

ATMOSPHERIC CHEMISTRY IN GIANT PLANETS, BROWN DWARFS, AND LOW-MASS DWARF STARS. II. SULFUR AND PHOSPHORUS

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Received 2005 October 28; accepted 2006 May 25

ABSTRACT

Thermochemical equilibrium and kinetic calculations are used to model sulfur and phosphorus chemistry in giant planets, brown dwarfs, and extrasolar giant planets (EGPs). The chemical behavior of individual S- and P-bearing gases and condensates is determined as a function of pressure, temperature, and metallicity. The results are independent of particular model atmospheres, and in principle, the equilibrium composition along the pressure-temperature profile of any object can be determined. Hydrogen sulfide (H_2S) is the dominant S-bearing gas throughout substellar atmospheres and approximately represents the atmospheric sulfur inventory. Silicon sulfide (SiS) is a potential tracer of weather in substellar atmospheres. Disequilibrium abundances of phosphine (PH_3) approximately representative of the total atmospheric phosphorus inventory are expected to be mixed upward into the observable atmospheres of giant planets and T dwarfs. In hotter objects, several P-bearing gases (e.g., P_2 , PH_3 , PH_2 , PH , and HCP) become increasingly important at high temperatures.

Subject headings: astrochemistry — planets and satellites: individual (Jupiter) — stars: individual (Gliese 229B, HD 209458) — stars: low-mass, brown dwarfs

1. INTRODUCTION

The relatively cool, dense atmospheres of substellar objects—gas giant planets, brown dwarfs, and extrasolar giant planets (EGPs)—are ideal environments for the formation of molecules and condensates and the establishment of equilibrium chemistry. For this reason, thermochemical models have been essential for interpreting and guiding spectroscopic observations of the atmospheres of giant planets (e.g., see Lewis 1969a, 1969b; Barshay & Lewis 1978; Fegley & Lewis 1979; Fegley & Prinn 1985, 1988; Fegley et al. 1991; Fegley & Lodders 1994) and brown dwarfs (e.g., Fegley & Lodders 1996). These models have also been useful for explaining how the optical and infrared spectra of substellar objects are influenced by CNO (Lodders & Fegley 2002), alkali (Lodders 1999a), Ti and V (Lodders 2002), and condensation (e.g., Lodders & Fegley 2006) chemistry.

After H, C, N, and O, sulfur and phosphorus are the next most abundant chemically reactive volatile elements in a solar system composition gas. Fegley & Lodders (1994, hereafter FL94) modeled the chemistry of all naturally occurring elements, including S and P, along the atmospheric profiles of Jupiter and Saturn. Recently, Lodders & Fegley (2002; hereafter LF02) modeled the CNO chemistry in substellar objects as a function of pressure, temperature, and metallicity. Here we continue and extend these studies by employing thermochemical equilibrium and kinetic calculations to model sulfur and phosphorus chemistry in the atmospheres of substellar objects.

Our approach is similar to that of LF02. We compute the chemistry of S- and P-bearing gases and condensates as a function of total pressure, temperature, and metallicity, and our abundance results are *independent* of any particular atmospheric profile. In principle, the pressure-temperature profile for any substellar object may be superimposed on our abundance contour diagrams to find the equilibrium composition along the profile.

The paper is organized as follows. In § 2 we describe our computational methods. In § 3 we describe sulfur chemistry in a solar system composition gas: we identify major gases and

condensates and discuss the chemistry of individual S-bearing species as a function of total pressure, temperature, and metallicity. We then apply our results by examining the sulfur species along the atmospheric profiles of representative substellar objects. A similar treatment of phosphorus chemistry follows in § 4. We discuss the relative roles of thermochemistry and photochemistry in § 5, and we conclude with a brief summary (§ 6).

2. COMPUTATIONAL METHODS

Thermochemical equilibrium calculations were performed using a Gibbs free energy minimization code, previously used for modeling the atmospheric chemistry of Saturn (Visscher & Fegley 2005). Where relevant, we considered the effects of vertical mixing on the abundances of gases (e.g., PH_3) that serve as chemical probes of the deep atmospheres of Jupiter and Saturn. This was done using a chemical dynamical model described in Fegley & Prinn (1985). We generally focus on temperatures of 1000 K and higher, where thermochemistry is expected to be much more important than photochemistry in the atmospheres of extrasolar giant planets close to their primary stars. Further discussion of thermochemical versus photochemical processes is given in § 5.

Thermodynamic data for the equilibrium calculations were taken from the compilations of Gurvich et al. (1989), Robie & Hemingway (1995), the fourth edition of the JANAF Tables (Chase 1998), and the thermodynamic database maintained in the Planetary Chemistry Laboratory (FL94; LF02). This database includes additional thermodynamic data from the literature for compounds absent from the other compilations, as well as several important data revisions for the sulfur and phosphorus species SH, S_2O , NS, PS, PH, PH_3 , PN, and $\text{Mg}_3\text{P}_2\text{O}_8(\text{s})$, which are incorrect in the JANAF tables (Lodders 1999b, 2004a). Thermodynamic data for P_4O_6 were taken from the JANAF tables for reasons cited in FL94.

All calculations were done with solar system (i.e., protosolar) elemental abundances from Lodders (2003). The effect of

metallicity on sulfur and phosphorus chemistry was examined by running computations at $[M/H] = -0.5$ dex (subsolar), $[M/H] = 0$ dex (solar), and $[M/H] = +0.5$ dex (enhanced) metallicities, where M is any element of interest (e.g., S, P, C, or O).¹ The metallicity factor, m , is defined as $\log m = [M/H]$. Stellar abundance determinations show that element abundance ratios $[M/H]$ for elements of interest here vary similarly to $[Fe/H]$ in the range $-0.5 \leq [Fe/H] \leq +0.5$ dex (Edvardsson et al. 1993; Gustafsson et al. 1999; Chen et al. 2000; Smith et al. 2001; Ecuivillon et al. 2004; Huang et al. 2005), consistent with what one may expect from Galactic chemical evolution models (e.g., Timmes et al. 1995). The slopes for fits of $[M/H]$ versus $[Fe/H]$ are about 0.61, 0.65, and 0.6 for $M = C, S,$ and O , respectively, which justifies our approach of “uniform” metallicity variations for these elements (e.g., $[S/H] \approx [P/H] \approx [C/H] \approx [O/H] \equiv [M/H]$) over the metallicity range considered here. Because phosphorus has weak lines, Galactic chemical evolution models are used to estimate P abundances as a function of metallicity (e.g., Timmes et al. 1995; Samland 1998). We thus assume a similar enrichment in phosphorus as for other heavy elements. However, the effects of metallicity on chemical equilibrium abundances are explicitly treated below and can be used to study effects from nonuniform elemental abundance enrichments.

For each S- and P-bearing species, we discuss how the most plausible representative net thermochemical formation reaction depends on temperature, total pressure, and metallicity. For example, consider the formation of the thioxophosphino radical (PS) via the net thermochemical reaction



This endothermic reaction proceeds toward the right with increasing temperature and the PS abundance increases. According to LeChâtelier’s principle, this reaction also proceeds toward the right with decreasing pressure, because there are 2 gas molecules on the left and 3.5 gas molecules on the right. Writing out the equilibrium constant (K_p) expression for PS in terms of the total pressure (P_T) and mole fractions,²

$$X_{PS} = (X_{PH_3}X_{H_2S}/X_{H_2}^{2.5})K_pP_T^{-1.5},$$

shows that the mole fraction of PS is proportional to $P_T^{-1.5}$. The metallicity dependence of X_{PS} enters only through the PH_3 and H_2S abundances, whereas the H_2 abundance is metallicity independent by definition. Phosphine and H_2S are typically the most abundant P- and S-bearing gases, respectively. Hence, X_{PH_3} and X_{H_2S} must each be expanded with a metallicity factor m , which results in an overall m^2 metallicity dependence for X_{PS} , assuming $[S/H] = [P/H]$ (see above). This basic approach is used to describe the equilibrium chemical behavior of each S- and P-bearing species throughout the paper.

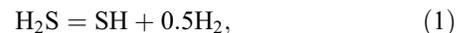
3. SULFUR CHEMISTRY

3.1. Sulfur Gas Chemistry

The sulfur equilibrium gas chemistry as a function of temperature and total pressure in a protosolar composition gas is illustrated in Figure 1. The most abundant gases are H_2S , SH, and monatomic S, and the P - T regions where each gas is dominant are

bounded by solid lines. Also shown are condensation curves (*dotted lines*) for S-bearing condensates (see § 3.2) and the $H_2 = H$ and $CH_4 = CO$ equal abundance curves (*dash-dotted lines*). Model atmosphere profiles for Jupiter ($T_{\text{eff}} = 124$ K, $\log g = 3.4$), the T dwarf Gliese 229B ($T_{\text{eff}} = 960$ K, $\log g = 5.0$; Marley et al. 1996), the close-orbiting EGP (or “Pegasi” planet) HD 209458b ($T_{\text{eff}} = 1350$ K, $\log g = 3.0$; Iro et al. 2005), an L dwarf ($T_{\text{eff}} = 1800$ K, $\log g = 5.0$; Burrows et al. 2006), and an M dwarf ($T_{\text{eff}} = 2600$ K, dust-free, $\log g = 5.0$; Tsuji et al. 1996) are indicated by dashed lines. The overall chemistry in the atmospheres of Jupiter and Gliese 229B differs slightly from the chemistry of a solar metallicity gas, because Jupiter has a heavy-element enrichment comparable to $[M/H] \approx +0.5$ dex (Lodders 1999a; LF02), whereas Gliese 229B likely has a subsolar metallicity of $[M/H] \approx -0.3$ dex (Saumon et al. 2000); their P - T profiles are shown here for reference. However, as described below, the P - T boundaries for the sulfur gases in Figure 1 are metallicity independent. This is because the P - T boundaries are defined by equal abundance *ratios* of the neighboring gases (e.g., H_2S/SH , SH/S , and H_2S/S), so that the metallicity dependence cancels out.

Hydrogen sulfide (H_2S) is the dominant S-bearing gas in substellar atmospheres under most P - T conditions considered here. The absolute H_2S abundance is of course metallicity dependent (see § 3.1.1). At high temperatures and low pressures, H_2S is replaced by SH via the net thermochemical reaction



and SH becomes the dominant sulfur gas. The equilibrium constant expression for reaction (1) is

$$K_1 = (X_{SH}X_{H_2}^{0.5}/X_{H_2S})P_T^{0.5}. \quad (2)$$

Rearranging and substituting for the temperature dependence of K_1 ($\log K_1 = 3.37 - 8785/T$ from 800 to 2500 K), the H_2S/SH ratio is given by

$$\log \left(\frac{X_{H_2S}}{X_{SH}} \right) = -3.37 + \frac{8785}{T} + 0.5 \log P_T + 0.5 \log X_{H_2}. \quad (3)$$

The H_2S/SH ratio is independent of metallicity, because the m dependence of each S-bearing gas in reaction (1) cancels out and the H_2 abundance is essentially constant ($X_{H_2} \approx 0.84$) over small metallicity variations. The solid line separating the H_2S and SH fields in Figure 1 shows where these two gases have equal abundances. With $X_{H_2S}/X_{SH} = 1$ and $X_{H_2} \approx 0.84$, equation (3) can be rewritten to give the $H_2S = SH$ equal abundance boundary,

$$\log P_T = 6.82 - 17,570/T, \quad (4)$$

which is independent of metallicity. The abundance of each sulfur gas does not drop to zero as this line is crossed; H_2S is still present within the SH field, and vice versa (see § 3.1.2).

With increasing temperatures, SH dissociates and monatomic S becomes the dominant sulfur-bearing gas via



Using $\log K_5 = 2.36 - 7261/T$ from 800 to 2500 K and rearranging, the SH/S abundance ratio is given by

$$\log \left(\frac{X_{SH}}{X_S} \right) = -2.36 + \frac{7261}{T} + 0.5 \log P_T + 0.5 \log X_{H_2}. \quad (6)$$

¹ We use the conventional notation $[M/H] \equiv \log(M/H) - \log(M/H)_{\text{solar}}$.

² The mole fraction abundance for a gas i is defined as $X_i = (\text{moles } i) / (\text{total moles of all gases})$.

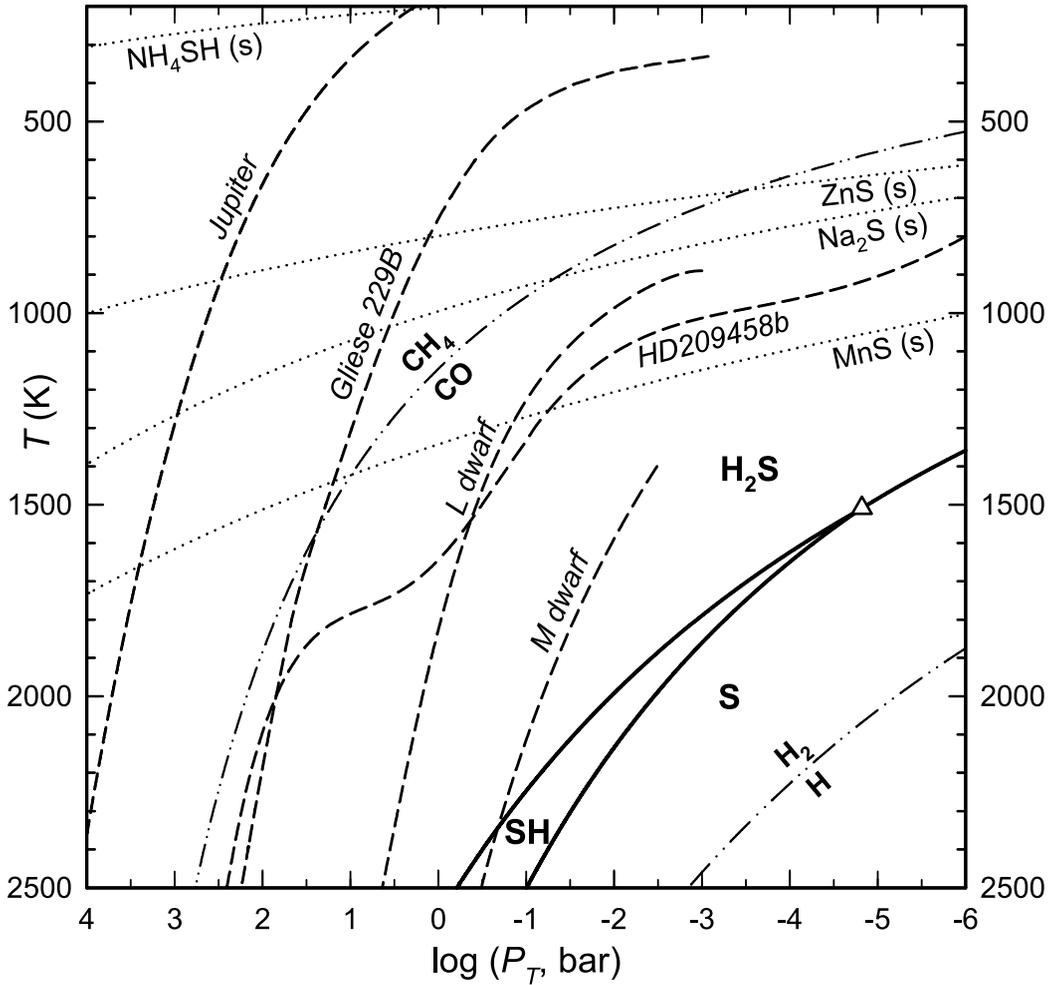


FIG. 1.—Overview of sulfur chemistry as a function of temperature and pressure in a solar system composition gas. The solid lines indicate where major S-bearing gases have equal abundances. The triangle denotes the position of the triple point where H_2S , SH , and S have equal abundances. Also shown are condensation curves for S-bearing compounds (*dotted lines*) and the $\text{H}_2 = \text{H}$ and $\text{CH}_4 = \text{CO}$ equal abundance lines (*dash-dotted lines*). Atmospheric profiles (*dashed lines*) are given for Jupiter ($T_{\text{eff}} = 124 \text{ K}$), Gliese 229B ($T_{\text{eff}} = 960 \text{ K}$), HD 209458b ($T_{\text{eff}} = 1350 \text{ K}$), an L dwarf ($T_{\text{eff}} = 1800 \text{ K}$), and an M dwarf ($T_{\text{eff}} = 2200 \text{ K}$).

This ratio is also independent of metallicity, because the m dependence of each S-bearing gas in reaction (5) cancels out. With $X_{\text{SH}}/X_{\text{S}} = 1$ and $X_{\text{H}_2} \approx 0.84$, equation (6) is rewritten to give the position of the metallicity-independent $\text{SH} = \text{S}$ equal abundance line,

$$\log P_T = 4.80 - 14,522/T. \quad (7)$$

At the lowest total pressures considered here, monatomic S is the major sulfur gas (see Fig. 1). At temperatures below $\sim 1509 \text{ K}$, H_2S directly converts to monatomic S via the net thermochemical reaction



The $\text{H}_2\text{S}/\text{S}$ abundance ratio follows from adding equations (3) and (6), as

$$\log\left(\frac{X_{\text{H}_2\text{S}}}{X_{\text{S}}}\right) = -5.73 + \frac{16,046}{T} + \log P_T + \log X_{\text{H}_2}, \quad (9)$$

and is independent of metallicity. Again, with $X_{\text{H}_2\text{S}}/X_{\text{S}} = 1$ and $X_{\text{H}_2} \approx 0.84$, the metallicity-independent position of the $\text{H}_2\text{S} = \text{S}$ boundary is approximated by

$$\log P_T = 5.81 - 16,046/T. \quad (10)$$

The $\text{H}_2\text{S} = \text{SH}$, $\text{SH} = \text{S}$, and $\text{H}_2\text{S} = \text{S}$ boundaries intersect at the H_2S - SH - S “triple point” at $T \sim 1509 \text{ K}$ and $P_T \sim 10^{-4.82}$ bars, indicated by the triangle in Figure 1 and represented by the net thermochemical equilibrium



The P - T position of the triple point is independent of metallicity, because the intersecting boundaries in equations (4), (7), and (10) are each independent of metallicity. At the triple point, all three gases have equal abundances $A(\text{H}_2\text{S}) = A(\text{SH}) = A(\text{S}) \approx \frac{1}{3}\Sigma\text{S}$ (where ΣS is the total elemental sulfur abundance) of one-third of the total sulfur abundance.

As noted above, the H_2 abundance is essentially constant ($X_{\text{H}_2} \approx 0.84$) over the small metallicity range considered here.

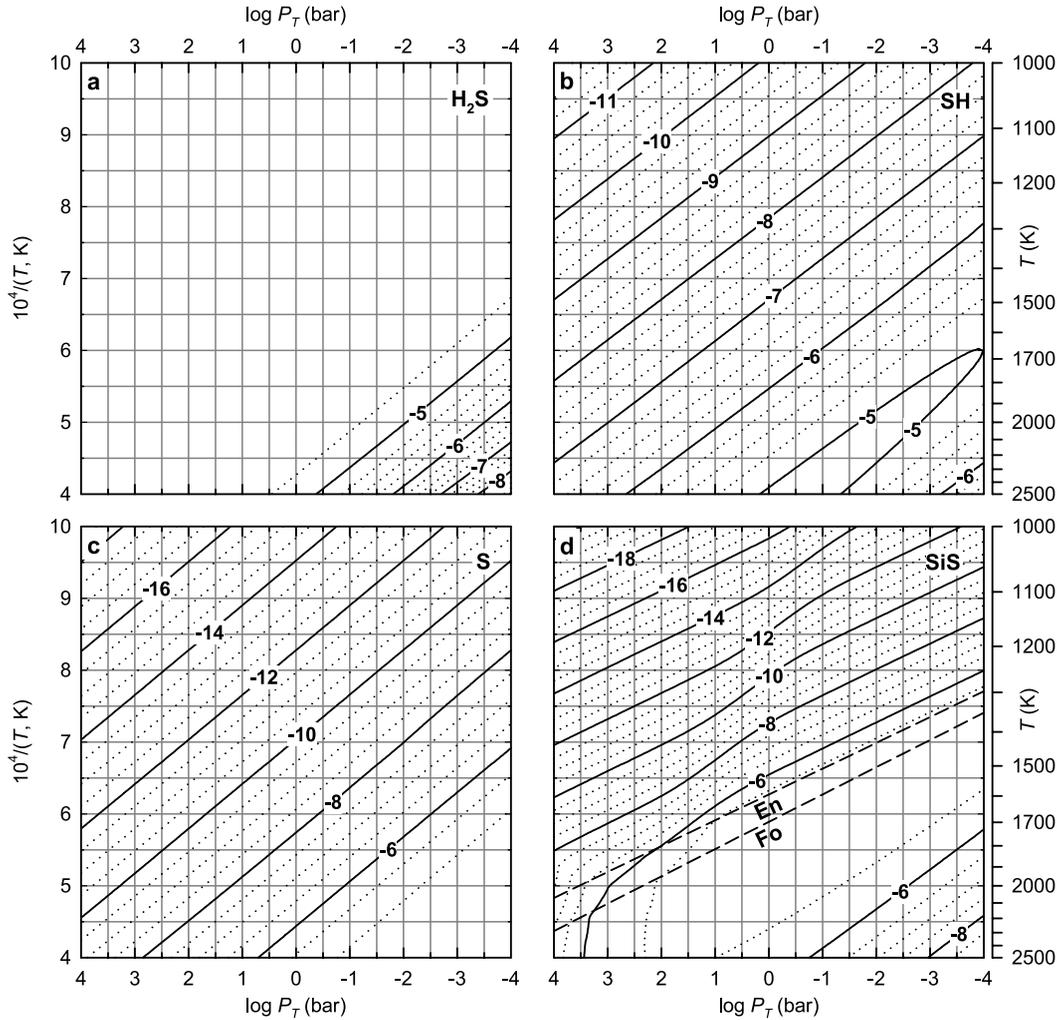


FIG. 2.—Mole fraction contours (on a logarithmic scale) for (a) hydrogen sulfide (H_2S), (b) mercapto radical (SH), (c) monatomic sulfur (S), and (d) silicon sulfide (SiS) as a function of pressure and temperature in a solar metallicity gas. The dashed lines labeled Fo and En in the SiS plot indicate the equilibrium condensation temperatures of forsterite (Mg_2SiO_4) and enstatite (MgSiO_3), respectively.

However, at high T and low P_T , H_2 thermally dissociates to H via the net thermochemical reaction



The position of the $\text{H}_2 = \text{H}$ equal abundance boundary is indicated by the dash-dotted line in Figure 1. The abundance of H_2 as a function of P_T and T in a solar system composition gas can be determined by solving the expression

$$X_{\text{H}_2} \approx \frac{1.9845 + 10^u - \sqrt{10^u(3.9690 + 10^u)}}{2.3670}, \quad (13)$$

where the variable u is given by

$$u = -23672/T - \log P_T + 6.2645. \quad (14)$$

At pressures and temperatures relevant for substellar atmospheres (Fig. 1), 10^u approaches zero and $X_{\text{H}_2} \approx 0.84$.

3.1.1. Hydrogen Sulfide, H_2S Gas

As shown in Figure 1, H_2S is expected to be the most abundant S-bearing gas throughout the atmospheres of substellar

objects (e.g., FL94; Fegley & Lodders 1996). Aside from minor amounts of sulfur ($\lesssim 9\%$) removed by metal sulfide clouds (see § 3.2), H_2S approximately represents the atmospheric sulfur inventory until it is removed by very low temperature cloud formation and/or photochemical destruction. The H_2S abundance also slightly decreases at atmospheric levels below the Mg silicate clouds, where SiS gas is relatively abundant (see §§ 3.1.4 and 3.3). Within the H_2S field and at the high temperatures below the metal sulfide clouds, the H_2S abundance is given by

$$\log X_{\text{H}_2\text{S}} \approx -4.52 + [\text{S}/\text{H}], \quad (15)$$

whereas above the metal sulfide clouds, the H_2S abundance is

$$\log X_{\text{H}_2\text{S}} \approx -4.56 + [\text{S}/\text{H}]. \quad (16)$$

Figure 2a gives mole fraction contours (on a logarithmic scale) of H_2S as a function of temperature and total pressure in a solar metallicity gas. The H_2S abundance at higher or lower metallicities can be found by substituting for $[\text{S}/\text{H}]$ in equations (15) and (16). As discussed above, H_2S dissociates to SH and S at high temperatures. Inside the SH and S fields, the H_2S abundance

remains proportional to m and decreases when moving toward higher temperatures and lower total pressures.

3.1.2. Mercapto, SH Gas

Mole fraction contours of SH as a function of T and P_T are shown in Figure 2b. Within the H_2S field ($X_{\text{H}_2\text{S}} \approx X_{\Sigma\text{S}}$ and $X_{\text{H}_2} \approx 0.84$), the mercapto radical is governed by reaction (1). The SH abundance is given by substituting equation (15) into equation (3) and rearranging to

$$\log X_{\text{SH}} \approx -1.11 - 8785/T - 0.5 \log P_T + [\text{S}/\text{H}], \quad (17)$$

proportional to $P_T^{-0.5}$ and m . At high temperatures, SH is replaced by S via reaction (5). Within the S field, the SH abundance is proportional to m and decreases when moving away from the SH-S boundary to higher T and lower P_T .

3.1.3. Monatomic Sulfur, S Gas

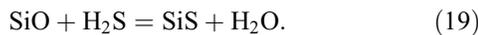
Mole fraction contours for monatomic S are shown in Figure 2c. Inside the H_2S field, monatomic sulfur gas is governed by reaction (8). The S abundance is given by rearranging equation (9), using $\log X_{\text{H}_2\text{S}}$ from equation (15) and $\log X_{\text{H}_2} \approx -0.08$ to give

$$\log X_{\text{S}} \approx 1.29 - 16,046/T - \log P_T + [\text{S}/\text{H}], \quad (18)$$

proportional to P_T^{-1} and m . As illustrated in Figure 1, monatomic S is the dominant S-bearing gas ($X_{\text{S}} \approx X_{\Sigma\text{S}}$) at high T and low P_T in a solar composition gas. Thermal ionization of S only becomes important at temperatures higher than those shown in Figure 1, e.g., $\text{S}^+/\text{S} \sim 1$ at 6974 K (10^{-2} bars), 5340 K (10^{-4} bars), and 4326 K (10^{-6} bars).

3.1.4. Silicon Sulfide, SiS Gas

The chemistry of SiS in a solar metallicity gas is shown in Figure 2d. Also shown are dashed lines for the condensation curves of forsterite (Mg_2SiO_4) and enstatite (MgSiO_3). Condensation of Mg silicates efficiently removes Si gases from the atmospheres of gas giant planets and cool brown dwarfs (Fegley & Prinn 1988; FL94). The SiS abundance is controlled by the net thermochemical reaction

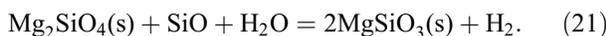


The SiS abundance at high temperatures below the Mg silicate clouds is given by

$$\log X_{\text{SiS}} \approx -1.07 + 666/T + [\text{M}/\text{H}] + \log X_{\text{H}_2\text{S}}, \quad (20)$$

assuming $[\text{O}/\text{H}] = [\text{S}/\text{H}]$ (see § 2). Below the clouds, X_{SiS} is relatively constant (~ 5 ppm [parts per million] at $[\text{M}/\text{H}] = 0$) until H_2S is replaced by monatomic S at high T and low P_T . The SiS abundance also decreases at $P_T \gtrsim 100$ bars, as CO is replaced by CH_4 (see Fig. 1). This conversion increases the H_2O abundance (see LF02) and drives reaction (19) toward the left to yield less SiS.

At lower temperatures, above the clouds, the SiO abundance is governed by the reaction



Combined with reaction (19), the abundance of SiS is given by

$$\log X_{\text{SiS}} \approx 5.38 - 28,151/T - \log P_T - 2 \log X_{\text{H}_2\text{O}} + [\text{S}/\text{H}]. \quad (22)$$

Although reaction (19) does not indicate a dependence on P_T and suggests a linear dependence on the H_2O abundance, the SiS abundance in equation (22) is proportional to P_T^{-1} and $X_{\text{H}_2\text{O}}^{-2}$. These dependencies enter through the SiO abundance governed by reaction (21). The H_2O abundance above the Mg silicate clouds is approximated by

$$\log X_{\text{H}_2\text{O}} \approx -3.58 + 0.46/(1 + 10^u) + [\text{O}/\text{H}], \quad (23)$$

where

$$u = -11,704/T - 2 \log P_T + 9.78. \quad (24)$$

Substituting $\log X_{\text{H}_2\text{O}}$ from equation (23) into equation (22) shows that X_{SiS} is proportional to m^{-1} , assuming $[\text{O}/\text{H}] = [\text{S}/\text{H}]$ (see § 2). Curvature in the SiS abundance contours results from the dependence of the H_2O abundance on the CH_4/CO equilibrium (see LF02). For reference, $X_{\text{H}_2\text{O}} \approx 10^{-3.12}$ in CH_4 -dominated objects and $X_{\text{H}_2\text{O}} \approx 10^{-3.58}$ in CO-dominated objects with solar metallicity in atmospheric regions above the Mg silicate clouds.

3.2. Sulfur Condensation Chemistry

With decreasing temperatures, sulfur condenses into MnS, Na_2S , ZnS, and NH_4SH cloud layers. Condensation affects the spectra of substellar objects by removing gases (and thus potential opacity sources) from the observable atmosphere and by introducing cloud particles (Marley et al. 1996; Lodders 1999a; Burrows et al. 2000a; Lodders & Fegley 2006).

The formation of a sulfur-bearing cloud requires that its constituent elements were not removed by condensation into more refractory cloud layers at deeper levels. For example, one might naively expect FeS cloud formation, because FeS is a well-known condensate in the equilibrium condensation sequence of the solar nebula gas. However, condensation of FeS is preceded by Fe metal condensation, and in the high-gravity environment of substellar objects, iron settles into a deep cloud layer at high temperatures (e.g., Prinn & Olaguer 1981; FL94; Lodders 1999a; LF02; Lodders & Fegley 2006). Hence, no Fe metal is left at lower temperatures when FeS could condense. Note that if FeS condensation did occur, all H_2S would be removed, because the Fe/S ratio is ≈ 1.9 . However, the measured H_2S abundance of ~ 2.4 times the protosolar $\text{H}_2\text{S}/\text{H}_2$ ratio in Jupiter's atmosphere (Niemann et al. 1998; Wong et al. 2004) requires Fe metal cloud formation at deep atmospheric levels.

Sulfur thus condenses as other sulfides with metals (Mn, Na, and Zn) that are not already removed into high-temperature condensates. The abundances of Mn, Zn, and Na are all lower than that of S, and condensation of these sulfides only depletes the atmosphere of $\sim 9\%$ of its entire sulfur inventory. Therefore, H_2S gas remains in T dwarfs, L dwarfs, and Pegasi planets and is only depleted in objects with low enough temperatures for NH_4SH condensation. Table 1 lists the calculated condensation temperatures of MnS, Na_2S , ZnS, and NH_4SH for HD 209458b and a model L dwarf with $[\text{M}/\text{H}] \approx 0$, for Jupiter ($[\text{M}/\text{H}] \approx +0.5$), and for Gliese 229B ($[\text{M}/\text{H}] \approx -0.3$), assuming uniform enrichments and/or depletions of heavy-element abundances.

3.2.1. Alabandite, MnS Condensation

The most refractory S-bearing condensate in substellar atmospheres is MnS (Fig. 1). Alabandite clouds form via the net thermochemical reaction

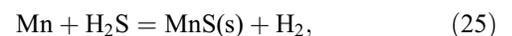


TABLE 1

EQUILIBRIUM CONDENSATION TEMPERATURES OF SULFUR-BEARING COMPOUNDS

Object	MnS	Na ₂ S	ZnS	NH ₄ SH
Jupiter.....	1800	1370	970	220
Gliese 229B.....	1380	1000	780	...
HD 209458b.....	1260	~800 ^a
L dwarf.....	1270
M dwarf.....

NOTE.—Condensation temperatures computed using $[M/H] \approx +0.5$ for Jupiter, $[M/H] \approx -0.3$ for Gliese 229B, and $[M/H] \approx 0$ for HD 209458b and the model L dwarf.

^a Nightside condensation.

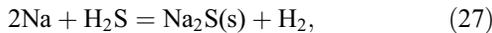
where the condensation temperature is approximated by

$$10^4/T_{\text{cond}}(\text{MnS}) \approx 7.45 - 0.42(\log P_T + [\text{Mn}/H] + [\text{S}/H]) \approx 7.45 - 0.42 \log P_T - 0.84[M/H], \quad (26)$$

assuming $[Mn/H] = [S/H]$ (see § 2). Because MnS condenses at sufficiently high temperatures (e.g., ~1340 K at 1 bar), MnS clouds are expected in most substellar atmospheres. The Mn abundance is 2% of that of sulfur, and thus MnS cloud formation removes all Mn and 2% of all sulfur from the atmosphere.

3.2.2. Sodium Sulfide, Na₂S Condensation

The Na₂S cloud layer forms via the net thermochemical reaction



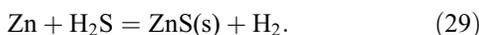
The condensation temperature of Na₂S as a function of P_T and metallicity is approximated by

$$10^4/T_{\text{cond}}(\text{Na}_2\text{S}) \approx 10.05 - 0.72(\log P_T + [\text{Na}/H] + 0.5[\text{S}/H]) \approx 10.05 - 0.72 \log P_T - 1.08[M/H], \quad (28)$$

assuming $[Na/H] = [S/H]$ (see § 2), and is shown in Figure 1 for a solar-metallicity gas. Below the Na₂S cloud, monatomic Na is the most abundant Na-bearing gas, followed closely by NaCl. With decreasing temperatures, NaCl becomes increasingly important, but its abundance never exceeds that of monatomic Na below the cloud (Lodders 1999a). Sodium sulfide condensation effectively removes all sodium and ~6.5% of all sulfur from the atmosphere, because the protosolar Na abundance is 13% of the protosolar S abundance.

3.2.3. Sphalerite, ZnS Condensation

Sphalerite clouds form by the net thermochemical reaction



The condensation temperature of ZnS as a function of P_T and metallicity is given by

$$10^4/T_{\text{cond}}(\text{ZnS}) \approx 12.52 - 0.63(\log P_T + [\text{Zn}/H] + [\text{S}/H]) \approx 12.52 - 0.63 \log P_T - 1.26[M/H], \quad (30)$$

assuming $[Zn/H] = [S/H]$ (see § 2). Sphalerite cloud formation effectively removes all Zn and ~0.3% of H₂S from the atmosphere.

3.2.4. Ammonium Hydrogen Sulfide, NH₄SH Condensation

Sulfur condenses as NH₄SH via the net thermochemical reaction



in the cool upper atmospheres of giant planets (Fig. 1), where H₂S and NH₃ are the major S- and N-bearing gases, respectively. The NH₄SH condensation temperature as a function of P_T and metallicity is approximated by

$$10^4/T_{\text{cond}}(\text{NH}_4\text{SH}) \approx 48.91 - 4.15(\log P_T + 0.5[\text{N}/H] + 0.5[\text{S}/H]) \approx 48.91 - 4.15 \log P_T - 4.15[M/H], \quad (32)$$

assuming $[N/H] = [S/H]$ (see § 2). This expression differs slightly from that of LF02 due to the revised solar elemental abundances of Lodders (2003). The formation of a NH₄SH cloud is expected to efficiently remove all sulfur from the atmosphere, because NH₃ is ~4.4 times more abundant than H₂S in a protosolar composition gas.

3.2.5. Hydrogen Sulfide, H₂S Condensation

Hydrogen sulfide cloud formation is only possible in cool objects (such as Uranus and Neptune) if NH₃ is absent or less abundant than H₂S, since ammonia will consume atmospheric sulfur to form NH₄SH via reaction (31) (e.g., see Fegley et al. 1991). At sufficiently low temperatures, H₂S condensation may occur via the net reaction



The H₂S condensation temperature is approximated by

$$10^4/T_{\text{cond}}(\text{H}_2\text{S}) \approx 86.49 - 8.54 \log P_T - 8.54[\text{S}/H]. \quad (34)$$

We found that no other S-bearing condensates are stable (OCS, SO₂, elemental S) over this P - T range in a protosolar composition gas.

3.3. Sulfur Chemistry in Substellar Objects

Figures 3a–3d summarize the equilibrium sulfur gas chemistry computed along the P - T profiles of four representative substellar objects: Jupiter ($T_{\text{eff}} = 124$ K), the T dwarf Gliese 229B ($T_{\text{eff}} = 960$ K), the Pegasi planet HD 209458b ($T_{\text{eff}} = 1350$ K), and an L dwarf ($T_{\text{eff}} = 1800$ K; see § 3.1). The profiles for Jupiter and Gliese 229B were computed at $[M/H] \approx +0.5$ and $[M/H] \approx -0.3$, respectively, assuming uniform enrichments and depletions in elemental abundances. The upper atmosphere of HD 209458b is heated by a large incoming stellar flux, which is responsible for the shape of this planet's P - T profile (Fig. 1) and hence the curvature in all gas abundances near 1800 K. Also shown are gases that are strongly affected by S-bearing cloud formation (e.g., Na, NaCl, Mn, and Zn). The condensation temperatures of Mg₂SiO₄ (Fo), MgSiO₃ (En), MnS, Na₂S, and ZnS are indicated by arrows (see Table 1). The Jupiter profile intersects the forsterite condensation curve at high temperatures outside the range of Figure 3a. The Gliese 229B profile intersects the ZnS condensation curve at 780 K, outside the range of Figure 3b. In contrast, ZnS does not condense in the atmospheres of HD 209458b and the L dwarf.

Hydrogen sulfide is the most abundant S-bearing gas throughout the atmospheres of substellar objects ($X_{\text{H}_2\text{S}} \approx X_{\text{S}}$). The H₂S

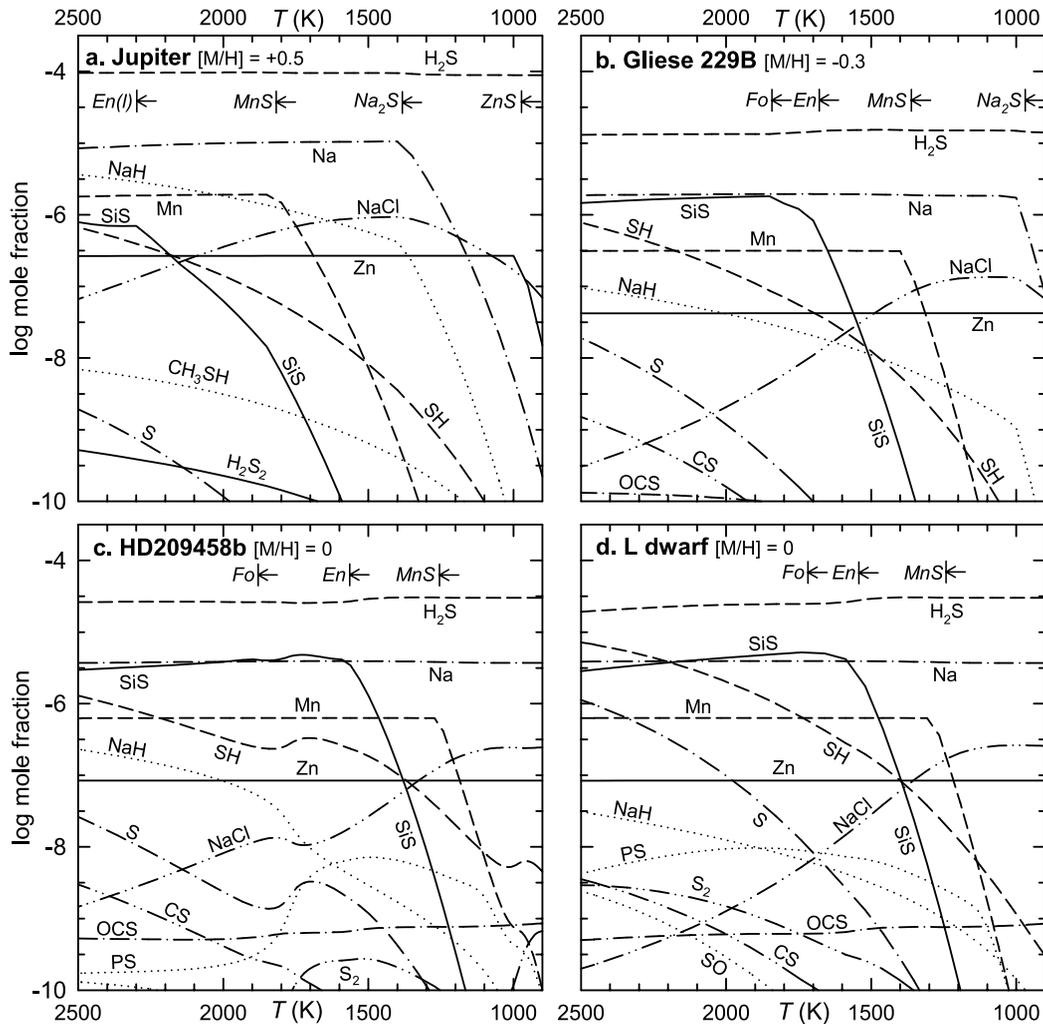


FIG. 3.—Sulfur chemistry along representative atmospheric pressure-temperature profiles from 900 to 2500 K for (a) Jupiter ($[M/H] \approx +0.5$), (b) Gliese 229B ($[M/H] \approx -0.3$), (c) HD 209458b ($[M/H] \approx 0$), and (d) an L dwarf ($[M/H] \approx 0$; $T_{\text{eff}} = 1800$ K), assuming uniform elemental enrichments and depletions. Also shown are the calculated condensation temperatures of forsterite (Fo; Mg_2SiO_4), enstatite (En; MgSiO_3), MnS, Na_2S , and ZnS. With the exception of forsterite (not shown) and enstatite on Jupiter, all condensates shown here condense as solids.

abundance slightly increases when silicon in SiS is removed by Mg silicate cloud formation (e.g., see Figs. 3b–3d) and slightly decreases when sulfur is removed by metal sulfide cloud formation (e.g., see Fig. 3a).

The *Galileo* entry probe measured H_2S down to the ~ 20 bar level on Jupiter (Niemann et al. 1998; Wong et al. 2004), where the observed H_2S abundance of 2.4 times the solar $\text{H}_2\text{S}/\text{H}_2$ ratio should represent the total sulfur inventory in Jupiter’s atmosphere (e.g., Barshay & Lewis 1978; FL94; Lodders 2004b). Ground-based observations have failed to detect H_2S on Jupiter and Saturn because of its removal by condensation, its short photochemical lifetime, and the lack of major H_2S features in the $5 \mu\text{m}$ window. Observations of Jupiter at $2.7 \mu\text{m}$ by Kuiper Airborne Observatory (KAO; Larson et al. 1984) and at $8.5 \mu\text{m}$ by *Voyager* (Bézar et al. 1983) provide only upper limits, because these wavelengths probe atmospheric levels where H_2S is depleted by NH_4SH condensation. The *Hubble Space Telescope* (*HST*) detection of H_2S in the Shoemaker-Levy 9 impact region suggested excavation of the Jovian atmosphere from regions below the NH_4SH cloud, where H_2S is more abundant (Noll et al. 1995; Zahnle et al. 1995).

Based on tropospheric NH_3 and H_2S abundances, NH_4SH cloud formation is expected to occur near the 220 K, 2.4 bar level

on Jupiter (see FL94). This should efficiently remove H_2S from the gas, because $\text{NH}_3/\text{H}_2\text{S} \sim 7.5 \pm 3.4$ in Jupiter’s atmosphere (Wong et al. 2004). The inferred NH_4SH cloud layer detected by the *Galileo* entry probe nephelometer was thin and tenuous, presumably due to the probe’s entry in a relatively clear $5 \mu\text{m}$ hot spot (West et al. 2004).

In contrast, NH_4SH cloud formation is not expected in the warmer atmospheres of brown dwarfs or Pegasi planets, because their P - T profiles do not intersect the NH_4SH condensation curve (see Fig. 1), and H_2S gas remains. Measurements of H_2S in these objects should therefore approximately represent their bulk atmospheric sulfur inventory (e.g., Fegley & Lodders 1996). Saumon et al. (2000) investigated the observability of H_2S and found that a H_2S feature at $2.1 \mu\text{m}$ is potentially detectable in the infrared spectrum of Gliese 229B. In the uppermost atmospheres of brown dwarfs and Pegasi planets, H_2S is plausibly destroyed by photochemistry (see § 5), as is expected for Jupiter (e.g., Prinn & Owen 1976).

Over the P - T range considered here, the next most abundant S-bearing gases after H_2S are SH (at low temperatures) or SiS (at high temperatures). The mercapto radical is generally the second or third most abundant sulfur gas throughout substellar

atmospheres. Yamamura et al. (2000) identified SH at $\sim 3.67 \mu\text{m}$ in the published infrared spectrum of R Andromedae, an S-type star. Their inferred SH/H ratio of $\sim 10^{-7}$ is consistent with thermochemical equilibrium (Tsuji 1973; Fig. 2b). Berdyugina & Livingston (2002) identified SH at $\sim 3280 \text{ \AA}$ in the Sun's photosphere. They do not give column densities, but computed synthetic spectra at 5250 and 4750 K. We calculated SH mole fractions of $\sim 9 \times 10^{-9}$ (5250 K) and $\sim 5 \times 10^{-9}$ (4750 K) using the solar model atmosphere of Edvardsson et al. (1993). Using the effective temperatures for reference, we also compute SH column densities of $\sim 7 \times 10^{12}$ (960 K), $\sim 2 \times 10^{17}$ (1350 K), and $\sim 2 \times 10^{17} \text{ cm}^{-2}$ (1800 K) on Gliese 229B, HD 209458b, and the L dwarf, respectively, versus the SH column density of $\sim 4 \times 10^{20} \text{ cm}^{-2}$ in R Andromedae (Yamamura et al. 2000). The equilibrium SH abundances expected for brown dwarfs and Pegasi planets may be too low for reliable quantitative analysis.

The relative importance of SiS increases with increasing temperature, and peak SiS abundances of ~ 6 ppm at $[\text{M}/\text{H}] = 0$ and ~ 60 ppm at $[\text{M}/\text{H}] = +0.5$ are achieved at P - T conditions close to the condensation temperatures of the Mg silicate clouds. With their condensation, silicon is removed from the atmosphere, and the abundance of SiS and other Si-bearing gases drop. This makes SiS a potential tracer of weather in Pegasi planets and L dwarfs, analogous to FeH in T dwarfs (Burgasser et al. 2002), and gaps in the Mg silicate cloud layers may expose regions where SiS is relatively abundant. In cooler objects, the SiS fundamental absorption band near $13.3 \mu\text{m}$ may be difficult to distinguish from ammonia features, as NH_3 replaces N_2 to become the dominant N-bearing gas; the first SiS overtone at $6.6 \mu\text{m}$ has been observed in the carbon giant WZ Cas (Aoki et al. 1998), although this feature will likely be overwhelmed by H_2O absorption in substellar atmospheres.

The increasing importance of NaCl instead of Na and the removal of Na by Na_2S cloud formation is a plausible cause of 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); this is further enhanced by pressure broadening of the Na I doublet (e.g., Tsuji et al. 1996; Burrows et al. 2000b; Liebert et al. 2000). Sodium sulfide is expected to condense at the ~ 1370 K level in Jupiter's atmosphere and the ~ 1000 K level in Gliese 229B (see Table 1). The L dwarf and the Pegasi planet HD 209458b are too warm for Na_2S condensation (assuming $[\text{M}/\text{H}] \approx 0$; see Fig. 1), and Na remains in the gas. This is consistent with the detection of Na in the atmosphere of HD 209458b (Charbonneau et al. 2002), although the chemistry results of Lodders (1999a) suggest that limited Na_2S cloud formation may occur on this planet if nightside temperatures are low enough (e.g., Fortney et al. 2003, 2005; Iro et al. 2005; Barman et al. 2005) or if its metallicity is sufficiently enhanced. However, while Na chemistry is strongly affected by Na_2S condensation, S chemistry remains almost unchanged, because Na_2S cloud formation only removes 6% of all sulfur (see § 3.2.2).

The formation of the MnS cloud layer effectively removes Mn from the atmospheres of substellar objects. Similarly, ZnS condensation removes Zn from the atmospheres of Jupiter ($[\text{M}/\text{H}] \approx +0.5$) and Gliese 229B ($[\text{M}/\text{H}] \approx -0.3$) above the ~ 980 K and ~ 780 K levels, respectively. In contrast, the atmospheres of L dwarfs and Pegasi planets are too warm for ZnS condensation, and Zn will remain in the gas.

4. PHOSPHORUS CHEMISTRY

4.1. Phosphorus Gas Chemistry

The phosphorus equilibrium gas chemistry as a function of temperature and total pressure in a protosolar composition gas

is illustrated in Figure 4. The P - T regions indicating the most abundant phosphorus-bearing gas are bounded by solid lines. Also shown is the condensation curve for $\text{NH}_4\text{H}_2\text{PO}_4$ (dotted line), model atmosphere profiles for representative substellar objects (dashed lines; see § 3.1), and the $\text{H}_2 = \text{H}$ and $\text{CH}_4 = \text{CO}$ equal abundance curves (dash-dotted lines). Phosphorus chemistry is considerably more complex than that for C, N, O, and S, and several P-bearing species become abundant at elevated temperatures (Barshay & Lewis 1978; Fegley & Lewis 1980; FL94).

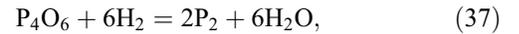
Under equilibrium conditions, P_4O_6 is the dominant phosphorus gas at low temperatures, and it is replaced by PH_3 or P_2 as temperatures increase. The conversion of P_4O_6 to PH_3 occurs by the net thermochemical reaction



In CH_4 -dominated objects, the $\text{PH}_3 = \text{P}_4\text{O}_6$ equal abundance boundary is approximated by

$$\begin{aligned} \log P_T &\approx -11.40 + 12,360/T + 2[\text{O}/\text{H}] + [\text{P}/\text{H}] \\ &\approx -11.40 + 12,360/T + 3[\text{M}/\text{H}], \end{aligned} \quad (36)$$

assuming $[\text{O}/\text{H}] \approx [\text{P}/\text{H}]$ (see § 2). The net reaction of P_4O_6 to P_2 occurs at lower P_T in CO-dominated objects via



and the position of the $\text{P}_2 = \text{P}_4\text{O}_6$ equal abundance boundary is approximated by

$$\begin{aligned} \log P_T &\approx 45.17 - 51,048/T - 6[\text{O}/\text{H}] - [\text{P}/\text{H}] \\ &\approx 45.17 - 51,048/T - 7[\text{M}/\text{H}], \end{aligned} \quad (38)$$

assuming $[\text{O}/\text{H}] \approx [\text{P}/\text{H}]$ (see § 2). The relative importance of reactions (35) and (37) depends on the position of an object's P - T profile relative to the PH_3 - P_4O_6 - P_2 triple point at $T \sim 1101$ K and $P_T \sim 10^{-1.20}$ bars, where all three gases have equal abundances $A(\text{PH}_3) = A(\text{P}_4\text{O}_6) = A(\text{P}_2) \approx \frac{1}{7}\Sigma\text{P}$. The positions of all the triple points shown in Figure 4 are listed in Table 2.

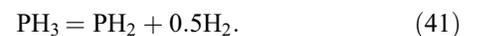
In L dwarf atmospheres, PH_3 and P_2 have similar abundances and are converted into each other by the net thermochemical reaction



The $\text{PH}_3 = \text{P}_2$ equal abundance boundary in a solar metallicity gas is approximated by

$$\log P_T \approx -1.56 \times 10^7/T^2 + 2.13 \times 10^4/T - 7.68, \quad (40)$$

from 1101 to 1330 K and shifts to higher P_T and lower T with increasing metallicity. At deeper atmospheric levels, PH_2 becomes the most abundant phosphorus gas. In T dwarfs and cool L dwarfs PH_2 replaces PH_3 via



The $\text{PH}_3 = \text{PH}_2$ boundary is given by

$$\log P_T \approx 7.71 - 10,888/T \quad (42)$$

and is independent of metallicity, because the m dependence for each P-bearing gas in reaction (41) cancels and the H_2 abundance is essentially constant over small metallicity variations.

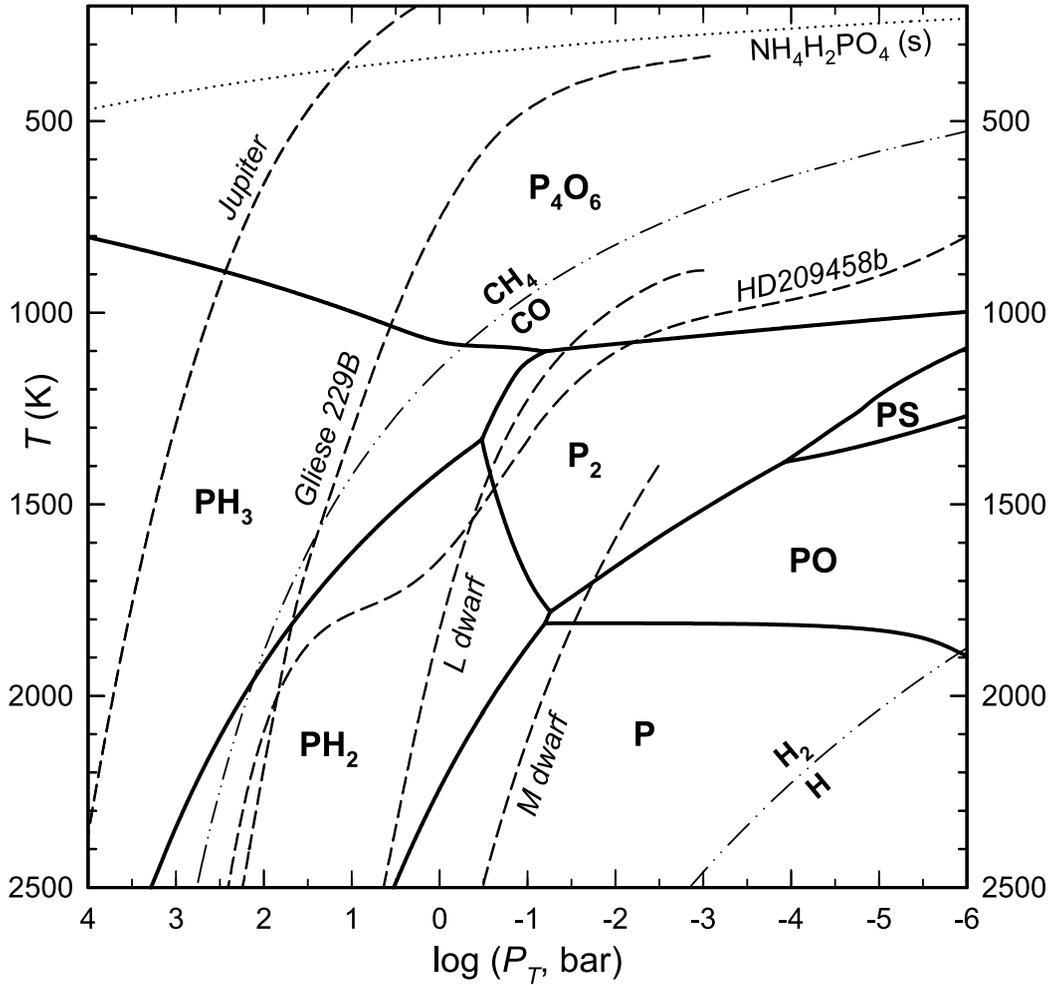


FIG. 4.—Overview of phosphorus chemistry as a function of temperature and pressure in a solar system composition gas. The solid lines indicate where major P-bearing gases have equal abundances. Also shown is the condensation curve for $\text{NH}_4\text{H}_2\text{PO}_4$ (dotted line) and the position of the $\text{H}_2 = \text{H}$ equal abundance boundary (dash-dotted line). Atmospheric profiles for representative substellar objects are shown for reference (dashed lines). See text for details.

In Pegasi planets and hot L dwarfs, PH_2 replaces P_2 via



The position of the $\text{P}_2 = \text{PH}_2$ boundary in a solar metallicity gas is approximated by

$$\log P_T \approx -1.68 \times 10^7 / T^2 + 2.62 \times 10^4 / T - 10.68 \quad (44)$$

TABLE 2
PHOSPHORUS EQUAL ABUNDANCE “TRIPLE POINTS”
IN A SOLAR METALLICITY GAS

Triple Point ^a	T (K)	$\log(P_T, \text{bar})$
$\text{PH}_3\text{-P}_4\text{O}_6\text{-P}_2$	1101	-1.20
$\text{PH}_3\text{-PH}_2\text{-P}_2$	1330	-0.48
$\text{P}_2\text{-PO-PS}$	1389	-3.93
$\text{P}_2\text{-PH}_2\text{-PO}$	1780	-1.26
$\text{PH}_2\text{-P-PO}$	1811	-1.20

^a For example, where $X_A = X_B = X_C$ for phosphorus-bearing gases A, B, and C.

from 1330 to 1780 K and shifts to higher P_T and T with increasing metallicity. The $\text{PH}_3 = \text{P}_2$, $\text{PH}_3 = \text{PH}_2$, and $\text{P}_2 = \text{PH}_2$ boundaries intersect at $T \sim 1330$ K and $P_T \sim 10^{-0.48}$ bars, where all three gases have equal abundances [$A(\text{PH}_3) = A(\text{PH}_2) = A(\text{P}_2) \approx \frac{1}{4}\Sigma\text{P}$].

At even higher temperatures, PH_2 thermally dissociates via



and monatomic P becomes the major P-bearing gas. The position of the $\text{PH}_2 = \text{P}$ boundary, given by

$$\log P_T \approx 5.00 - 11,233/T, \quad (46)$$

is independent of metallicity, because the m dependence for each P-bearing gas cancels out in reaction (45). As for sulfur, thermal ionization of P only becomes important at temperatures higher than those shown in Figure 4, e.g., $\text{P}^+/\text{P} \sim 1$ at 6088 K (10^{-2} bars), 4836 K (10^{-4} bars), and 4054 K (10^{-6} bars).

4.1.1. Tetraphosphorus Hexaoxide, P_4O_6 Gas

The equilibrium abundances of P_4O_6 as a function of T and P_T for solar metallicity are illustrated in Figure 5a. At high temperatures (≥ 1000 K), the P_4O_6 abundances depend on which

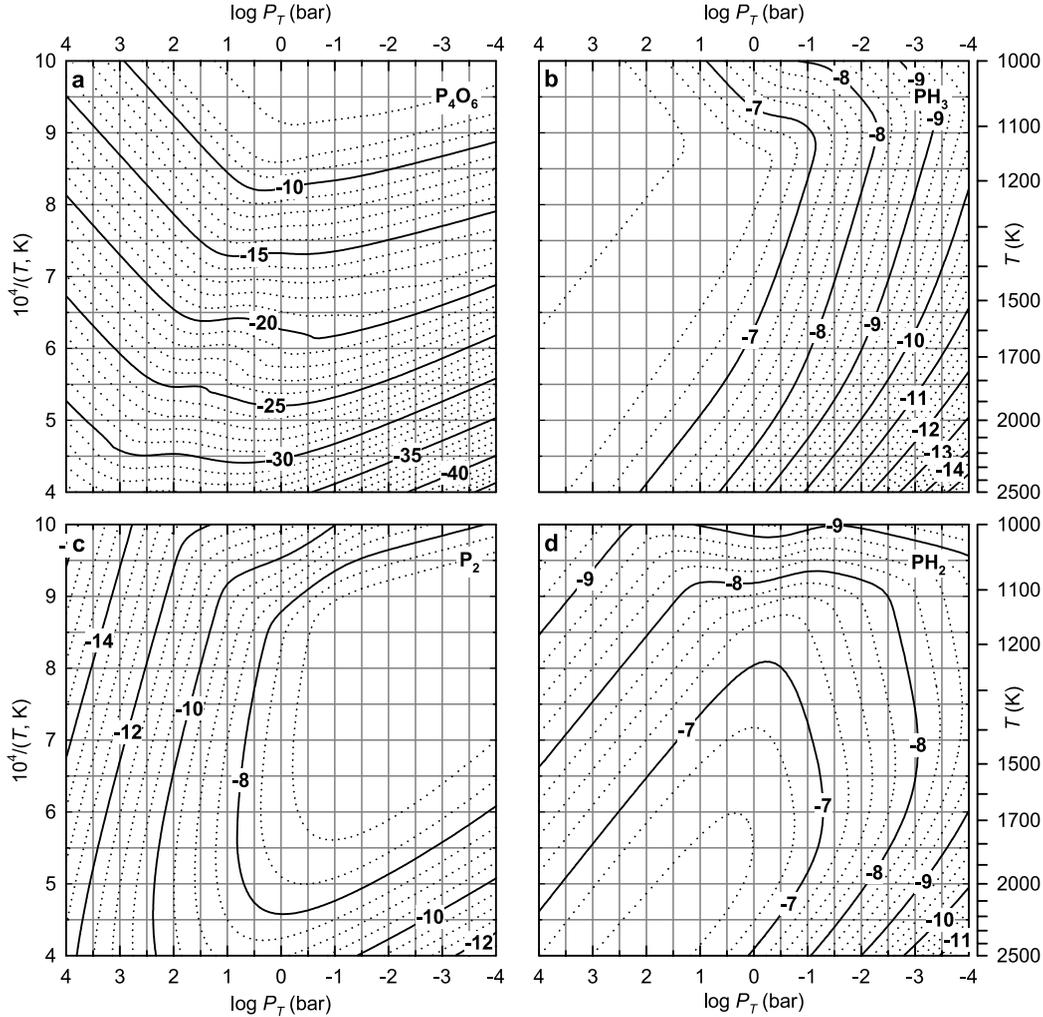


FIG. 5.—Mole fraction contours (on a logarithmic scale) for (a) tetraphosphorus hexaoxide (P_4O_6), (b) phosphine (PH_3), (c) diatomic phosphorus (P_2), and (d) the phosphino radical (PH_2) as a function of pressure and temperature in a solar metallicity gas. Gas abundances at higher or lower metallicities are given by the abundance expressions and/or the dependence on the metallicity factor m .

P-bearing gas is dominant. For example, within the PH_3 field, the P_4O_6 abundance is controlled by reaction (35) and is proportional to P_T^{-3} and m^{10} , assuming $[O/H] \approx [P/H]$ (see § 2). Inside the P_2 field, the P_4O_6 abundance is controlled by reaction (37) and is proportional to P_T and m^8 , assuming $[O/H] \approx [P/H]$ (see § 2). In both cases, the P_4O_6 abundance rapidly decreases with temperature and is strongly dependent on metallicity.

At low temperatures ($\lesssim 1000$ K), P_4O_6 is the dominant P-bearing gas at equilibrium (Fig. 4), and its abundance is proportional to m , assuming $[O/H] \approx [P/H]$ (see § 2). The maximum P_4O_6 abundance is $X_{P_4O_6} \approx \frac{1}{4} X_{\Sigma P}$, because each molecule of P_4O_6 contains four phosphorus atoms. However, completely insignificant amounts of P_4O_6 are expected in the upper atmospheres of giant planets and T dwarfs, because the PH_3 to P_4O_6 conversion is kinetically inhibited inside the PH_3 stability field, where essentially no P_4O_6 exists (see § 4.3).

4.1.2. Phosphine, PH_3 Gas

Chemical equilibrium abundances of PH_3 are shown in Figure 5b as a function of T and P_T . At high temperatures ($T \gtrsim 1000$ K), PH_3 abundances generally increase with P_T but decrease with T when other P-bearing gases are dominant. For

example, within the P_2 field the PH_3 abundance is governed by reaction (39) and is approximated by

$$\log X_{PH_3} \approx -9.03 + 3737/T + \log P_T + 0.5[P/H], \quad (47)$$

proportional to P_T and $m^{0.5}$. At higher total pressures, PH_3 is the dominant P-bearing gas (see Fig. 4), and its abundance is proportional to m . The maximum PH_3 abundance is $X_{PH_3} \approx X_{\Sigma P}$. Phosphine therefore approximately represents the total phosphorus inventory in the deep atmospheres of giant planets and T dwarfs. Furthermore, rapid vertical mixing and phosphine quenching from deep atmospheric regions where PH_3 dominates is expected to give disequilibrium abundances of $X_{PH_3} \approx X_{\Sigma P}$ in the observable atmospheres of giant planets and T dwarfs (see § 4.3).

4.1.3. Diatomic Phosphorus, P_2 Gas

Mole fraction contours for P_2 are given in Figure 5c as a function of T and P_T . In cooler objects (e.g., giant planets and T dwarfs), P_2 is governed by reaction (39), and the mole fraction abundance of P_2 within the PH_3 field is

$$\log X_{P_2} \approx -1.01 - 7474/T - 2 \log P_T + 2[P/H], \quad (48)$$

proportional to P_T^{-2} and m^2 . At lower total pressures ($\leq 10^{-0.48}$ bars), P_2 is the dominant P-bearing gas (see Fig. 4), and its abundance is proportional to m . The maximum P_2 abundance is $X_{P_2} \approx \frac{1}{2} X_{\Sigma P}$, because each molecule of P_2 contains two phosphorus atoms. With increasing temperatures, P_2 is replaced by PH_2 via reaction (43) in the atmospheres of L dwarfs and Pegasi planets.

4.1.4. Phosphino, PH_2 Gas

Figure 5*d* illustrates the abundances of the PH_2 radical, which is the most abundant P-bearing gas in the deep atmospheres of brown dwarfs and Pegasi planets. At lower temperatures, the PH_2 abundance within the PH_3 field is governed by reaction (41) and is given by

$$\log X_{PH_2} \approx -2.40 - 5444/T - 0.5 \log P_T + [P/H], \quad (49)$$

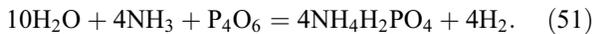
proportional to $P_T^{-0.5}$ and m . When P_2 is the dominant phosphorus gas, the PH_2 abundance is governed by reaction (43) and is given by

$$\log X_{PH_2} \approx -5.19 - 1707/T + 0.5 \log P_T + 0.5[P/H], \quad (50)$$

proportional to $P_T^{0.5}$ and $m^{0.5}$. Equations (49) and (50) show that the PH_2 abundances decrease with P_T when PH_3 dominates and increase with P_T when P_2 dominates. This explains the curvature of the PH_2 mole fraction contours in Figure 5*d*.

4.2. Phosphorus Condensation Chemistry

At low temperatures (Fig. 4), equilibrium condensation of $NH_4H_2PO_4$ is expected to occur via the net thermochemical reaction



The condensation temperature of $NH_4H_2PO_4$ as a function of P_T and metallicity is approximated by

$$\begin{aligned} 10^4/T_{\text{cond}}(NH_4H_2PO_4) &\approx 29.99 - 0.20(11 \log P_T \\ &\quad + 10[O/H] + 4[N/H] + 1[P/H]) \\ &\approx 29.99 - 0.20(11 \log P_T + 15[M/H]), \end{aligned} \quad (52)$$

assuming $[O/H] = [N/H] = [P/H]$ (see § 2). If equilibrium were attained (which is not the case for the giant planets in our solar system), $NH_4H_2PO_4$ condensation would efficiently remove phosphorus from the upper atmospheres of giant planets and the coolest T dwarfs, because oxygen and nitrogen abundances are typically much larger than that of phosphorus. We found that neither P_4O_{10} nor elemental P condenses under equilibrium conditions over this P - T range from a solar system composition gas.

4.3. Phosphorus Chemistry in Substellar Objects

Figures 6*a–d* illustrate equilibrium phosphorus gas chemistry along model atmosphere profiles of Jupiter, Gliese 229B, HD 209458b, and the L dwarf, as was done for sulfur in Figure 3. As before, the shape of the P - T profile of HD 209458b (Fig. 4) is responsible for the curvature in the phosphorus gas abundances near 1800 K.

Using the effective temperatures for reference, the major P-bearing gases expected from thermochemical equilibrium in the observable atmospheres are P_4O_6 in giant planets and cool T dwarfs ($T_{\text{eff}} \sim 100$ –1000 K), PH_3 in hot T dwarfs and cool L

dwarfs ($T_{\text{eff}} \sim 1000$ –1400 K), PH_2 in hot L dwarfs ($T_{\text{eff}} \sim 1400$ –2000 K), P_2 in Pegasi planets such as HD 209458b ($T_{\text{eff}} \sim 1350$ K), and monatomic P in cool M dwarfs (e.g., $T_{\text{eff}} \sim 2200$ K). The dominant P-bearing gas changes with increasing temperature, and the major phosphorus gases at depth are PH_2 in Pegasi planets, PH_2 and P in L dwarfs, PH_3 and PH_2 in T dwarfs, and PH_3 in giant planets (Fig. 4).

However, thermochemical equilibrium does not apply to phosphorus chemistry in the upper atmospheres of giant planets and T dwarfs, because the conversion from PH_3 to P_4O_6 is kinetically inhibited (Prinn & Owen 1976; Barshay & Lewis 1978; Prinn et al. 1984; FL94), and timescales for the PH_3 to P_4O_6 conversion (t_{chem}) are larger than typical convective mixing timescales (t_{mix}) in these atmospheres (Fegley & Prinn 1985; FL94; Fegley & Lodders 1996). The chemical lifetime of PH_3 as a function of T and P_T for solar metallicity is given in Figure 7, using PH_3 destruction kinetics described by Visscher & Fegley (2005). The quench temperature (where $t_{\text{chem}} = t_{\text{mix}}$) for PH_3 destruction is expected to be *inside* the PH_3 field in the deep atmospheres of giant planets and T dwarfs. As a result, virtually no P_4O_6 forms, and PH_3 is mixed upward into their observable atmospheres at abundances approximately representative of the total atmospheric phosphorus inventory ($X_{PH_3} \approx X_{\Sigma P}$). We therefore expect PH_3 (instead of P_4O_6) to be the major P-bearing gas in giant planets and T dwarfs.

Indeed, spectroscopic observations of PH_3 in the upper atmospheres of Jupiter and Saturn indicate tropospheric phosphine abundances of 1.1 ppm by volume on Jupiter (e.g., Lodders 2004b and references therein) and 4.5 ppm by volume on Saturn (e.g., Visscher & Fegley 2005 and references therein). These measured PH_3 abundances are ~ 30 orders of magnitude higher than expected from thermodynamic equilibrium and imply rapid vertical mixing from deeper atmospheric levels, where phosphine is more abundant. We expect PH_3 abundances of ~ 0.6 ppm (for solar metallicity) in the upper atmospheres of Jupiter-type giant planets and cool T dwarfs such as Gliese 229B (e.g., Fegley & Lodders 1996), and measurements of phosphine in these objects should approximately represent their bulk atmospheric phosphorus inventory. Noll & Marley (1997) discussed the observability of gases affected by vertical mixing and concluded that the 4.3 μm feature of PH_3 is potentially detectable in the infrared spectra of T dwarfs. Photochemistry may plausibly destroy PH_3 in the uppermost atmospheres of these objects (see § 5), as occurs on Jupiter and Saturn.

In hotter objects, PH_3 may no longer represent the total atmospheric phosphorus inventory when P equilibrium chemistry is established and other abundant P-bearing gases are present. Phosphine abundances of ~ 50 ppb (parts per billion; for solar metallicity) remain at the 1350 K level on HD 209458b and 1800 K in the model L dwarf. The PH_3 feature at 4.3 μm is potentially detectable in these objects if it can be distinguished from nearby CO bands (Noll & Marley 1997; Saumon et al. 2003).

The abundant P-bearing gases at higher atmospheric temperatures include P_2 , PH, PH_2 , PH_3 , and HCP (Figs. 6*a–d*). The phosphino radical (PH_2) is the dominant P-bearing gas in the observable atmosphere of the model L dwarf and in the deep atmospheres of T dwarfs and Pegasi planets. However, PH_2 only represents about half of the total atmospheric phosphorus inventory, because other P-bearing gases remain relatively abundant within the PH_2 field. Equilibrium PH_2 abundances of ~ 1 , ~ 50 , and ~ 300 ppb are expected (for solar metallicity) in the observable atmospheres of T dwarfs, Pegasi planets, and L dwarfs, respectively.

As temperatures decrease, PH_2 is replaced by PH_3 (in Gliese 229B, Fig. 6*b*) and/or P_2 (in HD 209458b and the L dwarf,

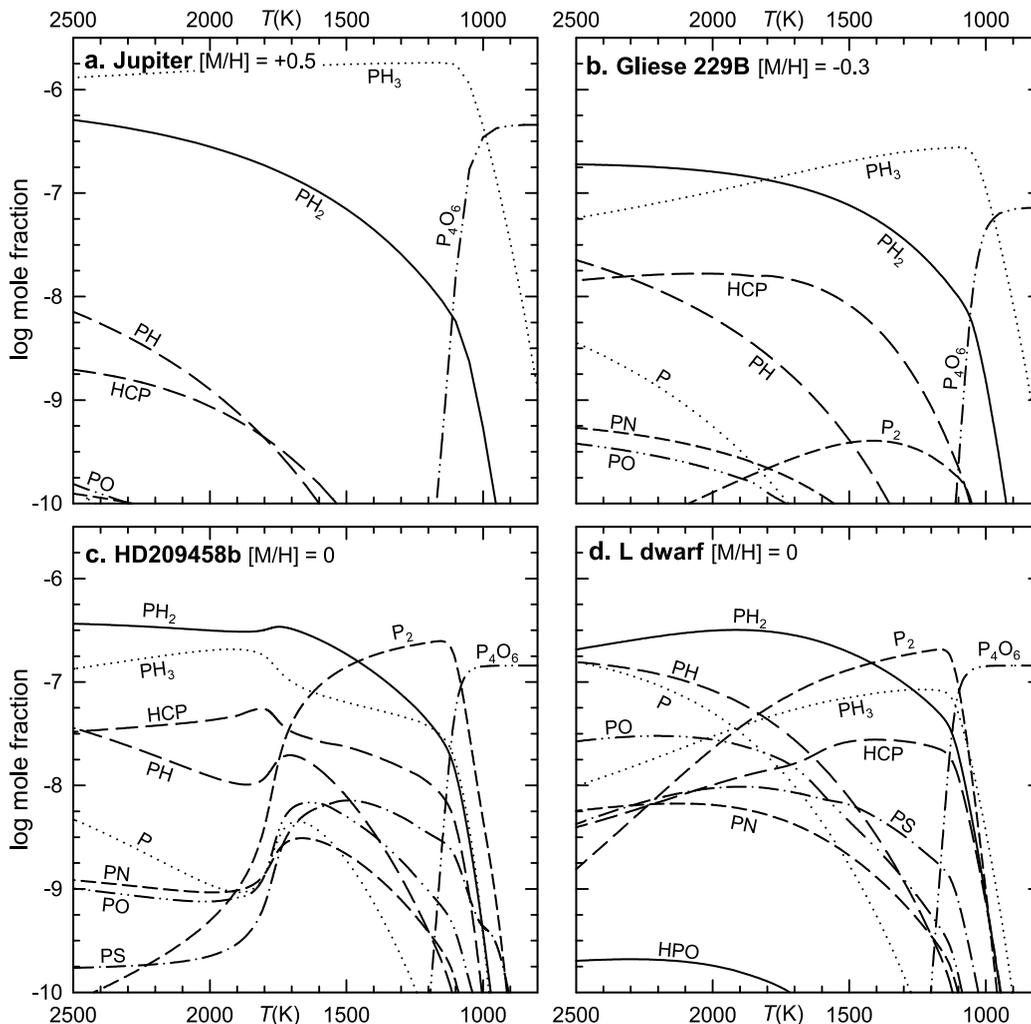


FIG. 6.—Phosphorus equilibrium chemistry along model atmosphere P - T profiles from 800 to 2500 K for (a) Jupiter ($[M/H] \approx +0.5$; $T_{\text{eff}} = 124$ K), (b) Gliese 229B ($[M/H] \approx -0.3$; $T_{\text{eff}} = 960$ K), (c) HD 209458b ($[M/H] \approx 0$; $T_{\text{eff}} = 1350$ K), and (d) an L dwarf ($[M/H] \approx 0$; $T_{\text{eff}} = 1800$ K), assuming uniform elemental enrichments and depletions. Note that the PH_3 to P_4O_6 conversion is kinetically inhibited in giant planets and T dwarfs, and that Jupiter's observable atmosphere lies outside the temperature range shown here.

Figs. 6c and 6d) as the major P-bearing gas, depending on the position of the atmospheric P - T profile relative to the PH_3 - PH_2 - P_2 triple point (see Fig. 4 and § 4.1). Although P_2 is expected to be the dominant P-bearing gas in the observable atmospheres of Pegasi planets ($X_{\text{P}_2} \sim 0.2$ ppm at 1350 K) and the upper atmospheres of L dwarfs, the P_2 bands expected near $0.2 \mu\text{m}$ (Carroll & Mitchell 1975) may be very difficult to detect in these objects. At temperatures below ~ 1000 K, P_2 is converted into P_4O_6 , which is plausibly destroyed by photochemical processes in the uppermost atmospheres of L dwarfs and Pegasi planets (see § 5).

The abundances of PH and HCP are negligible in the observable atmospheres of giant planets and T dwarfs. In warmer objects, these gases have equilibrium abundances (at solar metallicity) of ~ 2 (PH) and ~ 20 ppb (HCP) on HD 209458b (at 1350 K) and ~ 50 (PH) and ~ 15 ppb (HCP) in the L dwarf model atmosphere (at 1800 K).

Under equilibrium conditions, $\text{NH}_4\text{H}_2\text{PO}_4$ cloud formation would be expected near the 400 K level in the upper atmosphere of Jupiter (see Barshay & Lewis 1978; FL94), but is precluded by quenching of PH_3 (see above). Condensation of $\text{NH}_4\text{H}_2\text{PO}_4$ is not expected in the warmer atmospheres of Gliese 229B, HD

209458b, and the L dwarf, because their P - T profiles do not intersect the $\text{NH}_4\text{H}_2\text{PO}_4$ condensation curve (Fig. 4).

5. THERMOCHEMISTRY AND PHOTOCHEMISTRY

So far, our treatment of sulfur and phosphorus chemistry assumes the establishment of thermochemical equilibrium. The exception is phosphine, for which the kinetics of its destruction mechanism and convective vertical mixing must be considered for determining PH_3 abundances (§ 4.3). However, we must also consider photochemical reactions in the uppermost atmospheres of planets and brown dwarfs that are companions to stars. If ultraviolet flux causes photochemical reactions, the thermochemical reactions will be driven out of equilibrium. Photochemistry may also play a role in isolated brown dwarfs if their coronae are warm enough to produce an ultraviolet flux (Yelle 2000).

For example, in Jupiter's troposphere the major C-, N-, S-, and O-bearing gases expected from thermochemical equilibrium are CH_4 , NH_3 , H_2S , and H_2O , respectively (FL94). However, Jupiter's stratosphere contains photochemically produced hydrocarbons such as C_2H_6 , C_2H_2 , and C_2H_4 (Gladstone et al. 1996). Hence, we must examine the relative roles of thermochemistry and

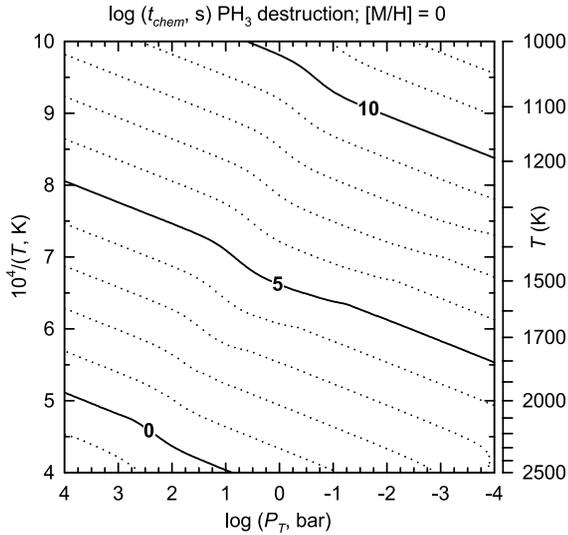
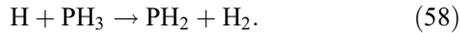
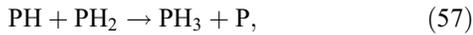
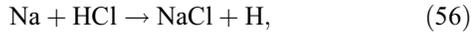
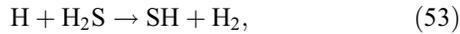


FIG. 7.—Logarithmic timescale (in seconds) for the chemical conversion of PH_3 to P_4O_6 in a solar metallicity gas. This conversion is kinetically inhibited in the upper atmospheres of giant planets and T dwarfs.

photochemistry on S and P compounds in brown dwarfs, EGPs, and related objects.

5.1. Thermochemistry in Substellar Objects

Thermochemical equilibrium is readily achieved in the hot, deep atmospheres of substellar objects, because gas-phase reaction rates are generally much faster than convective mixing rates (i.e., $t_{\text{chem}} \ll t_{\text{mix}}$). To illustrate this, we consider the kinetics of the following elementary reactions:



Here we use reaction (53) as an example for computing t_{chem} . The rate of disappearance of H_2S in reaction (53) is given by

$$\frac{d[\text{H}_2\text{S}]}{dt} = -k_{53}[\text{H}][\text{H}_2\text{S}], \quad (59)$$

where k_{53} ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) is the rate coefficient for reaction (53) and $[\text{H}_2\text{S}]$ and $[\text{H}]$ are the molecular number densities (molecules cm^{-3}) for H_2S and H . The chemical lifetime for H_2S is defined as

$$t_{\text{chem}}(\text{H}_2\text{S}) = -\frac{[\text{H}_2\text{S}]}{d[\text{H}_2\text{S}]/dt} = \frac{1}{k_{53}[\text{H}]} \quad (60)$$

and is the time required for a $1/e$ reduction in the H_2S abundance. Representative chemical lifetimes for reactions (53)–(57) at 1 bar total pressure and 1000, 1500, and 2000 K are listed in Table 3. Although the short chemical lifetimes in Table 3 indicate that these reactions proceed rapidly, we must also consider vertical mixing rates to determine whether equilibrium is established. The timescale for convective mixing t_{mix} is approximated by

$$t_{\text{mix}} \sim H^2/K_{\text{eddy}}, \quad (61)$$

where K_{eddy} is the eddy diffusion coefficient. The pressure scale height, H , is given by

$$H = RT/\mu g, \quad (62)$$

where R is the gas constant, μ is the mean molecular weight of the gas, and g is gravity. For a solar system composition gas, $\mu \approx 2.3 \text{ g mol}^{-1}$. A convective timescale of $t_{\text{mix}} \sim 10^6 \text{ s}$ is expected near the 1000 K level on Jupiter, using $H \sim 140 \text{ km}$ ($\log g = 3.4$) and $K_{\text{eddy}} \sim 10^8 \text{ cm}^2 \text{ s}^{-1}$ (Fegley & Prinn 1988). On Gliese 229B, we estimate $t_{\text{mix}} \sim 10^7 \text{ s}$ at the 1000 K level, assuming $H \sim 3.6 \text{ km}$ ($\log g = 5.0$; Saumon et al. 2000) and $K_{\text{eddy}} \sim 10^4 \text{ cm}^2 \text{ s}^{-1}$ (Griffith & Yelle 1999). Because of its low gravity ($\log g = 3.0$; Iro et al. 2005), HD 209458b has large mixing times of $\sim 10^7$ – 10^{11} s at the 1000 K level, depending on the assumed K_{eddy} value ($\sim 10^8$ – $10^4 \text{ cm}^2 \text{ s}^{-1}$). These timescales for convective mixing are typically many orders of magnitude greater than the chemical lifetimes listed in Table 3 (i.e., $t_{\text{chem}} \ll t_{\text{mix}}$). We therefore expect the rapid establishment of thermochemical equilibrium in the deep atmospheres of substellar objects. In instances where the rate of vertical mixing equals or exceeds the rate of chemical reactions ($t_{\text{chem}} \geq t_{\text{mix}}$), disequilibrium species (e.g., PH_3 ; see § 4.3) are mixed into the upper atmospheres of substellar objects, as occurs on Jupiter and Saturn (e.g., CO , HCN , PH_3 , GeH_4 , and AsH_3 ; FL94) and Gliese 229B (e.g., CO , PH_3 , and N_2 ; Fegley & Lodders 1996; Griffith & Yelle 1999; Saumon et al. 2000).

5.2. Photochemistry on Pegasi Planets

In order to examine the relative importance of photochemical versus thermochemical processes in substellar objects, we consider

TABLE 3
REPRESENTATIVE CHEMICAL LIFETIMES AT 1 BAR PRESSURE

REACTION	t_{chem}	CHEMICAL LIFETIME (s)			KINETIC DATA
		1000 K	1500 K	2000 K	
Eq. (53)	$t_{\text{chem}}(\text{H}_2\text{S})$	$10^{0.4}$	$10^{-3.8}$	$10^{-5.9}$	Yoshimura et al. (1992)
Eq. (54)	$t_{\text{chem}}(\text{SH})$	$10^{2.7}$	$10^{0.2}$	$10^{-0.2}$	Kurbanov & Mamedov (1995)
Eq. (55)	$t_{\text{chem}}(\text{S})$	$10^{1.7}$	$10^{-2.3}$	$10^{-4.3}$	Woiki & Roth (1994)
Eq. (56)	$t_{\text{chem}}(\text{Na})$	$10^{1.4}$	$10^{-1.6}$	$10^{-1.8}$	Husain & Marshall (1986)
Eq. (57)	$t_{\text{chem}}(\text{PH})$	$10^{4.2}$	$10^{1.2}$	$10^{1.0}$	Twarowski (1995)
Eq. (58)	$t_{\text{chem}}(\text{PH}_3)$	$10^{0.4}$	$10^{-3.5}$	$10^{-5.4}$	Arthur & Cooper (1997)

NOTES.—Convective mixing timescales (in seconds) are $t_{\text{mix}} \sim 10^{6.3}$ (1000 K), $10^{6.6}$ (1500 K), and $10^{6.9}$ (2000 K) for Jupiter, $10^{7.1}$ (1000 K), $10^{7.5}$ (1500 K), and $10^{7.7}$ (2000 K) for Gliese 229B, and $10^{7.1}$ – $10^{11.1}$ (1000 K), $10^{7.5}$ – $10^{11.5}$ (1500 K), and $10^{7.7}$ – $10^{11.7}$ (2000 K) for HD 209458b. See § 5.1 for details.

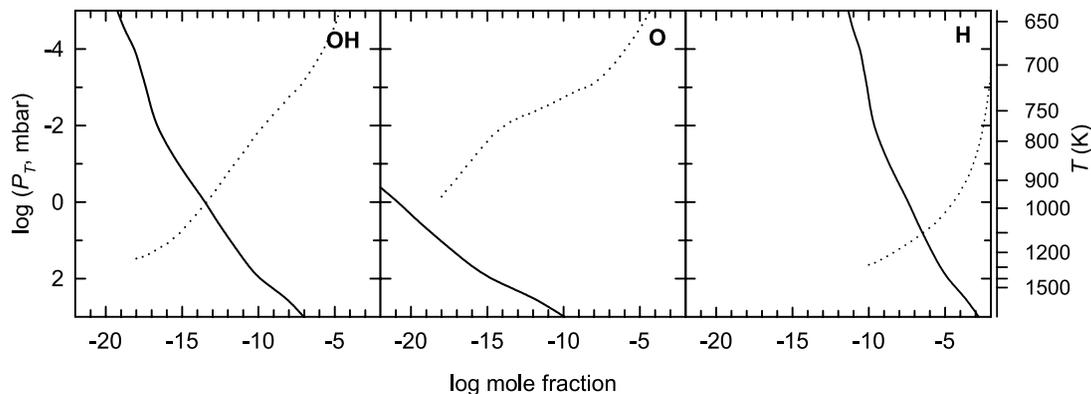


FIG. 8.—Comparison of thermochemical (*solid lines*) and photochemical (*dotted lines*; Liang et al. 2003) abundances for the reactive species OH, O, and H in the upper atmosphere of HD 209458b. See text for details.

an extreme example: the strongly irradiated upper atmosphere of HD 209458b. This Pegasi planet orbits a solar-type star at 0.05 AU and receives a stellar UV flux $\sim 10,000$ times that for Jupiter (e.g., Liang et al. 2003). To determine the depth in the atmosphere where thermochemical processes become important, we compared the thermochemical equilibrium abundances of the reactive species OH, O, and H in our model with photochemical equilibrium abundances from Liang et al. (2003) for HD 209458b. Plots comparing photochemical (*dotted lines*) and thermochemical (*solid lines*) abundances for these reactive species are shown in Figure 8, using the P - T profile for HD 209458b from Figure 1 of Liang et al. (2003).

At very low pressures, in the uppermost atmosphere of HD 209458b, photochemistry produces excess disequilibrium abundances of OH, O, and H, primarily via H_2O photolysis (Liang et al. 2003). Thermochemistry becomes increasingly important with depth, as pressures and temperatures increase and the available stellar flux decreases. Eventually, the predicted thermochemical abundances surpass the photochemical abundances, indicating the establishment of equilibrium chemistry. In other words, the photochemical reactions are no longer driving the thermochemical reactions out of equilibrium. As shown in Figure 8, this crossover occurs near the ~ 1 – 10 mbar levels ($T \sim 980$ – 1140 K) for the reactive species OH, O, and H. Thermochemical processes are therefore expected to be important at pressures of ~ 10 mbar and higher on HD 209458b, consistent with results showing that most of the incoming stellar flux is absorbed by the 1 bar level ($T \sim 1640$ K) in its atmosphere (Iro et al. 2005). Furthermore, Fortney et al. (2005, 2006) point out that the infrared spectra of Pegasi planets appear to be most sensitive to opacity near 10–100 mbar ($T \sim 1140$ – 1400 K). This suggests that thermochemical models will provide a useful basis for interpreting and guiding observations of Pegasi planet atmospheres.

6. SUMMARY

Thermochemistry governs the chemical behavior of sulfur and phosphorus species in the hot, deep atmospheres of substellar objects. Hydrogen sulfide is the most abundant sulfur-bearing gas throughout substellar atmospheres, and observations of H_2S in these objects should provide a good estimate of their atmospheric sulfur content. The condensation of metal sulfide clouds slightly lowers the atmospheric H_2S abundance to $\sim 91\%$ of the total S inventory. These clouds also affect opacity by introducing condensed particles and by removing absorbing gases from the observable atmosphere. The mercapto radical (SH) and SiS are the next most abundant sulfur gases after H_2S , and the relative importance of SiS increases with increasing effective temperature. Furthermore, the maximum SiS abundance occurs near the Mg silicate cloud base and is a potential tracer of weather in Pegasi planets and L dwarfs.

Phosphorus speciation is considerably more complex than that for C, N, O, or S, and several phosphorus gases become relatively abundant at high temperatures. Disequilibrium abundances of PH_3 are expected in the upper atmospheres of giant planets and T dwarfs via rapid vertical mixing from deeper levels. In addition, phosphine abundances in giant planets and T dwarfs are expected to approximately represent their atmospheric phosphorus inventories. In Pegasi planets and L dwarfs, P_2 is the dominant phosphorus gas until it is replaced by P_4O_6 at low temperatures or PH_2 at high temperatures. The phosphino radical (PH_2) is the most abundant phosphorus gas in the deep atmospheres of brown dwarfs and Pegasi planets.

This work was supported by the NASA Planetary Atmospheres Program and the McDonnell Center for Space Sciences at Washington University in St. Louis. Work by K. L. is supported by NSF grant AST 04-06963.

APPENDIX

ADDITIONAL COMPOUNDS

Here we list additional sulfur and phosphorus compounds investigated but not discussed in detail above. This list includes unstable condensates and minor gases predicted to have very low abundances in a solar system composition gas at temperatures and total pressures relevant for substellar atmospheres. Depending on the prevailing sulfur, carbon, and phosphorus chemistry, the abundances of key gases are P_T -independent: H_2S_2 within the H_2S field; OCS, CS, and CS_2 within the CO field; CH_3SH within the CH_4 field; and HPO, PH, and PN within the P_2 field. However, their abundances are generally too low to serve as useful temperature probes in brown

dwarf or EGP atmospheres. Some gases (H_2S_2 and CH_3SH) are potentially detectable via deep atmospheric entry probes on Jupiter and Saturn (FL94).

For a given metallicity, relatively constant OCS abundances are expected throughout the atmospheres of CO-dominated objects; however, maximum OCS abundances are only ~ 1 ppb (for solar metallicity) in L dwarfs and Pegasi planets. The equilibrium abundances of P, PO, and PS generally increase with T and decrease with P_7 . These gases only become important at the lowest total pressures considered here (see Fig. 4). The behavior of HCP is similar to that of PH_2 ; the maximum HCP abundances are ~ 50 ppb (for solar metallicity) over the P - T range considered here.

Sulfur.— S_2 , S_3 , S_4 , S_2O , SO , SO_2 , SO_3 , SOH , HSO , H_2SO , H_2SO_4 , SF , SF_2 , H_2S_2 , OCS , CS , CS_2 , CH_3SH , NS , PS , K_2S , CaS , FeS , MgS , MnS , TiS , VS , ZrS , SiS_2 , TiS_2 , ZrS_2 , S(s,l) , OCS(s,l) , and $\text{SO}_2(\text{s,l})$.

Phosphorus.— P_3 , P_4 , PO , PO_2 , P_2O_3 , P_2O_4 , P_2O_5 , P_3O_6 , P_4O_7 , P_4O_8 , P_4O_9 , P_4O_{10} , PCl , PCl_2 , PCl_3 , PF , PF_2 , PF_3 , HPO , HCP , CP , PH , PN , PS , P(s) , and $\text{P}_4\text{O}_{10}(\text{s,l})$.

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