1. INTRODUCTION

Thermochemical models have been used to describe alkali (Lodders 1999), titanium and vanadium (Lodders 2002), carbon, nitrogen, and oxygen (Lodders & Fegley 2002), sulfur and phosphorus (Visscher et al. 2006), and condensate (e.g., Lodders & Fegley 2006; Lodders 2009) chemistry in the atmospheres of giant planets, brown dwarfs, and low-mass dwarf stars. Here, we continue and extend these previous studies by using thermochemical equilibrium calculations to model the chemical behavior of Fe, Mg, and Si in substellar objects. Iron, magnesium, and silicon are the most abundant rock-forming elements in a solar composition gas, and—condensed as iron metal (Fe), and forsterite (Mg$_2$SiO$_4$) and enstatite (MgSiO$_3$) cloud formation. Monatomic Mg is the dominant magnesium gas throughout the atmospheres of EGPs and L dwarfs, and in the deep atmospheres of giant planets and T dwarfs. Mg- and Si-bearing gases are effectively removed from the atmosphere by forsterite (Mg$_2$SiO$_4$) and enstatite (MgSiO$_3$) cloud formation. Monatomic Mg is the dominant magnesium gas throughout the atmospheres of EGPs and L dwarfs, and in the deep atmospheres of giant planets and T dwarfs. Silicon monoxide (SiO) is the most abundant Si-bearing gas in the deep atmospheres of brown dwarfs and EGPs, whereas SiH$_4$ is dominant in the deep atmosphere of Jupiter and other gas giant planets. Several other Fe-, Mg-, and Si-bearing gases become increasingly important with decreasing effective temperature. In principle, a number of Fe, Mg, and Si gases are potential tracers of weather or diagnostic of temperature in substellar atmospheres.

Key words: astrochemistry – brown dwarfs – planets and satellites: individual (Jupiter) – stars: individual (Gliese 229B, HD 209458) – stars: low-mass

2. COMPUTATIONAL METHOD

Thermochemical equilibrium calculations were performed using a Gibbs free energy minimization code, previously used for modeling the atmospheric chemistry of Saturn (Visscher et al. 2006) and sulfur and phosphorus chemistry in substellar objects (Visscher et al. 2006). Thermodynamic data for the equilibrium calculations were taken from the compilations of Gurvich et al. (1989–1994), Robie & Hemingway (1995), the fourth edition of the JANAF Tables (Chase 1998), and the thermodynamic database maintained in the Planetary Chemistry Laboratory (Lodders & Fegley 2002). This database includes additional thermodynamic data from the literature for compounds absent from the other compilations.

As noted in Lodders & Fegley (2002) and Visscher et al. (2006), the cool, dense atmospheres of substellar objects
allow for the formation of molecules and condensates, and the establishment of equilibrium chemistry. Thermochemical equilibrium calculations therefore provide a very good first-order approximation of chemical speciation as a function of pressure, temperature, and metallicity for a wide variety of atmospheric systems (e.g., see references in Section 1). However, departures from equilibrium are commonly observed in substellar objects. For example, if an ultraviolet flux is present, photochemical reactions in the uppermost atmosphere will drive thermochemical reactions out of equilibrium—especially on highly irradiated objects such as close-in exoplanets. Vertical atmospheric transport may also yield departures from equilibrium if convective mixing rates become faster than temperature-dependent gas-phase reaction rates (that is, if the characteristic timescale for mixing is less than the characteristic timescale for a chemical reaction which creates or destroys a given species). Bearing these caveats in mind, we focus on higher temperatures (800 K and higher) when considering the chemical behavior of individual gases, where thermochemical processes are generally expected to dominate over disequilibrium processes such as photochemistry or atmospheric mixing (e.g., see Section 5 in Visscher et al. 2006).

All calculations were conducted using elemental abundances from Lodders (2003) for a solar system (i.e., protosolar) composition gas. The effect of metallicity on sulfur and phosphorus chemistry was examined by running computations at [Fe/H] = −0.5 dex (subsolar), [Fe/H] = 0 dex (solar), and [Fe/H] = +0.5 dex (enhanced) metallicities. The metallicity factor, m, is defined as \( m = [\text{Fe}/\text{H}] \). We assume that the elemental abundance ratios for Mg, Si, and other elements of interest vary similarly with [Fe/H] (e.g., [Mg/H] ≈ [Si/H] ≈ [Fe/H]) over the narrow range of metallicities considered here (see Edvardsson et al. 1993; Chen et al. 2000; Huang et al. 2005).

We assume that condensates settle gravitationally into a cloud layer and are removed from the cooler, overlying atmosphere. This equilibrium condensate scenario for the deep atmospheres of giant planets and brown dwarfs is supported by several lines of evidence (e.g., see Lodders & Fegley 2006, and references therein). First, the presence of germane (GeH₄) and the absence of silane (SiH₄) in the upper atmospheres of Jupiter and Saturn (even though Si is expected to be more abundant than Ge) can be explained by the removal of Si from the gas into silicate clouds deeper in the atmosphere, whereas Ge remains in the gas phase (Fegley & Prinn 1988; Fegley & Lodders 1994). Second, the detection of H₂S in Jupiter’s troposphere by the Galileo entry probe indicates that Fe must be sequestered into a cloud layer at deep atmospheric levels, because the formation of FeS would otherwise remove H₂S from the gas above the ~700 K level (Lodders & Fegley 2002; Visscher et al. 2006). Third, absorption from monatomic K gas in the spectra of T dwarfs (Burrows et al. 2000; Geballe et al. 2001) requires the removal of Al and Si at deeper atmospheric levels, because K would otherwise be removed from the observable atmosphere by the condensation of orthoclase (KAlSi₃O₈; Lodders & Fegley 2006). The presence of monatomic Na gas in brown dwarfs (Burrows et al. 2000; Geballe et al. 2001) requires the removal of Na by Na₂S cloud formation is consistent with the observed weakening of Na atomic lines throughout the L dwarf spectral sequence and their disappearance in early T dwarfs (e.g., Kirkpatrick et al. 1999; McLean et al. 2003; Visscher et al. 2006). Finally, as we note below, the disappearance of iron, magnesium, and silicon spectral features in later spectral types is consistent with removal of these elements into cloud layers. In our thermochemical model, the abundances of Fe-, Mg-, and Si-bearing gases above the clouds are computed assuming saturation (equilibrium) vapor pressure. If supersaturation occurs, a condensate will form and settle toward the cloud layer to restore equilibrium.

3. IRON CHEMISTRY

3.1. Overview of Iron Chemistry

Figure 1 illustrates model atmospheric profiles for an M dwarf \( (T_{\text{eff}} = 2600 \text{ K}, \log g = 5.0; \text{Tsuji et al.} 1996) \), an L dwarf \( (T_{\text{eff}} = 1800 \text{ K}, \log g = 5.0; \text{Burrows et al.} 2006) \), the hot, close-in (Pegasi) planet HD209458b \( (T_{\text{eff}} = 1350 \text{ K}; \text{Iro et al.} 2005) \), the T dwarf Gliese 229B \( (T_{\text{eff}} = 960 \text{ K}; \text{Marley et al.} 1996) \), and Jupiter \( (T_{\text{eff}} = 124 \text{ K}) \), indicated by dashed lines. We note that Jovian atmospheric chemistry differs slightly than that for a solar-metallicity gas because Jupiter has a heavy element enrichment comparable to \([\text{Fe}/\text{H}] \approx +0.5 \text{ dex} \) (Lodders 1999; Lodders & Fegley 2002).

Also shown in Figure 1 are lines indicating where \( \Delta(\text{CH}_3) = \Delta(\text{CO}) \) and \( \text{A}(\text{H}_2) = \text{A}(\text{H}) \). These boundaries are important because carbon and oxygen affect the chemical behavior of many Fe-, Mg-, and Si-bearing gases. Methane is the dominant carbon-bearing gas in Jupiter and T dwarfs (such as Gliese 229B) whereas CO is the dominant carbon-bearing gas in L dwarfs and Pegasi planets (such as HD209458b). Molecular hydrogen dissociates into monatomic H at high temperatures and low pressures (lower right corner of Figure 1). However, \( \text{H}_2 \) is the dominant form of hydrogen in substellar objects, and we therefore take \( \text{X}_{\text{H}_2} \approx \text{X}_{\text{H}} \approx 0.84 \) throughout the following. This approximation holds for metallicities up to \([\text{Fe}/\text{H}] \approx +0.5 \text{ dex} \); at higher metallicities, the \( \text{H}_2 \) mole fraction abundance
decreases as the relative abundance of heavy elements increases (e.g., $X_{\text{H}_2} \approx 0.82$ at $[\text{Fe}/\text{H}] \approx +1.0$ dex).

The dotted line in Figure 1 shows the condensation curve for Fe metal, with an open circle denoting its normal melting point (1809 K). Iron condensation occurs via

$$\text{Fe} = \text{Fe}(s,l).$$

The equilibrium condensation temperature ($T_{\text{cond}}$) of Fe is approximated by

$$10^4/T_{\text{cond}}(\text{Fe}) = 5.44 - 0.48 \log P_T - 0.48[\text{Fe}/\text{H}],$$

where higher pressures and/or metallicities lead to higher Fe condensation temperatures. Iron cloud formation effectively removes nearly all iron from the atmosphere, and the abundances of Fe-bearing gases above the clouds rapidly decrease with altitude.

Monatomic Fe gas is the dominant Fe-bearing gas in a protosolar composition gas until it is replaced by Fe(OH)$_2$ at low temperatures and high pressures. The conversion between Fe and Fe(OH)$_2$ is represented by the net thermochemical reaction

$$\text{Fe} + 2\text{H}_2\text{O} = \text{Fe(OH)}_2 + \text{H}_2,$$

and the solid line dividing the Fe and Fe(OH)$_2$ fields in Figure 1 indicates where these gases have equal abundances $A(\text{Fe}) = A(\text{Fe(OH)}_2) \approx \frac{1}{2} \Sigma \text{Fe}_{\text{gas}}$, where $\Sigma \text{Fe}_{\text{gas}}$ is the total amount of iron in the gas. The position of this line is given by

$$\log P_T = 11.94 - 12088/T - 2[\text{Fe}/\text{H}],$$

showing that an increase in metallicity will shift the Fe–Fe(OH)$_2$ boundary to higher temperatures and lower pressures. In other words, an increase in metallicity increases the stability field of Fe(OH)$_2$ for otherwise constant conditions.

3.2. Chemical Behavior of Iron-bearing Gases

3.2.1. Monatomic Iron, Fe

The mole fraction abundance of monatomic Fe at thermochemical equilibrium as a function of pressure and temperature is shown in Figure 2(a). As mentioned above, monatomic Fe is the dominant Fe-bearing gas over a wide range of pressures and temperatures in a solar system composition gas. Below the Fe clouds, the abundance of Fe gas is representative of the total iron content of the atmosphere ($X_{\text{Fe}} \approx X_{\text{Fe}^0}$), and its abundance is given by

$$\log X_{\text{Fe}} \approx -4.24 + [\text{Fe}/\text{H}].$$

Upon Fe metal condensation, the amount of iron in the gas rapidly decreases and the equilibrium Fe gas abundance is governed by its vapor pressure over solid or liquid iron, represented in reaction (1). The mole fraction abundance of monatomic Fe above the clouds is given by

$$\log X_{\text{Fe}} \approx 7.23 - 20995/T - \log P_T,$$

inversely proportional to $P_T$. The Fe gas abundance is independent of metallicity in this region because it depends solely on the temperature-dependent vapor pressure of iron. As described below (see Sections 3.2.2 and 3.2.3), this expression can be used with chemical equilibria to determine the abundances of other iron gases in substellar atmospheres. Equations giving the abundance of Fe (and other Fe-bearing gases) as a function of temperature, pressure, and metallicity below and above the Fe clouds are listed in Table 1.

Neutral monatomic Fe possesses several hundred spectral lines in the J and H bands (Meléndez & Barbuy 1999), and FeI features are observed in the spectra of brown dwarfs and low-mass dwarf stars (e.g., Cushing et al. 2005). The strong Fe feature at 1.189 μm weakens in mid- to late-type M dwarf spectra and generally disappears in mid-type L dwarfs (McLean et al. 2003; Cushing et al. 2005). This trend is consistent with the removal of iron from the gas into an Fe metal cloud deck located deeper below the photosphere in objects with low effective temperatures (e.g., Burgasser et al. 2002a).

3.2.2. Iron Hydride, FeH

The chemical behavior of FeH in a protosolar composition gas is illustrated in Figure 2(b). The conversion between Fe and FeH occurs via the net thermochemical reaction

$$\text{Fe} + 0.5\text{H}_2 = \text{FeH}.$$  (7)

Here, we show how chemical equilibria may be used to derive equations giving the abundance of Fe-bearing species as a function of temperature, pressure, and metallicity. Rearranging the equilibrium constant expression for reaction (7) yields

$$\log X_{\text{FeH}} = \log X_{\text{Fe}} + 0.5 \log X_{\text{H}} + 0.5 \log P_T + \log K_7.$$  (8)

Using the Fe abundance from Equation (5), the temperature dependence of $K_7$ (log $K_7 \approx -1.85 - 1905/T$ from 800 to 2500 K), and the hydrogen abundance ($X_{\text{H}} \approx 0.84$), the FeH abundance between the $\text{H}_2$–H boundary and the Fe cloud deck is given by

$$\log X_{\text{FeH}} \approx -6.13 - 1905/T + 0.5 \log P_T + [\text{Fe}/\text{H}],$$  (9)

proportional to $P_T^{0.5}$ and $m$. At high temperatures (>2000 K) and low pressures (<10$^{-2}$ bar) as monatomic H becomes increasingly abundant the H$_2$ abundance begins to decrease near the H$_2$–H boundary. The reduced H$_2$ abundance, in turn,
reduces FeH formation via reaction (7) and changes the chemical behavior of FeH at high temperatures and low pressures (i.e., the lower right corner of Figure 2(b)).

Above the iron clouds, the Fe abundance in Equation (6) is used in Equation (8) to give

$$\log X_{FeH} \approx 5.34 - 22900/T - 0.5 \log P_T,$$

where $X_{FeH}$ is proportional to $P_T^{-0.5}$ and independent of metallicity. The differences in chemical behavior of FeH below (Equation (9)) and above (Equation (10)) the Fe cloud deck are illustrated in the shape of the FeH abundance contours in Figure 2(b). The sharp bends in the contours correspond to the Fe condensation curve in Figure 1.

Absorption bands from FeH are common in the near-infrared spectra of brown dwarfs (e.g., Kirkpatrick et al. 1999; McLean et al. 2003; Cushing et al. 2003, 2005). The most prominent FeH feature is the band located at 0.9896 μm, which weakens throughout the L dwarf spectral sequence and in early T dwarfs (McLean et al. 2003; Nakajima et al. 2004;
Cushing et al. 2005), consistent with the removal of iron into a cloud located deeper and deeper in the atmosphere. This feature unexpectedly strengthens again in mid-type T dwarf spectra (Burgasser et al. 2002b, 2002a; Nakajima et al. 2004; Cushing et al. 2005), prompting different explanations for the shape of the color–magnitude diagram for brown dwarfs near the L–T transition. Nakajima et al. (2004) suggested that the strengthening FeH bands are caused by upward convective mixing of FeH gas from deeper levels where it is more abundant. However, as pointed out by Burgasser et al. (2002a) and demonstrated Lodders & Fegley (2006), the fragile Fe–H bond is unlikely to survive convective upwelling in a T dwarf atmosphere. Instead, the observations are plausibly explained by cloud disruption and clearing (in an ∼1 μm window) which allows the observation of FeH gas at deep atmospheric levels (Burgasser et al. 2002a; Lodders & Fegley 2006).

3.2.3. Iron Monohydroxide, FeOH

Mole fraction contours of FeOH are illustrated in Figure 2(c). The equilibrium between Fe and FeOH is represented by the net thermochemical reaction

\[ \text{Fe} + \text{H}_2\text{O} = \text{FeOH} + 0.5\text{H}_2, \]  

(11)

and expressions giving the FeOH abundance as a function of temperature, pressure, and metallicity are listed in Table 1. Above the iron clouds, the curvature in the FeOH abundance contours along the CH4–CO boundary results from the effect of carbon chemistry on the H2O abundance in reaction (11) (e.g., Lodders & Fegley 2002). For example, the atmospheric water abundance may be written as

\[ \log X_{\text{H}_2\text{O}} = \log X'_{\text{H}_2\text{O}} + [\text{Fe/H}], \]  

(12)

where \( X'_{\text{H}_2\text{O}} \) is the water abundance in a solar-metallicity gas, which is \( X'_{\text{H}_2\text{O}} \approx 10^{-3.12} \) inside the CH4 field and \( X'_{\text{H}_2\text{O}} \approx 10^{-3.58} \) inside the CO field in Figure 1. At temperatures and pressures near the CH4–CO boundary, \( X'_{\text{H}_2\text{O}} \) may be derived from CH4–CO equilibria (Lodders & Fegley 2002). Rearranging the equilibrium constant expression for reaction (11) gives

\[ \log X_{\text{FeOH}} = \log X_{\text{Fe}} + \log X_{\text{H}_2\text{O}} - 0.5 \log X_{\text{H}_2} + 0.5 \log P_T + \log K_{11}. \]  

(13)

Substituting for the Fe abundance from Equation (6), the H2O abundance from Equation (12), the H2 abundance (\( X_{\text{H}_2} \approx 0.8384 \)), and the temperature dependence of \( K_{11} \) (\( K_{11} \approx -2.25 + 2468/T \) from 800 to 2500 K), Equation (13) becomes

\[ \log X_{\text{FeOH}} \approx 5.02 - 18527/T - 0.5 \log P_T + 2[\text{Fe/H}] + \log X'_{\text{H}_2\text{O}}. \]  

(14)

This expression gives the FeOH abundance above the iron clouds and includes the effect of metallicity on the atmospheric water abundance. The kinks in the FeOH contours denote the position of the Fe condensation curve. As demonstrated in Equation (14) and shown in Figure 2(c), the mole fraction abundance of FeOH is proportional to \( P_T^{-0.5} \) throughout this region.

3.2.4. Iron Hydroxide, Fe(OH)2

The chemical behavior of Fe(OH)2 as a function of temperature and pressure is illustrated in Figure 2(d). The equilibrium conversion between Fe and Fe(OH)2 is represented by reaction (3). Below the Fe clouds (kinks in abundance contours), the Fe(OH)2 abundance increases with total pressure, and has a strong \( m^3 \) dependence on metallicity (see Table 1).

The Fe(OH)2 abundance in reaction (3) is very sensitive to the H2O abundance since the formation of one mole of iron hydroxide requires two moles of water. As a result, there is a large shift in the Fe(OH)2 abundance contours above the clouds (inflections in Figure 2(d)) when moving between the CH4 and CO fields. Within each field, the Fe(OH)2 abundance above the clouds is essentially pressure independent (see Table 1) and is therefore, in principle, diagnostic of atmospheric temperature.

As shown in Figure 1, Fe(OH)2 becomes the most abundant Fe-bearing gas at low temperatures and high pressures in a solar composition gas. Iron hydroxide is therefore expected to be the most abundant iron gas at \( T \lesssim 1600 \) on Jupiter ([Fe/H] \approx +0.5) and \( T \lesssim 1070 \) on Gliese 229B. However, we emphasize that the amount of iron remaining in the gas is greatly diminished by the condensation of Fe metal at deeper atmospheric levels. For example, even where it is the most abundant Fe-bearing gas, the predicted Fe(OH)2 mole fraction is \( \sim 10^{-13} \) at the 1000 K level in Jupiter’s atmosphere.

3.2.5. Iron Monoxide, FeO

Mole fraction abundance contours for FeO are shown in Figure 2(e) for a solar composition gas. Monatomic iron reacts with water to form FeO via the net reaction

\[ \text{Fe} + \text{H}_2\text{O} = \text{FeO} + \text{H}_2. \]  

(15)

Between the H2–H boundary and the Fe cloud deck, \( X_{\text{FeO}} \) is proportional to \( m^2 \) and is independent of pressure (see Table 1). In principle, the FeO abundance in this region is therefore diagnostic of either temperature or metallicity. Above the clouds, the FeO abundance decreases with pressure and increases with metallicity. As for FeOH and Fe(OH)2, the FeO abundance is sensitive to the H2O abundance and the FeO abundance contours display a subtle shift along the CH4–CO equal-abundance boundary.

3.2.6. Iron Sulfide, FeS

The abundance of FeS gas as a function of temperature and pressure is illustrated in Figure 2(f). The chemical behavior of FeS is governed by the reaction between Fe and H2S:

\[ \text{Fe} + \text{H}_2\text{S} = \text{FeS} + \text{H}_2. \]  

(16)

Above the iron clouds, H2S is the dominant sulfur-bearing gas (log \( X_{\text{H}_2\text{S}} \approx -4.52 + [\text{Fe/H}] \)), and the FeS abundance is proportional to \( P_T^{-1} \) and \( m \) (see Table 1). Below the Fe cloud deck, the FeS abundance is \( \sim 10 \) ppb and decreases at higher temperatures and lower pressures as H2S is replaced by SH and S (Visscher et al. 2006). Iron sulfide is predicted to be the second or third most abundant iron gas throughout L dwarf atmospheres and in the upper atmospheres (<1500 K) of Pegasi planets.

3.3. Iron Chemistry in Substellar Objects

Figures 3(a)–(d) summarize the iron gas thermochemistry in four representative substellar objects: Jupiter, the T dwarf Gliese 229B, the Pegasi planet HD209458b, and an L dwarf (\( T_{\text{eff}} = 1800 \) K). Iron chemistry in substellar objects is strongly affected by Fe metal or liquid condensation at deep atmospheric levels. Monatomic Fe is the dominant Fe-bearing gas in the
Figure 3. Iron chemistry along the atmospheric pressure–temperature profile from 1000 to 2500 K for (a) Jupiter, (b) Gliese 229B, (c) HD209458b, and (d) an L dwarf ($T_{\text{eff}} = 1800$ K). The vertical lines labeled Fe in panels (b)–(d) indicate the iron condensation temperature. Iron is condensed throughout the entire temperature range shown here for Jupiter (a).

Deep atmospheres of Jupiter and Gliese 229B, and throughout the atmospheres of HD209458b and the L dwarf. A number of Fe-bearing gases become relatively more abundant in objects with lower effective temperatures. On Jupiter and Gliese 229B, Fe(OH)$_2$ replaces Fe at lower temperatures. The Fe(OH)$_2$ and FeO abundances are pressure independent and thus potentially diagnostic of atmospheric temperature, respectively, above and below the iron clouds. For all four objects, iron hydride (FeH) is the second most abundant Fe-bearing gas at deep atmospheric levels, until it is replaced at lower temperatures by Fe(OH)$_2$, FeOH, or FeS. Because of its strong absorption and relatively high abundance near the iron condensation level, FeH is a tracer of weather in brown dwarfs (e.g., Burgasser et al. 2002a). Other Fe-bearing gases (e.g., Fe, FeOH, and FeS) are potential tracers of weather since they typically achieve their maximum abundance near iron cloud base.

4. MAGNESIUM CHEMISTRY

4.1. Overview of Magnesium Chemistry

Figure 4 gives an overview of Mg chemistry as a function of pressure and temperature in a protosolar composition gas. The dotted lines labeled Mg$_2$SiO$_4$(s,l), MgSiO$_3$(s,l), and MgO(s) show the equilibrium condensation curves for forsterite, enstatite, and periclase, respectively, and the open circles denote the normal melting temperatures for forsterite (2163 K) and enstatite (1830 K). Forsterite (Mg$_2$SiO$_4$) condenses via the net thermochemical reaction

$$2\text{Mg} + 3\text{H}_2\text{O} + \text{SiO} = \text{Mg}_2\text{SiO}_4(\text{s,l}) + 3\text{H}_2,$$

and its condensation temperature as a function of pressure and metallicity is approximated by

$$10^4/T_{\text{cond}}(\text{Mg}_2\text{SiO}_4) \approx 5.89 - 0.37 \log P_T - 0.73[\text{Fe/H}],$$

At slightly lower temperatures, enstatite (MgSiO$_3$) condensation occurs via the net reaction

$$\text{Mg} + 2\text{H}_2\text{O} + \text{SiO} = \text{MgSiO}_3(\text{s,l}) + 2\text{H}_2.$$

The enstatite condensation curve is approximated by

$$10^4/T_{\text{cond}}(\text{MgSiO}_3) \approx 6.26 - 0.35 \log P_T - 0.70[\text{Fe/H}],$$

where higher pressures and/or metallicities lead to higher condensation temperatures. At very high pressures, forsterite
and enstatite condensation temperatures are depressed as SiO is replaced by SiH₄ (see Section 5.1). Periclase (MgO) condenses via the net thermochemical reaction

$$\text{Mg} + \text{H}_2 \text{O} = \text{MgO(s)} + \text{H}_2, \quad (21)$$

at pressures greater than 10^{3.5} bar. The condensation curve for akermanite (Ca₂MgSi₂O₇) is not shown here because most Ca is expected to be removed at deeper atmospheric levels by the condensation of refractory calcium aluminates (e.g., Lodders 2002). If no calcium is removed, Ca₂MgSi₂O₇ condensation would consume ~3% of the total atmospheric Mg inventory. In the same way, olivine ([Mg,Fe]₂SiO₄) and fayalite (Fe₂SiO₄) are not expected in substellar atmospheres because nearly all Fe is removed from the gas phase by iron metal condensation at higher temperatures (e.g., Cushing et al. 2006; Lodders & Fegley 2006).

Magnesium-silicate cloud formation is very effective at removing nearly all (>99%) magnesium from the atmosphere, and the abundances of Mg-bearing gases rapidly decrease with altitude above the clouds. This behavior is generally consistent with the disappearance of Mg spectral features by early-type L dwarfs (see Section 4.2.1). Furthermore, Cushing et al. (2006) find a Si–O absorption feature at 10 μm in mid-type L dwarfs which is consistent with the presence of silicate grains and a weak 9.17 μm feature tentatively attributed to crystalline enstatite.

Monatomic Mg is the dominant Mg-bearing gas in substellar atmospheres until it is replaced by Mg(OH)₂ at low temperatures and high pressures. The conversion between Mg and Mg(OH)₂ is represented by the net thermochemical reaction

$$\text{Mg} + 2\text{H}_2\text{O} = \text{Mg(OH)}_2 + \text{H}_2, \quad (22)$$

and the solid line in Figure 4 indicates where Mg and Mg(OH)₂ have equal abundances. The dotted lines labeled Mg₂SiO₄(s,l) and MgSiO₃(s,l) show the condensation temperatures of forsterite and enstatite, with circles denoting their normal melting points of 1803 K (enstatite) and 2002 K (forsterite). If no calcium is removed, Ca₂MgSi₂O₇ condensation is expected to be removed at deeper atmospheric levels by the condensation of refractory calcium aluminates (e.g., Lodders 2006).

At higher temperatures (e.g., Cushing et al. 2006; Lodders & Fegley 2006) Fe is removed from the gas phase by iron metal condensation moving nearly all (>99%) Fe to lower pressures.

### 4.2. Chemical Behavior of Magnesium-bearing Gases

#### 4.2.1. Monatomic Magnesium, Mg

Figure 5(a) shows the chemical behavior of monatomic Mg as a function of pressure and temperature in a solar-metallicity gas. The chemical behavior of Mg is strongly affected by silicate cloud formation. Below the forsterite clouds, the abundance of Mg gas is given by

$$\log P_T = 10.96 - 10267/T - 2\text{[Fe/H]}, \quad (23)$$

where an increase in metallicity shifts the Mg–Mg(OH)₂ boundary to higher temperatures and lower pressures.

### Magnesium Gas Abundances

| Gas | $X_M$ | Reaction No. |
|-----|------|--------------|
| Mg | $-4.15 + \text{[Fe/H]}$ | \ldots |
| MgH | $-5.46 - 4236/T + 0.5\log P_T + \text{[Fe/H]}$ | 27 |
| MgOH | $-8.98 + 1672/T + 0.5\log P_T + 2\text{[Fe/H]}$ | 28 |
| Mg(OH)₂ | $-15.54 + 10267/T + \log P_T + 3\text{[Fe/H]}$ | 22 |
| MgO | $-6.12 - 7306/T + 2\text{[Fe/H]}$ | 29 |
| MgS | $-7.94 + 2\text{[Fe/H]}$ | 30 |
| Mg₂SiO₄ | $8.25 - 27250/T - \log P_T - \text{[Fe/H]} - \log X_{\text{H}_2\text{O}}$ | 17, 19 |
| MgH | $6.94 - 31486/T - 0.5\log P_T - \text{[Fe/H]} - \log X_{\text{H}_2\text{O}}$ | 27 |
| MgOH | $6.75 - 25578/T - 0.5\log P_T$ | 28 |
| Mg(OH)₂ | $3.53 - 16983/T + \text{[Fe/H]} + \log X_{\text{H}_2\text{O}}$ | 22 |
| MgO | $9.63 - 34556/T - \log P_T$ | 29 |
| MgS | $4.40 - 27250/T - \log P_T - \log X_{\text{H}_2\text{O}}$ | 30 |

### Notes

$X_{\text{H}_2\text{O}}$ is defined as the H₂O mole fraction in a solar-metallicity gas, where log $X_{\text{H}_2\text{O}} = -3.12$ within the CH₄ field and $-3.58$ within the CO field. The effect of metallicity on the atmospheric water abundance ($X_{\text{H}_2\text{O}}$) is included in the abundance equations. Expressions are valid for temperatures between 800 and 2500 K and metallicities up to [Fe/H] = 0.5 dex.

$X_M = \frac{\text{Mg}_{\text{gas}}}{\text{H}_{\text{gas}}} + \log X_{\text{H}_2\text{O}}$ and Mg(OH)₂ have equal abundances $A($Mg$) = A($Mg(OH)₂$) = \frac{\Sigma \text{Mg}_{\text{gas}}}{2}$, where $\Sigma \text{Mg}_{\text{gas}}$ is the total amount of magnesium in the gas. The position of the equal-abundance line is given by

$$\log P_T = 10.96 - 10267/T - 2\text{[Fe/H]}, \quad (23)$$

and comprises nearly 100% of the total elemental Mg content in the atmosphere ($X_M \approx X_{\Sigma \text{Mg}}$). Upon forsterite and enstatite condensation, the magnesium gas abundance is governed by its vapor pressure over rock, represented by reactions (17) and (19).

Curvature in the Mg mole fraction contours in Figure 5(a) occurs to higher temperatures and lower pressures. The Mg abundance is therefore

$$\log X_M \approx -4.15 + [\text{Fe/H}], \quad (24)$$

in CH₄-dominated objects.

$$\log X_M \approx 11.37 - 27250/T - \log P_T - [\text{Fe/H}], \quad (25)$$

in CO-dominated objects. We can use these expressions along with chemical equilibria to determine the abundances of other Mg-bearing gases in substellar atmospheres. Equations giving the abundance of Mg-bearing gases as a function of pressure,
Figure 5. Mole fraction contours (on a logarithmic scale) for (a) monatomic magnesium (Mg), (b) magnesium hydride (MgH), (c) magnesium monohydroxide (MgOH), and (d) magnesium hydroxide (Mg(OH)$_2$), (e) magnesium monoxide (MgO), and (f) magnesium sulfide (MgS) at thermochemical equilibrium, as a function of pressure and temperature in a solar-metallicity gas. The kinks in the abundance contours occur at the condensation temperature of Mg$_2$SiO$_4$ (forsterite).

4.2.2. Magnesium Hydride, MgH

Mole fraction contours for MgH are illustrated in Figure 5(b). The MgH abundance is governed by equilibrium with monatomic Mg, via the net thermochemical reaction

$$\text{Mg} + 0.5\text{H}_2 \rightarrow \text{MgH}.$$  \hspace{1cm} (27)

Between the H$_2$–H boundary and the Mg-silicate cloud base, the MgH abundance is proportional to $P_T^{1.5}$ and $m^{-1}$ (see Table 2). In contrast, the MgH abundance above the magnesium-silicate clouds is proportional to $P_T^{-0.5}$ and $m^{-1}$. The sharp bends in the temperature, and metallicity in a protosolar composition gas are listed in Table 2.

Several Mg absorption lines are present in the near-infrared spectra of M dwarfs, including the prominent feature at 1.183 μm (Jones et al. 1996; McLean et al. 2003; Cushing et al. 2005). These features weaken in mid- to late-type M dwarfs and generally disappear by ~L1 (Cushing et al. 2005), consistent with the removal of magnesium into Mg$_2$SiO$_4$ and MgSiO$_3$ clouds located at increasingly greater depths below the observable atmosphere (e.g., see Lodders 2004; Lodders & Fegley 2006).
MgH abundance contours occur at the condensation temperature of forsterite. Slight inflections in the MgH abundance occur along the CH₄–CO boundary because the Mg abundance in reaction (27) is sensitive to the H₂O abundance in reactions (17) and (19). Magnesium hydride is an important opacity source from 0.44 to 0.56 μm (Weck et al. 2003), and MgH bands at 0.48 and 0.52 μm have been found in the optical spectra of bright L dwarfs and extreme subdwarfs (Kirkpatrick et al. 1999; Reid et al. 2000; Kirkpatrick 2005).

4.2.3. Magnesium Monohydroxide, MgOH

The chemical behavior of MgOH as a function of pressure and temperature is shown in Figure 5(c). The equilibrium abundance of MgOH is governed by the reaction

\[
\text{Mg} + \text{H}_2\text{O} = \text{MgOH} + 0.5\text{H}_2, \quad (28)
\]

decreasing with temperature and proportional to \( P^{0.5} \) and \( m^2 \) below the Mg-silicate clouds. The kinks in the MgOH contours occur where forsterite condenses. Above the clouds, \( X_{\text{MgOH}} \) is proportional to \( P_T^{0.5} \) (see Table 2). Interestingly, the MgOH abundance in this region is independent of metallicity and shows no shift at the CH₄–CO boundary because these effects cancel out in reaction (28). For example, the H₂O abundance slightly decreases when moving from the CH₄ to the CO field (e.g., Lodders & Fegley 2002). However, as can be seen by comparing Equations (25) and (26), there is a corresponding increase in the Mg abundance, so the resulting MgOH abundance in reaction (28) remains unaffected by carbon chemistry. Magnesium monohydroxide is typically the third most abundant Mg-bearing gas in substellar atmospheres.

4.2.4. Magnesium Hydroxide, Mg(OH)₂

Mole fraction abundance contours for Mg(OH)₂ are shown in Figure 5(d) for a solar-metallicity gas. The equilibrium conversion between Mg and Mg(OH)₂ is represented by reaction (22). Below the Mg-silicate clouds, the Mg(OH)₂ abundance decreases with temperature and pressure, and has a very strong \( (m^2) \) dependence on metallicity. Above the magnesium-silicate clouds (the kinks in Figure 5(d)), the Mg(OH)₂ abundance contours show inflections along the CH₄–CO boundary, because Mg(OH)₂ is sensitive to the water abundance in reaction (22). Within either the CH₄ or CO field, the Mg(OH)₂ abundance is pressure independent. In principle, the abundance of Mg(OH)₂ is therefore diagnostic of atmospheric temperature if the object’s metallicity is known.

At low temperatures and high pressures, Mg(OH)₂ becomes the most abundant Mg-bearing gas, as illustrated in Figure 4. Magnesium hydroxide is thus expected to be the dominant magnesium gas below \( \sim 1550 \) K in the atmosphere of Jupiter (cf. Feddy & Lodders 1994) and below \( \sim 980 \) K on Gliese 229B.

4.2.5. Magnesium Monoxide, MgO

The abundance of MgO as a function of pressure and temperature is illustrated in Figure 5(e). Magnesium monoxide forms via the net thermochemical reaction

\[
\text{Mg} + \text{H}_2\text{O} = \text{MgO} + \text{H}_2, \quad (29)
\]

Below the Mg-silicate cloud deck, at pressures less than \( \sim 10 \) bar, the MgO abundance is effectively pressure independent and is therefore potentially diagnostic of atmospheric temperature if the metallicity is known.

For similar reasons as for MgOH (see Section 4.2.3), the MgO abundance above the magnesium-silicate clouds is independent of metallicity and is unaffected by the CH₄–CO boundary. For example, the Mg abundance decreases with metallicity, as shown by Equations (25) and (26), whereas the H₂O abundance increases with metallicity. These effects cancel out in reaction (29), with the result that MgO is unaffected by changes in metallicity or the prevailing carbon chemistry.

4.2.6. Magnesium Sulfide, MgS

Figure 5(f) displays mole fraction contours for MgS in protosolar composition gas. The equilibrium abundance of MgS is governed by the reaction

\[
\text{Mg} + \text{H}_2\text{S} = \text{MgS} + \text{H}_2, \quad (30)
\]

Near the silicate cloud base, the MgS abundance is \( \sim 10 \) ppb in a solar-metallicity gas and decreases at higher temperatures and lower pressures as H₂S is replaced by monatomic S. Above the Mg-silicate clouds, \( X_{\text{MgS}} \) is proportional to \( P_T^{-1} \) and is metallicity independent (see Table 2). Magnesium sulfide is typically among the more abundant Mg-bearing gases in brown dwarfs and extrasolar giant planets (EGPs), and becomes the second most abundant magnesium gas at temperatures below \( \sim 1600 \) K in the atmospheres of L dwarfs and Pegasi planets.

4.3. Magnesium Chemistry in Substellar Objects

Figures 6(a)–(d) illustrate magnesium gas chemistry at thermochemical equilibrium along the pressure–temperature profiles of Jupiter, Gliese 229B, HD209458B, and an L dwarf (\( T_{\text{eff}} = 1800 \) K). Monatomic Mg is the dominant Mg-bearing gas throughout the atmospheres of Pegasi planets and L dwarfs, and in the deep atmospheres of giant planets and T dwarfs. Furthermore, the Mg abundance below the Mg-silicate cloud deck is essentially constant and representative of the total magnesium abundance in the atmosphere. Upon condensation, the abundances of magnesium-bearing gases rapidly decrease with decreasing temperature above the magnesium-silicate clouds. In objects with lower effective temperatures, a number of other Mg-bearing gases become relatively abundant and Mg(OH)₂ replaces Mg as the most abundant magnesium gas at the \( \sim 1550 \) K level on Jupiter and the \( \sim 980 \) K level on Gliese 229B. Magnesium hydride (MgH) is the second most abundant magnesium gas in the deep atmospheres of substellar objects until it is replaced at lower temperatures by Mg(OH)₂ and MgOH (in giant planets and T dwarfs) or MgS (in L dwarfs and Pegasi planets). Magnesium hydroxide (Mg(OH)₂) and MgO are potential probes of atmospheric temperature, respectively, above and below the magnesium-silicate clouds.

5. SILICON CHEMISTRY

5.1. Overview of Silicon Chemistry

An overview of silicon chemistry as a function of pressure and temperature is illustrated in Figure 7. The dotted lines labeled \( \text{Mg}_2\text{SiO}_4(s,l) \) and \( \text{MgSiO}_3(s,l) \) show the condensation temperatures of forsterite and enstatite, which together remove nearly all silicon from the overlying atmosphere. Cushing et al. (2006) found that silicate absorption features near 10 μm in mid-type L dwarf spectra are consistent with the presence of these magnesium silicates, but noted the possibility of additional
Figure 6. Magnesium chemistry along the atmospheric pressure–temperature profile from 1000 to 2500 K for (a) Jupiter, (b) Gliese 229B, (c) HD209458b, and (d) an L dwarf (T_{eff} = 1800 K). The vertical lines labeled Fo and En denote the condensation temperatures of forsterite (Mg_2SiO_4) and enstatite (MgSiO_3), respectively. Forsterite is condensed throughout the entire temperature range shown here for Jupiter (a).

absorption by quartz (SiO_2) grains based upon the predictions of Helling et al. (2006). In contrast to the models of Helling et al. (2006, 2008), we find that quartz will not condense in the atmospheres of substellar objects unless enstatite condensation is suppressed. This is demonstrated in Figure 8, which shows the elemental distribution of Si in condensed phases at 1 bar total pressure in a solar-metallicity gas with (Figure 8(a)) and without (Figure 8(b)) enstatite condensation. As shown in Figure 8, Mg_2SiO_4 formation consumes nearly half of the total Si abundance because the solar elemental abundances of Mg and Si are approximately equal. Enstatite formation plausibly proceeds via reactions between SiO gas and pre-existing forsterite grains and continues until nearly all silicon is consumed. Thus, quartz (T_{cond} ~ 1550 K) can only form in the absence of enstatite (T_{cond} ~ 1600 K), because MgSiO_3 otherwise efficiently removes silicon from the gas phase. Even in the absence of gas–grain reactions between SiO and Mg_2SiO_4, the vapor pressures of Mg and SiO above forsterite (reaction (17)) remain high enough to drive enstatite cloud formation via the net thermochemical reaction (19), so that MgSiO_3 condenses instead of SiO_2. We therefore conclude that SiO_2 will not condense within the silicate cloud.

The most abundant Si-bearing gas over a wide range of pressures and temperatures is SiO, until it is replaced at higher pressures by silane, SiH_4 (see Figure 7). The equilibrium conversion between SiO and SiH_4 is

\[ \text{SiH}_4 + \text{H}_2\text{O} = \text{SiO} + 3\text{H}_2. \]  

The position of the line where SiO and SiH_4 have equal abundances \( A(\text{SiO}) = A(\text{SiH}_4) \approx \frac{1}{2} \Sigma \text{Si}_{\text{gas}} \) (where \( \Sigma \text{Si}_{\text{gas}} \) is the total amount of silicon in the gas) is given by

\[ \log P_T = 4.68 - 3086/T + 0.5[\text{Fe/H}]. \]  

As temperatures decrease, SiH_4 is replaced by SiH_3F via the net thermochemical reaction

\[ \text{SiH}_4 + \text{HF} = \text{SiH}_3\text{F} + \text{H}_2. \]  

This reaction is independent of pressure and the position of the SiH_4–SiH_3F boundary is given by

\[ T = 6948/(7.24 - [\text{Fe/H}]). \]  

and occurs at \( T \sim 960 \) K in a solar-metallicity gas. Meanwhile, the equilibrium between SiO and SiH_3F is

\[ \text{SiO} + \text{HF} + 2\text{H}_2 = \text{SiH}_3\text{F} + \text{H}_2\text{O}. \]
where the position of the SiO–SiH₃F line is given by

$$\log PT = 8.30 - 6560/T,$$  \hspace{1cm} (36)  

independent of the metallicity. The SiH₄–SiO, SiH₄–SiH₃F, and SiO–SiH₃F equal-abundance lines intersect to form a “triple point” at $T \sim 960$ K and $PT \sim 10^{1.47}$ bar in solar-metallicity gas, where all three gases have equal abundances $[A(SiO) = A(SiH_{3}F) \approx \Sigma Si_{gas}].$

At lower temperatures, SiH₂F₂ replaces SiH₃F via the net thermochemical reaction

$$SiH_{3}F + HF \rightarrow SiH_{2}F_{2} + H_{2},$$  \hspace{1cm} (37)

This reaction is also independent of pressure and the SiH₃F–SiH₂F₂ boundary is given by

$$T = 7040/(7.68 - [Fe/H]),$$  \hspace{1cm} (38)

and is located at $T \sim 917$ K in a solar-metallicity gas. The conversion between SiO and SiH₂F₂ takes place by the reaction

$$SiO + HF + H_2 \rightarrow SiH_{2}F_{2} + H_{2}O,$$  \hspace{1cm} (39)

where the position of the SiO–SiH₂F₂ boundary is given by

$$\log PT = 12.14 - 10080/T - 0.5[Fe/H].$$  \hspace{1cm} (40)

In a solar-metallicity gas, Equations (36) and (40) intersect to form the SiO–SiH₃F–SiH₂F₂ “triple point” at $T \sim 917$ K and $PT \sim 10^{1.15}$ bar, where all three gases have equal abundances. However, the abundances of SiH₃F and SiH₂F₂ in this region are extremely low ($X \sim 10^{-19}$ for $[Fe/H] = 0$) because most silicon is removed from the atmosphere by cloud formation at deeper levels.

5.2. Chemical Behavior of Silicon-bearing Gases

5.2.1. Silicon Monoxide, SiO

The chemical behavior of SiO in a protosolar composition gas is illustrated in Figure 9 as a function of pressure and temperature. Within the SiO field, the SiO abundance below the magnesium-silicate clouds is given by

$$\log X_{SiO} \approx -4.20 + [Fe/H],$$  \hspace{1cm} (41)

and SiO contains $\sim 100\%$ of the atmospheric silicon inventory ($X_{SiO} \approx X_{Si}$). Upon Mg-silicate condensation, silicon is efficiently removed from the gas phase and the SiO abundance rapidly decreases with decreasing temperature. Above the clouds, the SiO abundance is governed by its vapor pressure over rock. Curvature in the SiO contour lines along the CH₄–CO equal-abundance boundary results from the effect of carbon chemistry on the H₂O abundance in reactions (17) and (19). The SiO abundance is thus

$$X_{SiO} \approx 13.21 - 28817/T - \log PT - [Fe/H],$$  \hspace{1cm} (42)
in CH$_4$-dominated objects and

$$X_{\text{SiO}} \approx 13.67 - 28817/T - \log P_T - [\text{Fe/H}],$$  (43)

in CO-dominated objects, inversely proportional to pressure and metallicity. These expressions, along with chemical equilibria, are used to determine the equilibrium abundances of other Si-bearing gases. Expressions giving the abundances of silicon species as a function of temperature, pressure, and metallicity in a protosolar composition gas are listed in Table 3. We note that the types of cloud condensates present will affect the gas chemistry of SiO and subsequently all other Si-bearing gases. For example, as shown in Figure 10, SiO mole fraction abundances above the clouds are $\sim$0.5 dex higher if enstatite formation is suppressed and replaced by SiO$_2$ condensation (see Section 5.1). The SiO abundance is therefore potentially diagnostic of weather and cloud composition in brown dwarf atmospheres.

Silicon monoxide has not yet been detected in the atmospheres of brown dwarfs or giant planets, but has been observed in numerous objects (e.g., Campbell et al. 1995, and references therein), including molecular clouds, circumstellar envelopes, and sunspots, and in the photospheres of late-type stars (near $4 \mu$m; e.g., Wollman et al. 1973; Hinkle et al. 1976; Rinsland & Wing 1982). Abundant SiO gas was recently detected (by excess emission near $8 \mu$m) in the circumstellar disk of the β Pic analog HD172555 (Lisse et al. 2009).

### 5.2.2. Silicon Monosulfide, SiS

Mole fraction contours for SiS are shown in Figure 11(a) for a solar-metallicity gas. Silicon monosulfide is formed by the reaction between SiO and H$_2$S:

$$\text{SiO} + \text{H}_2\text{S} \rightarrow \text{SiS} + \text{H}_2\text{O}. \quad (44)$$

Below the Mg-silicate cloud deck, $X_{\text{SiS}} \sim 5$–10 ppm in a solar-metallicity gas. The SiS abundance decreases at higher temperatures and lower pressures as H$_2$S is replaced by SH and monatomic S (e.g., Visscher et al. 2006).

Above the clouds, the SiS abundance is inversely proportional to metallicity and total pressure (see Table 3). The SiS abundance contours in Figure 11(a) also display curvature along the CH$_4$–CO boundary. This shift is more pronounced for SiS than for SiO because the SiS abundance in reaction (44) depends on the SiO and H$_2$O abundances, both of which are affected by carbon chemistry. For example, when reaction (44) is at equilibrium, LeChâtelier’s principle shows that more SiS is produced either by adding SiO (or H$_2$S) or removing H$_2$O. When moving from the CH$_4$ field to the CO field in a protosolar composition gas, the SiO abundance increases and the H$_2$O abundance decreases, yielding a correspondingly large increase in the SiS abundance. Silicon sulfide is expected to be the second most

| Reaction No. | Below magnesium-silicate clouds; within SiO field |
|--------------|--------------------------------------------------|
| SiO          | $-4.20 + [\text{Fe/H}]$                         |
| SiS          | $-5.59 + 666/\text{T} + 2[\text{Fe/H}]$         |
| Si           | $-0.44 - 44738/\text{T}$                        |
| SiH          | $-2.64 - 11500/\text{T} + 0.5 \log P_T$         |
| SiH$_2$      | $-5.83 - 6422/\text{T} + \log P_T$              |
| SiH$_3$      | $-8.97 - 2770/\text{T} + 1.5 \log P_T$         |
| SiH$_4$      | $-13.33 + 6172/\text{T} + 2 \log P_T$          |
| SiH$_2$F     | $-20.57 + 13120/\text{T} + 2 \log P_T + [\text{Fe/H}]$ |
| SiH$_2$F$_2$ | $-28.25 + 20160/\text{T} + 2 \log P_T + 2[\text{Fe/H}]$ |

Notes: $X_{\text{H}_2\text{O}}$ is defined as the H$_2$O mole fraction in a solar-metallicity gas, where $\log X_{\text{H}_2\text{O}} \approx -3.12$ within the CH$_4$ field and $\approx -3.58$ within the CO field. The effect of metallicity on the atmospheric water abundance ($X_{\text{H}_2\text{O}}$) is included in the abundance equations. Expressions are valid for temperatures between 800 and 2500 K and metallicities up to [Fe/H] = +0.5 dex.
Figure 11. Mole fraction contours (on a logarithmic scale) for (a) silicon monosulfide (SiS), (b) monatomic silicon (Si), (c) silylidyne (SiH), (d) silylene (SiH₂), (e) the silyl radical (SiH₃), and (f) silane (SiH₄) at thermochemical equilibrium, as a function of pressure and temperature in a solar-metallicity gas. The bends in the abundance contours occur where magnesium-silicate clouds (MgSiO₃, Mg₂SiO₄) condense.

5.2.3. Monatomic Silicon, Si

Figure 11(b) illustrates the chemical behavior of monatomic Si gas as a function of pressure and temperature. The abundance of Si is governed by the net thermochemical reaction

$$\text{SiO} + \text{H}_2 = \text{Si} + \text{H}_2\text{O}. \quad (45)$$

Below the Mg-silicate cloud deck and at pressures less than ~10 bar, the Si abundance is effectively independent of pressure and metallicity and thus potentially diagnostic of atmospheric temperature. Above the clouds, the Si abundance rapidly decreases with decreasing temperature and is proportional to $P_T^{-1}$ and $m^{-2}$ (see Table 3). A number of Si absorption bands are observed in the near-infrared spectra of low-mass dwarf stars. These features...
generally weaken and disappear in late-type M dwarfs (Cushing et al. 2005), consistent with the removal of silicon into Mg$_2$SiO$_4$ and MgSiO$_3$ clouds deeper in the atmosphere.

5.2.4. Silyldyne, SiH

The abundance of SiH as a function of pressure and temperature is illustrated in Figure 11(c). The SiH abundance is governed by the net thermochemical reaction

$$\text{SiO} + 1.5\text{H}_2 = \text{SiH} + \text{H}_2\text{O}.$$  

(46)

Below the Mg-silicate clouds, the SiH abundance is proportional to $P_T^{1.5}$ and is independent of metallicity. Above the clouds, the SiH abundance is proportional to $P_T^{-0.5}$ and $m^{-2}$ (see Table 3). When moving from the CH$_4$ to the CO field, the SiO abundance increases and the H$_2$O abundance decreases in reaction (46). Both effects serve to increase the SiH abundance, resulting in a shift in the SiH contour lines along the CH$_4$–CO boundary. The $m^{-2}$ dependence on metallicity means that for every [Fe/H] = +1 dex increase in metallicity, the SiH abundance decreases by a factor of 100 at a given pressure and temperature.

5.2.5. Silylene, SiH$_2$

Mole fraction contours for SiH$_2$ are shown in Figure 11(d). The equilibrium between SiO and SiH$_2$ is given by the reaction

$$\text{SiO} + 2\text{H}_2 = \text{SiH}_2 + \text{H}_2\text{O}.$$  

(47)

Beneath the magnesium-silicate cloud deck, the metallicity-independent silylene abundance increases with total pressure. Upon rock condensation, the amount of SiH$_2$ remaining in the gas rapidly decreases with decreasing temperature. As for SiH, the SiH$_2$ abundance is sensitive to the SiO and H$_2$O abundances in reaction (47) and thus a shift occurs in the SiH$_2$ contour lines when moving between the CH$_4$ and CO fields. Within each field, the SiH$_2$ abundance is pressure independent (see Figure 11 and Table 3), and thus potentially diagnostic of temperature if the metallicity is known and SiH$_2$ is thermochemical in origin.

5.2.6. Silyl Radical, SiH$_3$

The chemical behavior of the SiH$_3$ radical in a solar-metallicity gas is illustrated in Figure 11(e). The abundance of SiH$_3$ is governed by the reaction

$$\text{SiO} + 2.5\text{H}_2 = \text{SiH}_3 + \text{H}_2\text{O}.$$  

(48)
Between the H2–H boundary and the Mg-silicate cloud base, the SiH4 abundance is proportional to $P^{-1.5}_T$. Above the clouds, the SiH3 abundance is proportional to $P^{-1.5}_T$ and $m^{-2}$ (see Table 3). There is curvature in the SiH3 contour lines along the CH4–CO boundary because the prevailing carbon chemistry affects both the SiO and H2O abundances in reaction (48).

5.2.7. Silane, SiH4

Mole fraction abundance contours for SiH4 are illustrated in Figure 11(f). The equilibrium conversion between SiO and SiH4 is represented by reaction (31), and expressions giving the SiH4 abundance as a function of pressure, temperature, and metallicity are listed in Table 3. Below the clouds, the silane abundance has a strong ($P^{-2}_T$) dependence on total pressure. Upon Mg-silicate cloud formation, there is an inflection in the SiH4 contour lines, and the SiH4 abundance above the clouds is proportional to $P_T$ and $m^{-2}$. Curvature in the SiH4 contour lines along the CH4–CO boundary results from the effect of carbon chemistry on the SiO and H2O abundances in reaction (31).

At high pressures and temperatures ($>960$ K for [Fe/H] = 0), SiH4 becomes the most abundant silicon-bearing gas. We thus expect SiH4 to be the dominant silicon gas below the 1031 K level in the deep atmosphere of Jupiter ([Fe/H] $\approx +0.5$). However, we again emphasize the efficiency with which rock condensation removes silicon from the gas, and we expect an abundance of $X_{\text{SiH}_4} \sim 10^{-17}$ near the 1031 K level on Jupiter. At lower temperatures, SiH4 is surpassed by SiH3F and SiH2F2. Silane is expected to be the third most abundant Si-bearing gas in the deep atmosphere of Gliese 229B.

We also point out the trend in pressure dependence for the silicon hydrides below ($X_{\text{SiH}_4} \propto P^{-0.5}_T$, $X_{\text{SiH}_3} \propto P^{-1}_T$, $X_{\text{SiH}_2} \propto P^{-1.5}_T$, and $X_{\text{SiH}} \propto P^{-2}_T$) and above the silicate clouds ($X_{\text{SiH}_4} \propto P^{-0.5}_T$, $X_{\text{SiH}_3} \propto P^{-0.5}_T$, $X_{\text{SiH}_2} \propto P^{-1.5}_T$, and $X_{\text{SiH}} \propto P^{-2}_T$), which is evident in the shapes of the contour lines in Figures 11(c)–(f). The abundance of each of the silicon hydrides is metallicity independent below the Mg-silicate clouds and proportional to $m^{-2}$ above the clouds.

5.3. Silicon Chemistry in Substellar Atmospheres

Figures 12(a)–(d) summarize the chemical behavior of silicon gases, as predicted by thermochemical equilibrium, along the pressure–temperature profiles of Jupiter, the T dwarf Gliese 229B, the Pegasi planet HD209458b, and an L dwarf ($T_{\text{eff}} = 1800$ K). There is a clear trend in silicon chemistry as a function of effective temperature. On Jupiter, SiH4 is the dominant Si-bearing gas throughout the deep atmosphere, and is replaced by SiH3F and SiH2F2 at lower temperatures (see Figure 7). The second most abundant Si-bearing gas is SiO, followed by SiS and a number of other silicon gases. In the warmer atmosphere of Gliese 229B, SiO is the dominant Si-bearing gas, followed by SiS and SiH4. The relative importance of SiH4 decreases with increasing effective temperature, and SiO and SiS are the most important silicon gases throughout the atmospheres of Pegasi planets and L dwarfs. The abundances of all the silicon gases shown in Figure 12 rapidly decrease with decreasing temperature above the silicate clouds, which explains the nondetection of SiH4 and other silicon species in the atmospheres of Jupiter and Saturn. Silylene (SiH2) and monatomic silicon (Si) are potentially diagnostic of atmospheric temperature above and below, respectively, the magnesium-silicate clouds. The important silicon gases SiO and SiS typically achieve their maximum abundance just below the cloud base and are therefore potential tracers of weather in brown dwarfs and Pegasi planets.

6. SUMMARY

Thermochemical equilibrium calculations provide a very good first-order approximation of the chemical behavior of Fe, Mg, and Si in the atmospheres of substellar objects. The chemical behavior of iron species in substellar atmospheres is strongly affected by Fe metal condensation, which efficiently removes most iron from the gas phase. Similarly, most magnesium and silicon is removed from the gas by forsterite (Mg2SiO4) and enstatite (MgSiO3) cloud formation. The equilibrium abundances of Fe-, Mg-, and Si-bearing gases rapidly decrease with increasing altitude (and decreasing temperature) above the clouds.

Monatomic iron is the dominant Fe-bearing gas throughout the atmospheres of L dwarfs and Pegasi planets. Other less abundant iron gases become increasingly important in objects with lower effective temperatures, and Fe(OH)2 replaces Fe at low temperatures in T dwarfs and giant planets. Magnesium gas chemistry is similar to that of iron. Monatomic Mg is the most abundant magnesium gas throughout the atmospheres of L dwarfs and Pegasi planets and in the deep atmospheres of giant planets and T dwarfs, where Mg is replaced by Mg(OH)2 at lower temperatures. A number of Mg-bearing gases become relatively abundant with decreasing effective temperature. Silicon monoxide (SiO) is the most abundant Si-bearing gas, followed by SiS, through the atmospheres of L dwarfs and Pegasi planets and in the deep atmospheres of T dwarfs. In objects with lower effective temperatures, a number of other silicon gases become increasingly important and SiH4 is the dominant silicon gas in the deep atmosphere of Jupiter. At high pressures and low temperatures, SiH4 and SiO are replaced by SiH3F and/or SiH2F2.

The abundances of several Fe-, Mg-, and Si-bearing gases are pressure independent and thus, in principle, diagnostic of atmospheric temperature. These include Fe(OH)2, Mg(OH)2, and Si below the clouds and FeO, MgO, and SiO2 above the clouds. In addition, a number of gases (e.g., Fe, FeH, FeOH, FeS, Mg, MgH, MgOH, MgS, SiO, and SiS) may serve as indicators of weather since they generally reach their maximum abundance just below the iron metal or magnesium-silicate cloud decks. This may be particularly useful for late M dwarfs and early L dwarfs in which the metal and silicate clouds are located at relatively shallow depths below the photosphere.

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