abundances of each of about 330 gas-phase species, including the monatomic forms of the elements, and of about 120 specified condensates. These calculations are performed at each of about 2000 temperature-pressure points for every atmosphere model.

Table 1 lists the abundances by number for the 27 elements used in these calculations. With the exception of lithium, rubidium, and cesium, the list covers nearly all the most abundant elements anticipated to be in brown dwarf atmospheres. Lithium is added because it is an important brown dwarf indicator (Rebolo, Martin, & Magazzù 1992). Rubidium and cesium are added because they have recently been detected in cool objects (Oppenheimer et al. 1998; Tinney et al. 1998). Their very low excitation and ionization potentials make them good temperature indicators in a range where many other elements are associated into molecules or have condensed out.

The same methods were used as in Sharp & Huebner (1990), but the improved version of the original computer code SOLGASMIX (Besmann 1977) used in that paper was further improved in the current work by including more species, incorporating a number of error traps, and adding features to make the code more user friendly. Using the multidimensional Newton-Raphson method of White, Johnson, & Dantzig (1958), the equilibrium abundances of gas-phase and condensed-phase species at a given temperature, pressure, and elemental composition were obtained by minimizing the total free energy of the system. After subtracting the constraint equation in the manner of Lagrange’s method of undetermined multipliers and linearizing, SOLGASMIX uses Gaussian elimination with pivoting to iteratively solve the resulting matrix equations. The free energy of each species at a particular temperature is obtained by evaluating a polynomial of the form

$$
\Delta G_{\phi i}(T) = \frac{a}{T} + b + cT + dT^2 + eT^3,
$$

where $a$, $b$, $c$, $d$, and $e$ are fitted coefficients and $\Delta G_{\phi i}(T)$ is the Gibbs free energy of formation at temperature $T$ of species $i$ in phase $\phi$, relative to its constituent atoms in their monatomic neutral gaseous state. For instance, for $H_2S$ the reference states of the elements are monatomic hydrogen and sulfur in the gas phase, whose energies of formation are zero by definition. If the species being considered is in the gas phase and is monatomic, all the coefficients on the right side of equation (1) are zero.

In the original work of Sharp & Huebner (1990), the total free energy of the system was expressed quite generally in terms of the gas (g) phase, several liquid or solid solutions (each containing at least two species), and distinct condensed (c) phases of invariant stoichiometry (each containing a single species). In our current work, because of the large number of species considered, we decided to simplify the calculations and omitted solutions such as the solid solution of melilitite ($Ca_2Al_2SiO_7$ with $Ca_2MgSi_2O_7$). Thus, given a value of $\Delta G_{\phi i}(T)$ from equation (1) for each chemical species, the elemental composition, and initial trial values of the species abundances, the total equilibrium free energy of the system is found by minimizing

$$
\frac{G(T)}{RT} = \frac{m}{i=1} \left\{ n_{\phi i} \left[ \frac{\Delta G_{\phi i}(T)}{RT} + \ln P + \ln \left( \frac{n_{\phi i}}{N} \right) \right] \right\}_{\phi=1} + \frac{1}{RT} \sum_{\phi=2}^{s+1} \left[ n_{\phi i} \Delta G_{\phi i}(T) \right]_{i=1},
$$

where $R$ is the gas constant, $P$ is the total pressure in atmospheres, and $N$ is the total number of moles in the gas phase. The first sum is over $m$ species in the gas phase with $\phi = 1$, the second sum is over $s$ condensed phases (numbered 2 to $s + 1$), and $n_{\phi i}$ is the number of moles of species $i$ in phase $\phi$. Each condensed phase is in fact only a single species, so $i = 1$ in the second sum, since we need to distinguish between, for example, $H_2O(g)$ and $H_2O(liquid)$, which are considered to be separate species. The subsidiary mass balance relations are satisfied for each element $j$ of the total number of elements, $k$, as follows:

$$
\sum_{i=1}^{m} \left[ \nu_{\phi i} n_{\phi i} \right]_{i=1} + \sum_{\phi=2}^{s+1} \left[ \nu_{\phi i} n_{\phi i} \right]_{i=1} = b_j \text{ for } j = 1 \rightarrow k,
$$

where $\nu_{\phi i}$ is the stoichiometric coefficient of element $j$ in species $i$ in phase $\phi$ and $b_j$ is the number of gram atoms of element $j$. As in equation (2), the first sum is over the gas-phase species ($\phi = 1$), and the second sum is over all the single-component ($i = 1$) condensates.

Most of the thermodynamic data were obtained from the JANAF tables (Chase 1982; Chase et al. 1985). Data on no condensates not available in these tables were obtained from Turkdogan (1980), and data on the two condensates NaAlSi$_2$O$_8$ (high albite) and KAlSi$_3$O$_8$ (high sanidine) were obtained from Robie & Waldbaum (1968). Tsuji (1973) was the source of data for the gas-phase molecules CaH, CrH, MnH, NiH, MnO, NiO, MnS, TiS, TiN, SiH$_2$, and SiH$_3$, together with some carbides of little importance in the brown dwarf context. Our database currently holds information on 1662 species, of which about 450 are followed in these calculations. For those species for which the JANAF tables were used, the coefficients in equation (1) were obtained from a database generated in Sharp & Huebner (1993) in which the free energies were renormalized relative to the monatomic gaseous phase of each element rather than relative to standard reference states. A polynomial with up to five coefficients, as in equation (1), was fitted over the tabulated temperature range of each species. Using the redefined free energies has the advantage of removing any discontinuities associated with phase changes in the reference states, permitting polynomial fits to be made over large temperature ranges.

In Sharp & Huebner (1990), the only alkali elements considered were sodium and potassium, together with their most important compounds. In this work, we include all the other alkali elements except francium, together with their most important compounds, in particular their chlorides and fluorides, in both gas and condensed phases. With the exception of rubidium, all the data were obtained from the JANAF tables. As no useful data on rubidium and its compounds are available in the JANAF tables, including in the more recent compilations in Chase et al. (1985), we used Barin (1995).

The JANAF tables are deficient in a number of important volatile condensates, the most important being $H_2O(ice)$.
prescription for water from Eisenberg & Kauzmann (1969) was modified and incorporated into our code. A second important volatile condensate is NH$_3$(ice). The pure liquid phase of NH$_3$, together with a number of its hydrated liquid phases, were not considered. The data for NH$_3$ were obtained from the CRC Handbook (Weast & Astle 1980) in the form of vapor-pressure coefficients. Another important volatile condensate is ammonium hydrogen sulfide, NH$_4$SH, which is believed to be an important component in the Jovian atmosphere (Lewis 1969). As with NH$_3$(ice), we obtained the data for NH$_4$SH from the CRC Handbook in the form of vapor-pressure coefficients. However, unlike either NH$_3$ or H$_2$O, which on vaporization remain the same compound, NH$_4$SH decomposes into two gaseous components, NH$_3$ and H$_2$S. In addition, we added NH$_4$Cl, which decomposes into NH$_3$ and HCl, but this species proves to be unimportant at the temperatures and pressures encountered in giant planet and brown dwarf atmospheres. Except for the data originating from Tsuji (1973) and our newly added data on the condensed phases of H$_2$O, NH$_3$, NH$_4$SH, and NH$_4$Cl, which were expressed in different forms, all data were converted to the same form as equation (1) before the evaluation of equations (2) and (3). Furthermore, we replaced the polynomial fit for the gaseous species CO found in the JANAF tables with a polynomial fit based on its spectroscopic constants, as the spectroscopic data are very well known for this molecule (Sharp 1985).

We assume that the gas is ideal, i.e., that the activity of each species is the same as the partial pressure in atmospheres and, with the exception of liquid H$_2$O, only solid condensates are included in the calculations. We consider the neglect of the liquid phases to be quite reasonable, as the difference between the free energies of formation of the liquid and solid phase of a species is generally much smaller than the difference between the free energies of one of the condensed phases and the gas phase. For example, for iron in the range 1000–2000 K, the change in the free energy when converting the vapor into the liquid is at least 5 orders of magnitude larger than the corresponding change when converting the liquid to the solid. In the case of TiO, the ratio of the change in the free energy between vapor and liquid to between liquid and solid is much smaller but is still at least 1 order of magnitude in the same range (although in detailed calculations other condensed oxides form). Additionally, the inclusion of ionization slows down the calculations substantially in any temperature region that involves both marginal ionization and condensation, as is the case in this work, and since ionized species play a negligible role at the lower temperatures of substellar atmospheres, we omit them.

The main object of this work is to derive the abundance profiles for models of the atmospheres of cool brown dwarfs and giant planets, given their temperature-pressure profiles, both ignoring rainout to create a limiting, true equilibrium reference and including rainout with an ad hoc prescription, with a particular focus on the brown dwarf Gl 229B (Nakajima et al. 1995). Since we start with temperature-pressure profiles with specified gravities and effective temperatures from Burrows et al. (1997), to obtain such profiles for given ages and masses we interpolate using the evolutionary calculations from that work. Given a profile corresponding to the required model, we calculate the abundances by minimizing the free energy of the system. Starting at the high-temperature end of the profile, the code uses approximate trial values based on the element abundances to start the calculations. On convergence, the abundances of selected species are written to a file for later graphical treatment. These abundances are then used as trial values for the next calculation 1 K lower in temperature, and at selected temperature intervals, typically 100 K, additional data are printed out. This process is repeated for progressively lower temperatures and pressures in the atmosphere until the end of the data file is reached. At the high-temperature end, convergence is usually rapid, since the gas consists of atomic and simple molecular species, and few, if any, condensates. At progressively lower temperatures, as more species condense out and the chemistry becomes more complicated, convergence is slower and more "delicate." If the starting values before each iteration are too far away from the solution, there is a risk of nonconvergence. It is for this reason that the calculations are always started at the high-temperature end of a profile.

However, even with the above method convergence problems can arise. It is found that between 1100 and 1200 K for pressures less than about 0.1 atmospheres the program may fail to converge. For higher pressures the code generally operates successfully until temperatures below 600 K are reached. In the first case, nonconvergence is often associated with the refractory condensate Ca$_2$MgSi$_2$O$_7$, and in the second case it is often associated with the less refractory (and very low abundance) condensate LiAlO$_2$. In both cases, these condensates appear in true chemical equilibrium at higher temperatures, only to disappear into other species before the problems are encountered. On removal of these and many other similar species, such as Al$_2$O$_3$, which is present only above about 1800 K in most models and disappears into other aluminum-bearing species at lower temperatures, the problems are often solved. These problems are caused by a too-rapid change in abundance associated with condensation or a phase change. Unfortunately, it is often not possible without doing the calculations to know ab initio which species are likely to be unimportant and can be neglected. Fortunately, removing gas-phase species of negligible abundance can speed up the calculations. After removing redundant species, iterations can be restarted.

If it is still not possible to obtain successful convergence after removing one or more redundant species, condensates that are present but can be considered inert can be removed from the calculations, which can be restarted with trial values from a previous dump file. In the process of removing a condensate from the calculations, the corresponding abundances of each element tied up in the species are removed. For example, if the condensate spinel, MgAl$_2$O$_4$, is present and is to be removed from the calculations, then given $N$(Mg) and $n$(MgAl$_2$O$_4$), which are, respectively, the number of gram atoms of Mg in all forms in the calculations and the number of moles of spinel, the corrected total abundance of Mg is $N$(Mg)–$n$(MgAl$_2$O$_4$), that of Al is $N$(Al)–2$n$(MgAl$_2$O$_4$), and that of O is $N$(O)–4$n$(MgAl$_2$O$_4$), from which the relative element abundances can be obtained.

However, it was often found that at a lower temperature, removing a condensate changed the chemistry. A very good example is iron, which in our equilibrium calculations normally forms the solid metal at high temperatures. If iron is retained in the calculations, at 718 K iron metal reacts with H$_2$S to form FeS, which is then the main compound of sulfur and substantially depletes sulfur from the gas phase.
If iron is removed from the calculations when it initially condenses (rains out), as is likely, much more sulfur remains in the gas phase, which is then available to form the volatile condensate, \( \text{NH}_4\text{SH} \), at lower temperatures. Hence, the presence of \( \text{NH}_4\text{SH} \) clouds and \( \text{H}_2\text{S} \) inferred in Jupiter’s atmosphere may be an indirect consequence of the rainout of iron metal to deeper regions.

3. COMPOSITION BOUNDARIES AND ABUNDANCE PROFILES

Figure 1 depicts temperature-pressure profiles for 5, 10, 20, and 40 \( M_J \) atmosphere models from Burrows et al. (1997), for ages of 0.1, 1.0, and 10.0 Gyr. Only the 5 and 10 \( M_J \) models are given at 0.1 Gyr. The dots identify the positions of the photospheres. This set of profiles represents the general trends in brown dwarfs and EGPs. Note that the concept of a photosphere is ambiguous, since the opacities are stiff functions of wavelength. Radiation at different wavelengths decouples from a variety of disparate pressure levels. By photosphere we mean here the level at which the temperature equals the effective temperature, defined via Stefan’s law. This approach provides us with a sensible average position but should not be overinterpreted.

Higher mass models generally reside at higher entropies, i.e., at a given temperature level the gas is at lower pressures. However, as Figure 1 demonstrates, cooling in the radiative zones above the photosphere at lower temperatures can result in a reversal of this behavior. Furthermore, for a given mass the older a substellar object, the lower the effective temperature, and the higher the photospheric pressure. In addition, for a given age the higher the mass, the higher the photospheric pressure. However, and importantly, although the effective temperature is a strong function of age and mass, the corresponding pressure at the photosphere is only weakly dependent on these quantities and varies within about half a dex of 1 atmosphere. Consequently, the abundances of species at the photosphere of a brown dwarf or EGP are governed almost entirely by the temperature. This is an important conceptual simplification.

Figures 2–4 depict the regions of transition from one chemical species to another in temperature-pressure space for a variety of important constituents of equilibrium substellar atmospheres. Anders & Grevesse (1989) solar abundances are assumed (Table 1). Only a subset of the calculated and interesting composition boundaries are depicted. Nevertheless, these figures summarize some of the diagnostic chemical sequences and transitions encountered in theoretical substellar atmospheres and the reservoirs of the major elements. Superposed on these plots are atmospheric profiles of 5, 10, 20, and 40 \( M_J \) models at 1 Gyr from
Fig. 2.—Condensation or chemical transformation boundaries for major species in temperature-pressure space. Superposed on the figure are atmospheric profiles, shown as solid curves, from Fig. 1 for a number of giant planet and brown dwarf models with an age of 1 Gyr. The models of Burrows et al. (1997) were employed. Included are a present-day Jupiter profile and 1 Gyr adiabats for M dwarf models with masses of 0.08, 0.09, and 0.115 $M_\odot$ ($1 M_\odot = 1047 M_J$). The black filled circles indicate the location of the photosphere. The region to the left of a circle spans the atmosphere above the photosphere. Note that for the red dwarfs we have extrapolated temperatures somewhat above the height of the photosphere, assuming an adiabatic law. In reality, this is in the radiative regime, and the profile pressures at a given temperature should be lower, as are those for the substellar models. Chemical boundary curves indicate when a condensed species forms or when a ratio of abundances is unity. The condensates are written in braces to distinguish them from gas-phase species. A condensate forms on and immediately to the left of each indicated curve and in some cases may disappear into another phase at lower temperatures, but is not shown. The curve labeled by a ratio, such as $\text{CH}_4/\text{CO}$, indicates where these two species have equal abundances, with the ratio greater than unity to the left. See text for further explanations.

Figure 1. Also shown for comparison on Figures 2–4 are adiabats above and below the photospheres for more massive M dwarf models of Burrows et al. (1993) at 0.08, 0.09, and 0.115 $M_\odot$ and 1 Gyr. As is demonstrated in Figure 1 for a broad range of objects and ages, the narrow band around 1 atmosphere is relevant when looking at the compositions near the photosphere. Furthermore, the near verticality of the transition curves confirms that composition is most closely linked with temperature.

Figures 5–14 depict theoretical chemical equilibrium composition profiles versus temperature for Gl 229B–like models (see Marley et al. 1996; Allard et al. 1996) as a function of $T_{\text{eff}}$ and gravity. For these profiles, no algorithm for heavy elements depletion or rainout has been employed. (A discussion of rainout is postponed to § 4.) These results are meant to be true chemical equilibrium benchmarks that represent limits against which depleted atmospheres with clouds, fundamentally nonequilibrium animals, can be compared and contrasted. To avoid confusion, only a subset of the major compounds are included in the plots. Implicit are the corresponding pressures from the atmosphere models of Burrows et al. (1997). The odd-numbered figures depict the gravity dependence for $T_{\text{eff}} = 950$ K, and the even-numbered figures depict the $T_{\text{eff}}$ dependence for a gravity of 1000 m s$^{-2}$. The figures are approximately in order of decreasing elemental abundance. Hence, Figures 5–14 and the curves on those figures follow the rough sequence: O, C, N, Mg, Si, Fe, S, Al, Ca, Na, P, K, Ti, V, Li, Rb, and Cs. We will describe each of these figures in turn, but even though they depict the range of theoretical limiting equilibrium abundance profiles for Gl 229B models, they demonstrate that the sequence of chemical reservoirs of the major elements as a function of temperature varies little with model. This is a consequence of the weak pressure and gravity dependence of the equilibrium abundances and the steepness of the transition boundary curves in Figures 2–4 relative to the model temperature-pressure profiles. Hence, the sequence of dominant chemical species for an element along the entire brown dwarf/EGP continuum and the transition temperatures from one species to another are very approximately universal. Note that the proximity of a species to the photosphere and its importance in the emergent spec-
trum does vary importantly as a function of age and mass or gravity and $T_{\text{eff}}$. Tables 2a and 2b provide useful lists of the major chemical species of each of the most abundant elements found in the equilibrium atmospheres of substellar objects if heavy-element depletion is ignored.

### TABLE 2a

| Element | Major Chemical Species |
|---------|------------------------|
| H ...... | H$_2$                  |
| He ...... | He                     |
| Li ...... | Li, LiCl, LiF, LiAlO$_2$* |
| C ...... | CO, CH$_4$             |
| N ...... | N$_2$, NH$_3$, NH$_3$* |
| O ...... | H$_2$O, CO, H$_2$O*    |
| F ...... | HF, LiF, NaF, KF, RbF, CsF, Na$_3$AlF$_6$* | LiF* |
| Ne ...... | Ne                     |
| Na ...... | Na, NaCl, NaCl*, NaAlSi$_3$O$_8$*, Na$_3$AlF$_6$* |
| Mg ...... | Mg, MgH, MgSiO$_3$*, Mg$_2$SiO$_4$*, MgAl$_2$O$_4$*, CaMgSi$_2$O$_6$*, Ca$_2$MgSi$_2$O$_7$*, Mg$_3$P$_2$O$_8$*, MgTi$_2$O$_5$* |
| Al ...... | Al, AlH, AlOH, Al$_2$O, Al$_2$O$_3$, MgAl$_2$O$_4$, Ca$_2$Al$_2$Si$_2$O$_8$, NaAlSi$_3$O$_8$, KAlSi$_3$O$_8$, Na$_3$AlF$_6$*, LiAlO$_2$* |
| Si ...... | SiO, MgSiO$_3$, Mg$_2$SiO$_4$, Ca$_2$Al$_2$Si$_2$O$_8$, Ca$_2$Si$_2$O$_5$, CaMgSi$_2$O$_6$, Ca$_2$MgSi$_2$O$_7$, NaAlSi$_3$O$_8$, KAlSi$_3$O$_8$, MnSiO$_3$* |
| P ...... | P$_2$O$_5$, PN, Mg$_3$P$_2$O$_8$* |
| S ...... | H$_2$S SH SiS MnS*, FeS*, NH$_3$, SH* |

* The species marked by asterisks are condensates, and the gas-phase species are given first. Otherwise, the order of the species is generally unimportant, although some condensates of less importance are given last.

3.1. Oxygen, Carbon, Nitrogen, Iron, Chromium, Sulfur, Titanium, and Vanadium

As Figures 5 and 6 demonstrate, the major reservoir for oxygen in substellar atmospheres is gaseous H$_2$O. The only...
significant competitor for abundant oxygen is CO, but CO is converted into CH₄ between temperatures of 1100 and 2000 K. Only at temperatures below ~300 K does H₂O condense: as a liquid above 273.15 K, otherwise as ice. As is well known (Fegley & Lodders 1996), Jupiter has condensed H₂O below its photosphere. As is not so well known and as is demonstrated in Figure 2, at 1 Gyr a 10 M_J object may have condensed H₂O in its atmosphere. In fact, as Figure 2 suggests, all but the youngest EGPs and those not at elevated temperatures due to proximity to a primary (e.g., 51

| Table 2b |
| --- |
| **CONTINUATION OF THE LISTING OF THE MOST IMPORTANT SPECIES ASSOCIATED WITH EACH ELEMENT**

| Element | Major Chemical Species |
| --- | --- |
| Cl | HCl, LiCl, NaCl, KCl, RbCl, KCl, AlCl, MgCl, CaCl, NaCl*, RbCl*, CsCl* |
| Ar | Ar |
| K | K, KCl, KAlSi₃O₈* |
| Ca | Ca, CaH, CaOH, Ca₂Al₂SiO₇*, Ca₂SiO₄*, Ca₃MgSi₂O₇*, Ca₃MgSi₂O₆* |
| Ti | Ti, TiO, Ti₂O₃*, Ti₂O₅*, Ti₂O₇*, MgTi₂O₅*, CaTi₂O₄* |
| V | V, VO, VO*, V₂O₅*, VN* |
| Cr | Cr, CrH, Cr*, Cr₂O₃* |
| Mn | Mn, MnH, MnS*, MnSiO₃* |
| Fe | Fe, FeH, Fe*, FeS* |
| Co | Co, Co* |
| Ni | Ni, NiH, Ni* |
| Rb | Rb, RbCl, RbF, RbCl* |
| Cs | Cs, CsCl, CsF, CsCl* |

* Species marked by asterisks are condensates, and the gas-phase species are given first. Otherwise, the order of the species is generally unimportant, although some condensates of less importance are given last.
Fig. 5.—Plots of the abundance profiles for several of the most abundant chemical species, \( \text{H}_2\text{O}, \text{CH}_4, \text{CO}, \text{NH}_3, \) and \( \text{N}_2 \), for brown dwarf models with an effective temperature of 950 K but with the gravities of 300, 1000, and 3000 m s\(^{-2}\). These are true equilibrium results, in which no ad hoc assumption for heavy-element depletion is assumed, and serve as reference benchmarks against which to compare rainout calculations. The temperature of 950 K is chosen because it is near that of the brown dwarf Gl 229B. Temperature-pressure profiles for the underlying dwarf models are implicit and are from Burrows et al. (1997). Each curve is a plot of \( \log_{10} \) of the number fraction of a particular species out of all species, including any condensates, as a function of level temperature. An increase in temperature generally corresponds to an increase in pressure and depth. Each set of curves is labeled by the chemical species \( \text{CO}, \text{and} \), and the numbers 300, 1000, and 3000 correspond to each model’s gravity. For example, the set of curves labeled \( \text{CO} \) and 300, \( \text{H}_2\text{O}, \text{CH}_4, \text{N}_2, \) and \( \text{N}_2 \), and 1000, and 3000 show the profiles for \( \text{CO} \) for the three models. The two most abundant species, \( \text{He} \), would be above the top of the figure and are not plotted. For clarity, the profile for \( \text{CO} \) is shown as a dashed curve, and the label of 1000 is omitted from the plots of \( \text{He} \). The vertical line at 950 K shows the position of the photosphere. The condensates are identified here and in the following figures by being enclosed in braces.

Pegasi b, τ Bootis b) should have water clouds (Burrows et al. 1997). This may importantly affect their albedos and reflected spectra (Marley et al. 1998).

As is alluded to above and shown in Figures 5 and 6, the major reservoirs of carbon are \( \text{CO} \) and \( \text{CH}_4 \). The reaction

\[ \text{CO} + 3\text{H}_2 \rightarrow \text{H}_2\text{O} + \text{CH}_4 \]

and Le Chatelier’s principle indicate that for a given temperature \( \text{CO} \) is favored at low pressures and gravities. \( \text{CO} \) is also favored at high temperatures and for models with high \( T_{\text{eff}} \)'s. From Figures 5 and 6 it is expected that in Gl 229B \( \text{CO} \) will convert into \( \text{CH}_4 \), between temperatures of 1300 and 1800 K, depending on \( T_{\text{eff}} \) and gravity. To put equilibrium \( \text{CO} \) closer to the photosphere in Gl 229B, high \( T_{\text{eff}} \)'s and lower gravities are preferred. This makes the interpretation of the detection in Gl 229B of CO at 4.67 μm (Noll, Geballe, & Marley 1997) problematic, as \( \text{CO} \) is not expected in great abundance near the photosphere for \( T_{\text{eff}} \)'s near 950 K. This may imply that the higher \( \text{CO} \) abundances at the higher temperatures at depth are being advected out of equilibrium into the cooler regions of the photosphere, and the kinetics of the reaction might have to be considered. Be that as it may, \( \text{CH}_4 \) should be the major atmospheric reservoir of carbon for all but the youngest and hottest (\( T_{\text{eff}} \geq 1300 \) K) brown dwarfs and EGPs.

Nitrogen is in the form of \( \text{N}_2 \) for temperatures above 800 K but is converted into \( \text{NH}_3 \), between 600 and 800 K (Figs. 5 and 6). In Figure 2 we see that the \( \text{NH}_3/\text{N}_2 \) boundary coincides with the typical atmospheric pressure level (\( \sim 1 \) atmosphere) near the Fe → FeS transition. This flags the \( \sim 700 \) K level in a substellar object as another interesting transition for equilibrium atmospheres. From Figures 2, 7, and 8, we see that for iron the first condensate to form (at \( T_{\text{eff}} \geq 2200 \) K) is the metal, followed at much lower temperatures by the solid sulfide, FeS. FeH should also be present in abundance but is not in our calculations (Fegley & Lodders 1996). The major equilibrium reservoir for sulfur above 718 K is gaseous \( \text{H}_2\text{S} \). As Guillot et al. (1997) have shown, at lower temperatures \( \text{ZnS} \) forms. Note that although \( \text{Na}_2\text{S(c)} \) and \( \text{K}_2\text{S(c)} \) are in our equilibrium calcu-
lations, they never appear in great abundance (see § 3.2). In 
equilibrium without depletion, FeS always forms at 718 K 
because of the reaction of iron metal with H$_2$S. The 
pressure-independence of this reaction follows from simple 
mass action arguments applied to the reaction 

$$\text{Fe(c)} + \text{H}_2\text{S} \rightarrow \text{H}_2 + \text{FeS(c)}$$

and assumes that metallic iron is available in the equilibria 
to react with the buffer gas H$_2$S (but see § 4.).

At $\sim 2000$ K chromium exists predominantly in the form 
of gaseous CrH but is converted in large part into the metal 
nearing 1560 K ($\pm 15$ K, depending on the pressure [gravity]). 
Near and below 1500 K the dominant compound of chromium 
is solid Cr$_2$O$_3$. At 1500 K, CrH exists but involves 
only a few percent by number of the available element. 
Hence the disappearance of CrH(g) occurs around 1400–
1500 K.

At temperatures below $\sim 200$ K, NH$_3$ condenses into 
clouds. Such clouds are seen in Jupiter and Saturn, but as is 
implied in Figure 2, they may be present in the lowest mass 
EGPs with $T_{\text{eff}}$'s below $\sim 300$ K.

The ratio [Ti$_\text{gaseous}$]/TiO in Figure 2 indicates where the 
abundance of one or more titanium condensates is equal to 
those of the gas-phase TiO, as the first titanium condensate 
to form with decreasing temperature depends on the press-
ure. Note that for pressures corresponding to red dwarf 
atmospheres, perovskite, CaTiO$_3$, is the first titanium con-
densate to appear, whereas for substellar objects this is 
replaced by Ti$_3$O$_5$. As is indicated in Figure 2, there is a 
range of pressures where both form. At lower temperatures 
in undepleted equilibrium, the first titanium condensate 
to form would change into other compounds (Ti$_3$O$_5$, Ti$_2$O$_3$, 
Ti$_4$O$_7$, and MgTi$_2$O$_5$). Equilibrium abundance profles for 
these species for various models of Gl 229B are shown in 
Figures 11 and 12. The Ti transition sequence starting from 
$\sim 2400$ to $\sim 2100$ K is quite general for substellar objects 
with $T_{\text{eff}}$'s below $\sim 2000$ K. For $T_{\text{eff}}$'s above $\sim 2000$ K, per-

ovskite replaces Ti$_3$O$_5$ as the first condensed species into 
which TiO is transformed, and titanium is depleted.

The main gas-phase species of vanadium and the first 
condensate to appear are both VO, and the curve on Figure 
2 labeled by [VO]/VO shows where these two phases have 
equal abun-
dance. The condensed phase of VO first appears 
off the lef of the curve. Abundance profles for V com-
ponds for a range of equilibrium Gl 229B models are 
depicted in Figures 11 and 12. VO is depleted into solid VO, 
then into V$_3$O$_5$, but its depletion sequence starts near 1800 
K, at lower temperatures than for titanium. Hence, we 
expect that in brown dwarfs and EGPs (and presumably in 
M dwarfs), the abundance of gaseous VO will decrease 
(near $T_{\text{eff}}$'s of 2100–2400 K), then (near 1800 K) the abun-
dance of gaseous VO will decrease because of its depletion 
into solid VO. This depletion order should manifest itself in 
the spectral sequence of cool objects.

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**Fig. 6**—Same as Fig. 5 for the same five species but for five models with the efffective temperatures of 800, 850, 900, 950, and 1000 K for a fixed gravity of 
1000 m s$^{-2}$. Each set of curves is labeled by the species, with 800 and 1000 indicating the coolest and hottest models in the sequence, with the other models 
lying in between. The five photospheric temperatures are shown as short tick marks at the bottom of the figure.
3.2. Silicates, Phosphorus, Sodium, and Potassium

In Figure 3, the condensates MgSiO$_3$ (enstatite), Mg$_2$SiO$_4$ (fosterite), and MgAl$_2$O$_4$ (spinel) are shown and are the most important condensates of magnesium, silicon, and aluminum. In the undepleted equilibrium calculations, these condensates are found to persist to lower temperatures and, unlike those of titanium and vanadium, do not change into other compounds. Figures 7 and 8 depict the equilibrium abundance profiles of enstatite and fosterite for the range of Gl 229B models. Figures 9 and 10 show the same for the more refractory silicates. Also included in Figures 3, 9, and 10 are the two main high-temperature condensates of sodium and potassium, NaAlSi$_3$O$_8$ (high albite) and KAlSi$_3$O$_8$ (high sanidine) that would exist in true equilibrium atmospheres if the rainout of aluminum and silicon compounds at even higher temperatures is ignored.

As is indicated in Figures 9 and 10, the most refractory compounds are the calcium aluminum silicates (e.g., akermanite), followed by the calcium magnesium (iron) silicates. These condensates can be found from temperatures of ~2300 down to ~1800 K. Above ~2000 K, a major reservoir of Si is gaseous SiO (not shown in the figures), which is progressively sacrificed to form the refractories as the temperature decreases. Below 1800 K, among the classical refractories only spinel, enstatite, fosterite, and diopside (CaMgSi$_2$O$_6$) remain in abundance. In equilibrium, diopside is the low-temperature reservoir of calcium, while that of aluminum transitions from spinel to high albite back to spinel as the temperature decreases. The latter transition occurs below the minimum temperature shown in Figures 9 and 10. The aluminum-bearing compound, corundum (Al$_2$O$_3$), is not a major component of brown dwarf atmospheres. As Figure 3 demonstrates, enstatite and fosterite would appear near the photospheres of equilibrium brown and M dwarf atmospheres at temperatures from 1700 to 1900 K. In fact, as the relevant figures imply, classical silicate grains form in a temperature range from 2400 to 1500 K. This is just the $T_{\text{eff}}$ transition regime between stars and brown dwarfs and serves to emphasize the importance of grain opacity and cloud structure and extent in determining the properties of transition objects and in setting the $T_{\text{eff}}$ and luminosity of the main-sequence edge. Its role has yet to be precisely delineated, but Burrows et al. (1993) note that at the edge $T_{\text{eff}}$ is decreased by ~250 to ~1750 K when the approximate effects of grains are included.

At high temperatures, sodium and potassium are in monatomic form, but at temperatures of 1300–1500 K (Figs. 3, 9, and 10) NaAlSi$_3$O$_8$ and KAlSi$_3$O$_8$ would condense in undepleted atmospheres. Figure 4 depicts the Na/NaCl(g) and...
K/KCl(g) transition boundaries that occur in the 1000–1500 K temperature range and near the photosphere for \( T_{\text{eff}} \)'s of 1200–1400 K. Not shown in Figure 4, these chlorides condense below 800 K. Hence, as the temperature decreases, the major sodium species in true equilibrium atmospheres are first atomic Na, then gaseous NaCl and solid NaAlSiO\(_3\), and finally solid NaCl. Potassium shows a similar sequence. The presence of condensed NaCl and KCl at low temperatures (below the inferred \( T_{\text{eff}} \)) of Gl 229B is quite suggestive, and we will return to this in § 4.

Figures 9 and 10 depict representative abundance profiles for the dominant equilibrium phosphorus compounds, and Figure 3 depicts the major chemical transitions phosphorus undergoes. The \( \text{PH}_3 \rightarrow \text{P}_4\text{O}_6 \rightarrow \text{Mg}_3\text{P}_2\text{O}_8 \) transformations occur in the temperature range of 800–1200 K. The chemistry of phosphorus is particularly interesting, as the condensation temperature of \( \text{Mg}_3\text{P}_2\text{O}_8 \) (magnesium orthophosphate) is only weakly dependent on pressure and forms very close to the photosphere of many of the depicted equilibrium brown dwarf models. The predominant gas-phase species of phosphorus at about 1200 K is \( \text{PH}_3 \) (phosphine). Except at pressures above about 30 atmospheres, \( \text{PH}_3 \) is rapidly oxidized by \( \text{H}_2\text{O} \) to form the gas-phase oxide \( \text{P}_4\text{O}_{10} \), which becomes by far the dominant compound of phosphorus until \( \text{Mg}_3\text{P}_2\text{O}_8 \) condenses (ignoring Mg depletion by higher temperature refractories). At higher pressures, \( \text{Mg}_3\text{P}_2\text{O}_8 \) would first condense, then the remaining gas-phase phosphorus forms the oxide. The curve on Figure 3 labeled \( \left( \text{P}_4\text{O}_6 + \{\text{Mg}_3\text{P}_2\text{O}_8\}\right)/\text{PH}_3 \) indicates where the abundance of \( \text{PH}_3 \) is the same as the sum of the abundances of the oxide and the condensate, which, except for the highest pressures where \( \text{Mg}_3\text{P}_2\text{O}_8 \) condenses first, is where the ratio \( \text{P}_4\text{O}_6/\text{PH}_3 \) is unity. Note that the phosphorus equilibrium can be represented by the reaction,

\[
4\text{PH}_3 + 6\text{H}_2\text{O} \rightarrow \text{P}_4\text{O}_6 + 12\text{H}_2,
\]

which involves more gas-phase molecules on the right-hand side than the left. Hence, Le Chatelier’s principle can be used to explain why the slope of the phosphorus curve is anomalously positive, unlike that of the other curves in Figure 3.

However, according to Borunov, Dorofeeva, & Khodakovskiy (1995), the thermodynamic data for the gaseous species \( \text{P}_4\text{O}_6 \) in the JANAF tables may be in error and may result in an overestimate of its abundance. In their work they report a less negative value for the enthalpy of formation of \( \text{P}_4\text{O}_6 \), which would be reflected in a lower abundance. We have been using the data from the JANAF tables and find that with decreasing temperature \( \text{P}_4\text{O}_6 \) replaces phosphine, \( \text{PH}_3 \), as the dominant gas-phase phosphorus-bearing compound below about 1100 K in brown dwarf atmosphere models, until the condensate magnesium orthophosphate, \( \text{Mg}_3\text{P}_2\text{O}_8 \), would form in undepleted atmospheres between about 800 and 900 K, as is shown in Figure 3 (assuming other magnesium condensates are available to react with phosphorus-bearing species). It may be that the
abundance of $P_4O_6$ is overestimated in our calculations. However, for a present-day equilibrium Jupiter model and other similar undepleted models, magnesium orthophosphate would condense near to or above the temperature at which the phosphorus chemistry of the gas phase switches over from being dominated by $PH_3$ to being dominated by $P_2O_6$, so it appears that $P_2O_6$ may not in any case play an important role. In Figure 3, the curves indicating the phosphorus chemistry clearly show that at high pressures the condensation of $Mg_3P_2O_8$ would overlap with the formation of $P_4O_6$ if rainout were ignored.

3.3. Lithium, Cesium, Rubidium, Chlorine, and Fluorine

Figure 4 depicts the atomic to gaseous chloride transitions for the alkali metals and compares them with model temperature-pressure profiles from Burrows et al. (1997) at 1 Gyr. Figures 13 and 14 show the abundance profiles for Li, Cs, and Rb species for various Gl 229B models. The chemistry of these metals is similar, but since the elemental abundances are quite different (Table 1), there is the natural ordering (Li, Rb, Cs) depicted in the figures. Lithium is in atomic form above $\sim 1700$ K but is converted first into LiOH, then into LiCl at lower temperatures. Below $\sim 700$ K, in strict equilibrium lithium resides in LiAlO$_2$. Hence, at sufficiently low temperatures, the “lithium” test at 6708 Å is of less use (Martin et al. 1992). Below $T_{\text{eff}}$’s of perhaps 1300–1600 K, atomic lithium will be depleted, and the strength of the standard lithium line will abate. Below temperatures of 1200 K the abundance of atomic lithium will be about one hundredth of solar. Interestingly, at these low $T_{\text{eff}}$’s spectral signatures of the chlorides may be detectable in the mid-IR. The consequence of this is to nullify the standard lithium test for the majority of brown dwarfs and EGPs unless they are caught early in their lives (e.g., in young clusters) or are “massive” and near the transition edge.

Rubidium and cesium form the chloride as well but at temperatures that are 200–300 K lower than does Li. Nevertheless, the alkali metals survive in atomic form to lower temperatures than do the other true metals. Since they are less refractory and survive in monatomic form for a longer stretch of temperature, the alkali metals should manifest themselves in the spectra of transition objects after the other metals (e.g., Fe, Ca, Ti, V, Mg, and Al) are depleted and rain out, as is described above and in § 4. Very
approximately, the order of disappearance of the atom with decreasing temperature from \( \sim 1500 \text{ to } \sim 1200 \text{ K} \) should be: Li, Na, Cs, Rb, K, with Cs, Rb, and K disappearing at about the same temperature. (Note that Na and K could be depleted into high albite and sanidine as well.) Something like this seems to be what is being observed by the 2MASS (Kirkpatrick et al. 1998) and DENIS (Tinney et al. 1998) collaborations in the spectra of newly discovered substellar (?) and transition objects in the field.

From Figures 4, 13, and 14 we would predict that atomic cesium would be weak or nonexistent in the spectrum of Gl 229B itself. However, two cesium lines are clearly visible in its spectrum (Oppenheimer et al. 1998). Along with the anomalous (see Figs. 2, 5, and 6) detection of CO in the cold atmosphere of Gl 229B alluded to above, the atomic cesium detections may imply that its convective zone extends below \( 1500 \text{ to } 1200 \text{ K} \) and that some of its chemistry is not in equilibrium. In principle, grain and cloud opacities can extend the convective zone beyond the range theoretically predicted without them (Burrows et al. 1997), but until detailed calculations including grain opacities are available, this suggestion must be treated as speculative. The necessity to include chemical kinetics in the convective zones would further complicate the theoretical treatment of brown dwarf atmospheres.

Because of its small abundance, fluorine is not a very important element, but its chemistry is similar to that of chlorine. In these calculations, most of fluorine is in HF, with much of the remainder being in the gas-phase alkali fluorides. Chlorine is combined in HCl, with much of the rest at low temperatures being in the gas-phase alkali metal chlorides.

4. RAINOUT

The equilibrium abundance calculations we presented in § 3 are fiducial reference models in the study of the atmospheric compositions of brown dwarfs and EGPs in general and of Gl 229B in particular. Tables 2a and 2b and Figures 2–14 summarize the results and the major trends. However, as is demonstrated in the Gl 229B campaign and in attempts to fit its spectrum, there is strong evidence that heavy metals such as Ca, Fe, Ti, V, Si, Al, and Mg are depleted in Gl 229B’s atmosphere (Marley et al. 1996). In addition, such depletions are manifested in the atmospheres of Jupiter and Saturn. This is altogether to be expected, since the grains that condense below temperatures of \( \sim 2500 \text{ K} \) should form droplets and rain out of the atmosphere. This rainout will carry the condensate’s elements to depth. The lower boundary of the grain cloud deck should be near where the object’s temperature-pressure profile intersects the condensate’s Clausius-Clapyron lines (see Figs. 2–4), but its upper boundary is more difficult to determine. The physical extent of the clouds is a function of the character of convection and the meteorology of the atmo-
sphere. The droplet sizes are determined by the poorly understood processes of nucleation, coagulation, and breakup. Furthermore, the high opacity of the grains can turn an otherwise radiative zone into a convective zone and thereby influence the cloud extent and composition. In principle, if a convective zone were well mixed and the chemical kinetics were suitably fast, the compositions in the convective zones would closely follow the equilibrium abundance patterns described in § 3. This is the philosophy behind presenting such true equilibrium profiles. However, the condensables are likely to settle and concentrate at depth. In short, because of the low temperatures of substellar atmospheres, we would expect a variety of cloud layers with a variety of compositions both above and below their photospheres. Which clouds dominate is expected to be a function of the object’s effective temperature, gravity, and metallicity.

The equilibrium calculations are a straightforward guide in determining the likely cloud chemicals and layers as a function of depth (temperature). However, it is not known where the tops of these cloud decks will reside. This is important. The condensates that form from temperatures of ~2400–1400 K (e.g., akermanite, spinel, Fe, enstatite, festerite, the titanates, MnS, and high albite) have in a Gl 229B column total grammages above a few g cm$^{-2}$. The optical depth of a column of monodispensed grains is approximately

$$\tau \sim \frac{Pf}{\rho_o g a} Q_{ext} \sim \frac{G}{\rho_o a} Q_{ext},$$  \hspace{1cm} (4)$$

where $P$ is the pressure at the base of the cloud layer of a given composition, $f$ is the mixing ratio of the cloud particles, $g$ is the gravity, $Q_{ext}$ is the extinction parameter in Mie theory, $G$ is the cloud grammage, $\rho_o$ in the density of a grain, and $a$ is the grain radius. The term with $P$ in it assumes that the atmosphere is completely depleted in the corresponding refractory down to the cloud base. From equation (4) we can readily calculate that the predominantly silicate and iron cloud layers below the photosphere of Gl 229B are quite optically thick ($\gtrsim 10^3$), the precise thickness depending crucially on grain radius. Grain radii would have to exceed 1 cm in order to render these clouds transparent, whereas it is expected that the mean $a$ will be below 100 $\mu$m (Lunine et al. 1989). These regions might be more vigorously convective than would be expected without grain opacity, and the convective zone may extend to lower pressures and temperatures. This phenomenon, yet to be verified, may help to explain the anomalous detections of Cs (Oppenheimer et al. 1998) and CO (Noll et al. 1997) in Gl 229B, particularly if disequilibrium chemistry is involved.
Fig. 12.—Abundances of the same titanium and vanadium species depicted in Fig. 11 are plotted for models with effective temperatures of 800, 850, 900, 950, and 1000 K for a fixed gravity of 1000 m s$^{-2}$, as in Fig. 6. Note that in these models CaTiO$_3$ does not form.

Though a detached convective zone (Marley et al. 1996) may also be implicated.

However, the rainout of a high-temperature refractory will leave the upper regions of brown dwarf and EGP atmospheres depleted in the refractory’s constituent elements in stoichiometric ratios. The lower temperature chemical species will be assembled from the depleted elemental mixture. As a consequence, chemical abundances will be altered from the values assuming an Anders & Grevesse (1989) mixture at all altitudes ($\delta$ 3). We attempt to explore this process with a series of artificial rainout calculations in which we progressively sequester from the calculation the elements involved in grain formation. From some starting temperature (either 1000, 1400, or 2000 K) that defines each of three separate “trials” (trials 1, 2, or 3), every 200 K we deplete the atmosphere (in stoichiometric ratios) of the elements found in the chemical species that indeed condense in that temperature interval. For instance, when MgSiO$_3$ condenses, we decrease the Mg, Si, and O elemental abundances out of which the remaining compounds form in the ratio 1:1:3. In the lower 200 K interval we perform the equilibrium calculations with a composition depleted in the constituent elements of the higher temperature refractories. In a sense, via this procedure we are artificially forming cloud decks every 200 K comprised of the species that condense in that 200 K interval. This simulates in a crude way the progressive depletion and rainout of refractory elements from the entire atmosphere as we go down to lower temperatures (higher altitudes, lower pressures). For example, for trial 3 we progressively deplete from the atmosphere the constituents of the refractories formed at 2000, 1800, 1600, 1400, 1200, 1000, 800, and 600 K. For trial 1 we do the same for 1000, 800, and 600 K but with an Anders & Grevesse mixture, leave in equilibrium the layers at higher temperatures. One motivation for this exercise is the identification of likely condensates in the upper atmosphere of Gl 229B, below temperatures of 1000 K, that may be implicated wholly or in part in muting the “optical” spectrum observed from $\sim$1 to $\sim$0.8 $\mu$m (Oppenheimer et al. 1998).

The different trials represent our attempt to bracket the results, with trial 3 representing the almost total and immediate sequestration of a condensate once first formed and trial 1 allowing for the maintenance of true chemical equilibrium and rapid kinetics in and out of the solid phases down to the 1000 K level. If this procedure consistently identifies specific low-temperature refractory compounds below $\sim$1000 K at useful cloud grammages, then we may have a clue concerning spectroscopically important aerosols in the upper atmosphere.

Tables 3a and 3b depict the results of these trials below 1000 K. The temperature-pressure profile used is for a Gl 229B model with a $T_{\text{eff}}$ of 950 K and a gravity of $10^5$ cm s$^{-2}$ (Burrows et al. 1997). The species listed have condensed either in the 800–1000 K range (Table 3a) or in the 600–800.
Fig. 13.—Abundances of lithium, rubidium, cesium, and their most abundant compounds for an effective temperature of 950 K and the three gravities employed in Fig. 5. At the lowest temperatures plotted, the condensate RbCl forms, with the 300 m s$^{-2}$ model being labeled.

The K range (Table 3b) after the corresponding depletions have been carried out at depth by the described procedure. Certain features are readily apparent. First, the grammages of the clouds formed at altitude are significantly below the few g cm$^{-2}$ for silicates at depth. This is encouraging, since only modest optical depths are needed to explain the shorter wavelength Gl 229B data. From equation (4), a grammage of only $10^{-5}$ g cm$^{-2}$ with a particle radius of 0.1 μm provides close to unit optical depth. (Note that small particles are expected in radiative zones.) Second, the “abundant” low-temperature refractories are predominantly the chlorides and sulfides. In particular, KCl, NaCl, NaF, and SiS$_2$ stand out, with SiS$_2$ dominating for trial 3. Without depletion, SiS$_2$ would not form in abundance, but

### TABLE 3a
Inferred Cloud Grammages (g cm$^{-2}$) for Species that Condense Between 1000 and 800 K for the Three Rainout Trials$^a$

| Condensate | A1 | A2 | A3 | Grammages 1 | Grammages 2 | Grammages 3 |
|------------|----|----|----|-------------|-------------|-------------|
| MnO        | 927| 875| 125| 2.09 x 10$^{-10}$ | 6.90 x 10$^{-11}$ |          |
| FeS        | 924| 922| 921| 1.26 x 10$^{-9}$  | 2.14 x 10$^{-8}$   | 2.01 x 10$^{-5}$ |
| NaF        | 836| 25 | 825| 6.74 x 10$^{-5}$  | 5.53 x 10$^{-9}$   |          |
| Ni$_3$S$_4$| 800| 863| 862| 1.18 x 10$^{-7}$  | 2.45 x 10$^{-8}$   | 1.15 x 10$^{-7}$ |
| Fe$_2$O$_3$| 835| 862| 862| 1.18 x 10$^{-7}$  | 2.45 x 10$^{-8}$   | 1.15 x 10$^{-7}$ |
| NiS$_2$    | 800| 863| 863| 1.18 x 10$^{-7}$  | 2.45 x 10$^{-8}$   | 1.15 x 10$^{-7}$ |

$^a$ A1, A2, and A3 are the temperatures in K when the condensate first appears for the first, second, and third rainout trials, respectively.
progressive depletion starting at the highest temperatures is needed for it to become important. If SiS$_2$ forms, it does so around 743 K, whereas NaF forms near 920 K, NaCl forms near 800 K, and KCl forms near 740 K. Be that as it may, the sodium and potassium salts emerge as cloud candidates in Gl 229B’s upper atmosphere, with grammages that may range from $\sim 10^{-4}$ to $\sim 4 \times 10^{-6}$ g cm$^{-2}$. In trial 3, although the KCl cloud is thin, the SiS$_2$ is thick. These

**TABLE 3b**

| Condensate | A1   | A2   | A3   | Grammage 1     | Grammage 2     | Grammage 3     |
|------------|------|------|------|----------------|----------------|----------------|
| NaCl       | 776  | 701  | 701  | $1.04 \times 10^{-5}$ | $2.44 \times 10^{-7}$ |
| KCl        | 730  | 740  | 728  | $4.62 \times 10^{-6}$ | $3.68 \times 10^{-5}$ | $4.20 \times 10^{-6}$ |
| LiF        | 700  | 613  | 613  | $2.68 \times 10^{-7}$ | $4.94 \times 10^{-8}$ |
| RbCl       | 613  | 613  | 613  | $4.94 \times 10^{-8}$ |
| Mn         | 768  | 768  |      | $2.16 \times 10^{-9}$ | $2.12 \times 10^{-9}$ |
| LiOH       | 745  |      |      | $3.15 \times 10^{-7}$ |
| Fe$_2$O$_3$| 726  |      |      | $1.72 \times 10^{-10}$ |
| MgF$_2$    | 636  |      |      | $5.77 \times 10^{-10}$ |
| KF         | 605  |      |      | $5.03 \times 10^{-9}$ |
| SiS$_2$    | 743  |      |      | $4.13 \times 10^{-3}$ |
| Co$_3$O$_4$| 684  |      |      | $5.52 \times 10^{-9}$ |
| LiCl       | 638  |      |      | $2.63 \times 10^{-7}$ |
| CaF$_2$    | 627  |      |      | $1.77 \times 10^{-10}$ |
| MgCl$_2$   | 615  |      |      | $8.85 \times 10^{-10}$ |

* A1, A2, and A3 are the temperatures in Kelvin when the condensate first appears for the first, second, and third rainout trials, respectively.
calculations suggest that thin clouds of nonsilicate, low-temperature refractories can and do exist in the upper atmosphere of Gl 229B. Furthermore, they may also reside in the atmospheres of brown dwarfs with \( T_{\text{eff}} \)’s below about 1800 K (7). Hence, it is expected that many cloud layers with different compositions are formed both above and below the photospheres of brown dwarfs and EGPs. At times, from the lowest effective temperatures up, clouds of either \( \text{NH}_3 \) (\( T_{\text{eff}} \leq 250 \text{ K} \)), \( \text{H}_2\text{O} \) (\( T_{\text{eff}} \leq 400 \text{ K} \)), chlorides, sulfides, iron, or silicates should be found in these exotic substellar and late M dwarf atmospheres.

5. DISCUSSION AND CONCLUSIONS

In the Appendix we present useful analytic expressions for the abundances of the main gaseous compounds \( \text{CH}_4, \text{CO}, \text{NH}_3, \text{N}_2, \text{and} \ H_2\text{O} \) in terms of temperature, pressure, and chemical composition. These formulae will prove useful to those interested in approximating the abundances of the major gas-phase species in substellar atmospheres of almost any metallicity. In this paper we have explored in detail the abundance profiles and compositions expected in the atmospheres of solar-metallicity brown dwarfs and EGPs, with rainout and in the limit of true equilibrium (no depletion). In chemical equilibrium, the major reservoirs of the dominant elements shift with pressure and, most importantly, with temperature in ways reflected in Figures 2–14 and in Tables 2a and 2b. Unlike in any other stellar context, chemistry and molecules assume a central role in determining the character of the atmospheres of substellar objects. As the temperature decreases with increasing height in such an atmosphere, molecules not encountered in M dwarfs or in standard stellar atmospheres form. At higher temperatures, the standard refractories, such as the silicates, spinel, and iron, condense out into grain clouds, which by their large opacity lower the \( T_{\text{eff}} \) and luminosity of the main-sequence edge (Burrows et al. 1993) and alter in detectable ways the spectra of objects around the transition mass (Jones & Tsuji 1997). As \( T_{\text{eff}} \) decreases below that at the stellar edge, the classical refractories are buried progressively deeper below the photosphere, and less refractory condensates and gas-phase molecules come to dominate (Marley et al. 1996; Burrows et al. 1997).

Below temperatures of \( \sim 1500 \text{ K} \) our calculations suggest that the alkali metals, which are not as refractory as \( \text{Fe, Al, Ca, Ti, V, and Mg} \), emerge as important atmospheric and spectral constituents. At still lower temperatures, chlorides and sulfides appear, some of which will condense in the cooler upper atmosphere and form clouds that will affect emergent spectra and albedos. Cloud decks of many different compositions at many different temperature levels are expected, depending on \( T_{\text{eff}} \) and weakly on gravity. We expect that clouds of chlorides and sulfides (not silicates) at temperature levels below \( \sim 1000 \text{ K} \) are responsible for the steeper slope observed in the spectrum of Gl 229B at the shorter wavelengths (Oppenheimer et al. 1998).

As \( T_{\text{eff}} \) decreases (either as a given mass cools or, for a given age, as we study objects with lower masses) the major atmospheric constituents of brown dwarfs and EGPs change. This change is reflected in which spectral features are most prominent and in the albedos of substellar objects near their primaries. Hence, specific mixes of atoms, molecules, and clouds can serve as approximate \( T_{\text{eff}} \) and temperature indicators, and a composition scale can be established. In order to do this definitively, synthetic spectra with the atmospheres we have calculated are required. However, the composition trends we have identified are suitably dramatic that reasonable molecular indicators of spectral type can be suggested. A workable sequence might be: \( \text{TiO} \) disappears (at 2300–2000 K), refractory silicates and \( \text{Fe} \) appears (at 2300–2000 K), \( \text{Mg}_2\text{SiO}_4 \) appears (at 1900 K), \( \text{VO}(g) \) disappears (at 1700–1900 K), MgSO \(_3\) appears (at 1700 K), silicates rain out (at \( \sim 1400 \text{ K} \) [7]), CrH disappears (\( \sim 1400 \text{ K} \)), \( \text{Li} \rightarrow \text{LiCl} \) (\( \leq 1400 \text{ K} \)), \( \text{CO} \rightarrow \text{CH}_4 \) (1200–1500 K), \( \text{Rb, Cs, K} \rightarrow \text{chlorides} \leq 1200 \text{ K} \)), \( \text{PH}_3 \rightarrow (\text{P}_2\text{O}_9) \) (\( \leq 1000 \text{ K} \)), formation of \( \text{NaF, NaCl, and KCl} \) clouds and various sulfire clouds (\( \sim 700–1100 \text{ K} \)), \( \text{N}_2 \rightarrow \text{NH}_3(g) \) (\( \sim 700 \text{ K} \)), \( \text{H}_2\text{O}(g) \rightarrow \text{H}_2\text{O}(c) \) (\( \sim 350 \text{ K} \)), and \( \text{NH}_3 \rightarrow (\text{NH}_2[c], \text{NH}_2\text{SH}[c]) \) (\( \sim 200 \text{ K} \)).

Disequilibrium chemistry and convection and differences in the spectroscopic strengths of the various indicators will no doubt partially alter the \( T_{\text{eff}} \) order of this spectral scale. Note that objects with \( T_{\text{eff}} \)’s higher than the temperatures quoted above may nevertheless, because of the lower temperatures that can be achieved at lower optical depths, manifest lower temperature compounds and/or transitions in their atmospheres and spectra. Gl 229B with a \( T_{\text{eff}} \) of \( \sim 950 \text{ K} \) is a case in point, if lower temperature chlorides and sulfide refractories are to be invoked to explain its spectrum. How much higher the appropriate \( T_{\text{eff}} \) should be for a given chemical transition to be fully manifest will depend on consistent atmosphere models. Clearly, the above temperatures for the appearance or disappearance of species should be used with great caution when estimating \( T_{\text{eff}} \).

Very crudely, the “L” spectral type suggested by Kirkpatrick et al. (1998) would correspond to between \( \sim 1500 \text{ and } 2200 \text{ K} \). None but the youngest and most massive brown dwarfs and only the very youngest EGPs could have this proposed spectral designation. Most brown dwarfs and EGPs will be of an even later spectral type, yet to be coined: a spectral type that would include Gl 229B.

In the future, more consistent atmospheres and a detailed spectral sequence need to be calculated. Furthermore, we need to expand our inventory of possible compounds and explore the effect of metallicity. Importantly, credible cloud models, incorporating realistic grain size distributions and their altitude dependence, will be required to explain the spectral and photometric data on brown dwarfs and extrasolar giant planets that has already been obtained and that can be anticipated in the near future. Given the ambiguities in cloud physics and theoretical meteorology, new observations will be crucial to educate and guide theory concerning the true nature of substellar atmospheres. Nevertheless, it is clear that brown dwarfs and giant planets occupy an exciting new realm of science midway between astronomy and planetary studies in which new insights and for which new tools must be developed. The theoretical study of substellar objects with \( T_{\text{eff}} \)’s between those of Jupiter and the stars has only just now begun in earnest.

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APPENDIX

ANALYTIC ABUNDANCE ESTIMATES OF THE MAIN COMPOUNDS OF C, N, AND O

Here we present analytic expressions for the abundances of the main gaseous compounds CH$_4$, CO, NH$_3$, N$_2$, and H$_2$O in terms of temperature, pressure, and chemical composition. Our method assumes that temperatures are below about 2500 K, that pressures are high enough for the dissociation of H$_2$ to be neglected, and that the composition ratios are approximately solar with $N_O > N_C + N_Si$. ($N_O, N_C,$ and $N_Si$ are the abundances by number of oxygen, carbon, and silicon, respectively.) This method does not involve any iterations, and the abundances are obtained by directly evaluating a few simple expressions, without recourse to free-energy minimization. Throughout we define abundances by number relative to hydrogen for an solar with $N_C/N_H$, the partial pressure in atmospheres of gas Y as $P_Y$, and the ratio of the partial pressure of gas Y to that of H$_2$ as $B_Y = P_Y/P_{H2}$. Note that $P_{H2}$ is the partial pressure of H$_2$, not the total pressure of the gas.

A1. CO, CH$_4$, AND H$_2$O ABUNDANCES

Given the equilibrium, CO + 3H$_2$ ⇌ H$_2$O + CH$_4$, the equilibrium constant is

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

(A1)

where $\Delta G_1(T)$ is the Gibbs free-energy change in calories per mole associated with the equilibrium, and $R$ is the gas constant in cal mol$^{-1}$ K$^{-1}$. Assuming that all the carbon is in CO and CH$_4$ and that all the oxygen is in CO and H$_2$O, equation (A1) can be solved analytically, yielding the results

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

(A2)

$$B_{CH4} = 2A_C - B_{CO} ,$$

(A3)

and

$$B_{H2O} = 2A_O - B_{CO} ,$$

(A4)

where

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

(A5)

and $a_1, b_1, c_1, d_1,$ and $e_1$ are equal to 1.106131 × 10$^6$, $-5.69895 \times 10^4$, 62.656, $-5.81396 \times 10^{-4}$, and $2.346515 \times 10^{-8}$, respectively. These coefficients are obtained by fitting the Gibbs free energies of formation for each of the species in the equilibrium, then combining them according to the stoichiometry. In the limit that $K_1 \to 0$, i.e., when all the carbon is in CH$_4$ (favored at low temperatures or high pressures), equation (A2) indeed yields that $B_{CO} = 0$. In the limit that $K_1 \to \infty$, i.e., when all the carbon is in CO (favored at high temperatures or low pressures), equation (A2) indeed gives us that $B_{CO}$ equals $2A_C$. Note that the H$_2$O abundance is bounded by the inequalities $2(A_O + A_C) \leq B_{H2O} \leq 2A_O$.

A2. N$_2$ AND NH$_3$ ABUNDANCES

Given the equilibrium N$_2$ + 3H$_2$ ⇌ 2NH$_3$, we obtain

$$K_2(T) = \frac{P_{N2} P_{H2}^3}{P_{NH3}^2} = \exp \left( -\Delta G_2(T)/RT \right) ,$$

(A6)

where $\Delta G_2(T)$ is the Gibbs free-energy change associated with the equilibrium. Assuming that all nitrogen is in N$_2$ and NH$_3$, equation (A6) can be solved analytically, yielding the result

$$B_{N2} = A_N + \frac{P_{H2}^2}{8K_2(T)} - \sqrt{\frac{A_N + P_{H2}^2}{8K_2(T)}} - A_N^2 ,$$

(A7)

and

$$B_{NH3} = 2(A_N - B_{N2}) ,$$

(A8)

where

$$K_2(T) = \exp \left[ (a_2/T + b_2 + c_2 T + d_2 T^2 + e_2 T^3)/RT \right] ,$$

(A9)

and $a_2, b_2, c_2, d_2,$ and $e_2$ are equal to 8.16413 × 10$^3$, $-2.9109 \times 10^4$, 58.5878, $-7.8284 \times 10^{-4}$, and $4.729048 \times 10^{-8}$, respectively. Given equation (A7), the abundance of NH$_3$ can be found from equation (A8). In the limit that $K_2 \to 0$, i.e., when all the nitrogen is in NH$_3$, equation (A7) returns 0, and in the limit that $K_2 \to \infty$, i.e., when all the nitrogen is in N$_2$, equation (A7) returns $A_N$.

Since some oxygen is removed from the gas phase at low temperatures by refractory condensates, notably those of silicon and magnesium, we may correct for this, yielding even more accurate analytic abundances for CO and CH$_4$ below about 1700
K. If $N_0$ is the abundance of the available oxygen after removal of oxygen in silicates, $N_0 = N_O - x_{Si}N_{Si}$, where $x_{Si}$ is the average number of oxygen atoms removed from the gas phase by each silicon atom. Below $\sim 1700$ K, assuming solar ratios, $x_{Si}$ is found to be 3.28, i.e., slightly more than three oxygen atoms per silicon atom are removed from the gas phase. This is consistent with the stoichiometry of the most abundant condensate, MgSiO$_3$. Because of the presence of other condensates, such as Mg$_2$SiO$_4$, $x_{Si}$ is not exactly 3. Reducing in $A_O$ the oxygen abundance by $3.28N_{Si}$ when the temperature is below $\sim 1500$ K, the agreement between the analytic abundances of H$_2$O, CO, and CH$_4$ and the numerical results is better than 0.4%. Above temperatures at which silicates condense, setting $N_0$ equal to $N_O$ is accurate to no worse than $\sim 5\%$. In fact, the analytic formulae for the nitrogen compounds are good to better than 0.8% for the entire temperature and pressure regime.

The formulae of this appendix comprise a simple algorithm for calculating the abundances of five of the main compounds of carbon, nitrogen, and oxygen for a wide range of temperatures, pressures, and compositions without recourse to matrix inversion or Gibbs minimization. Hence, together with the abundances of H$_2$, He, and Ne, the eight most abundant species in brown dwarf and giant planet atmospheres can be derived analytically.

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