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ATMOSPHERIC CHEMISTRY OF THE BROWN DWARF GLIESE 229B: THERMOCHEMICAL EQUILIBRIUM PREDICTIONS

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ABSTRACT

Thermochemical equilibrium calculations of gas abundances and condensation cloud formation are used to model the atmospheric chemistry of Gliese 229B. The calculations, which are analogous to our prior modeling of atmospheric chemistry of the Jovian planets in our solar system, predict the abundances of gases that are potentially observable by Earth-based and Earth-orbital telescopes. The calculations indicate that refractory elements such as Ca, Al, Ti, V, the lanthanides, Mg, Si, and Fe are removed by condensate cloud formation at temperatures above 1600 K and that gases containing these elements should not be observed. The major H, O, C, N, S, P, Cl, and F gases are predicted to be H_2, H_2O, CO (temperatures $T > 1470$ K), CH_4 ($T < 1470$ K), N_2 ($T > 630$ K), NH_3 ($T < 630$ K), H_2S, PH_3 ($T > 1155$ K), P_4O_6 ($T < 1155$ K), HCl, and HF. By analogy with the Jovian planets in our solar system, we expect that rapid vertical mixing may quench the destruction of species such as CO, N_2, HCN, and PH_3, leading to abundances greater than thermochemical equilibrium values at low temperatures in the atmosphere of Gliese 229B. In principle, observations of CO, N_2, the NH_3/CH_4 ratio, HCN, and PH_3 could constrain such rapid vertical mixing and current models of the atmospheric thermal profile.

Subject headings: infrared: stars — stars: abundances — stars: atmospheres — stars: individual (Gliese 229B) — stars: low-mass, brown dwarfs

1. INTRODUCTION

Gliese 229B (Gl 229B), a proper-motion companion to the star Gl 229A, was discovered recently by Nakajima et al. (1995) and identified by them as a cool brown dwarf. The initial observation of CH_4 and H_2O absorption features in the atmosphere of Gl 229B (Oppenheimer et al. 1995), subsequent IR observations of CH_4 and H_2O absorption features (Geballe et al. 1996), IR broadband photometry (Matthews et al. 1996), and theoretical models of the atmospheric structure and spectra of Gl 229B (Allard et al. 1996; Marley et al. 1996) support its identification as a brown dwarf.

Here we present some results of thermochemical equilibrium modeling of the atmospheric chemistry of Gl 229B. The calculations predict the abundances of spectroscopically observable gases and the condensation cloud chemistry in the atmosphere of Gl 229B as a function of temperature, pressure, and elemental composition. The results thus provide a foundation for interpreting the existing spectroscopic observations and for guiding future spectroscopic studies of this cool brown dwarf.

2. THERMOCHEMICAL EQUILIBRIUM CALCULATIONS

The thermochemical equilibrium calculations displayed in Figures 1 and 2 were done using the CONDOR computer code (Fegley & Lodders 1994). CONDOR calculates the distribution of elements among different molecules, radicals, atoms, and ions at thermochemical equilibrium for a given temperature, pressure, and elemental composition. It does this by considering simultaneously the constraints of chemical equilibrium, electroneutrality, and mass balance. The operation of the code and the thermodynamic database used are described in Fegley & Lodders (1994). At present, over 2500 compounds of all naturally occurring elements are included in the database. The CONDOR code has been used previously to model atmospheric chemistry of the Jovian planets (Fegley & Lodders 1994; Lodders & Fegley 1994), condensation chemistry in the solar nebula (Lodders & Fegley 1993), molecular abundances in the atmospheres of white dwarf stars (Schmidt, Bergeron, & Fegley 1995), gas chemistry, and grain condensation in the atmospheres and circumstellar outflows of carbon stars (Lodders & Fegley 1995; Bernatowicz et al. 1996).

The calculations reported here assume solar elemental abundances (Anders & Grevesse 1989) and the best-fit pressure (P)–temperature (T) profile (with $T_{\rm eff} = 960$ K and $g = 1000$ m s^{-2}) of Marley et al. (1996) to model the atmosphere of Gl 229B. Small variations from solar composition do not alter our conclusions significantly.

3. DISCUSSION

Here we summarize a subset of our results for the 10 most abundant chemically reactive elements (H, O, C, N, Mg, Si, Fe, S, Al, Ca) and for the less abundant volatile elements P, Cl, and F in solar composition material. Figure 1 displays the best-fit P-T profile of Marley et al. (1996) for the atmosphere of Gl 229B and the P-T profile for the atmosphere of Jupiter as well as several important thermochemical phase boundaries. Figure 2 shows equilibrium abundances for important gases along the adopted thermal profile for Gl 229B. We discuss first the significance of the thermochemical phase boundaries in Figure 1 and then their implications for atmospheric chemistry of Gl 229B.

The line labeled $CaTiO_3$ shows the condensation curve for perovskite and is representative of the pressure-dependent temperatures at which other refractory elements such as Al, Zr, V, and the lanthanides condense from a solar gas. The intersection of the thermal profile for Gl 229B with the perovskite condensation curve occurs at high temperatures and pressures and thus indicates that refractory elements are condensed out of the gas deep in the atmosphere of Gl 229B. Spectral features of TiO, VO, and other refractory oxide gases

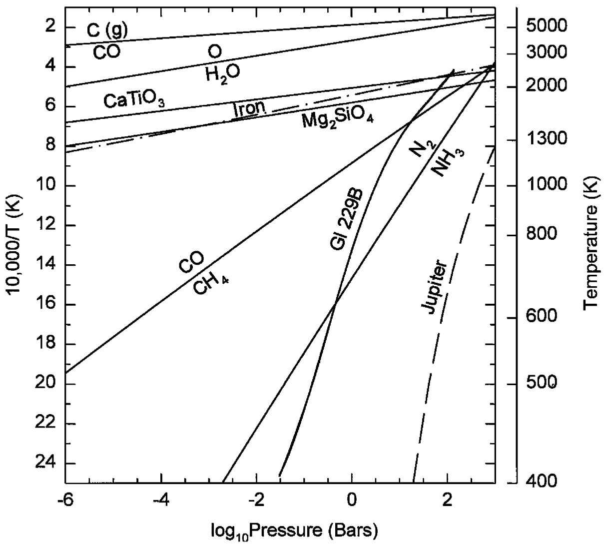

FIG. 1.—A comparison of the pressure (P)–temperature (T) profiles for the atmospheres of Gl 229B ($T_{\rm eff} = 960$ K and $g = 1000$ m s^{-2} from Marley et al. 1996) and Jupiter with some important thermochemical phase boundaries in a solar composition gas. As explained in the text, the lines labeled C/CO, CO/CH_4, O/H_2O, and N_2/NH_3 are boundaries along which these carbon, oxygen, and nitrogen gases have equal abundances. The $CaTiO_3$ (perovskite) condensation line is representative of the pressure-dependent temperatures at which other refractory elements such as Al, Zr, V, and the lanthanides condense from a solar gas. The abundant rock-forming elements (Mg, Si, Fe) condense as iron and Mg_2SiO_4 (forsterite).

are thus expected to be absent in spectra of Gl 229B. The abundant rock-forming elements (Mg, Si, Fe) condense as iron and Mg_2SiO_4 (forsterite). The condensation of these refractory phases at high temperatures plausibly removes Ca, Ti, Al, Mg, Si, Fe, and other less abundant but refractory elements from the observable atmosphere of Gl 229B.

This is a similar situation as on Jupiter, where thermochemical modeling predicts that the more volatile rock-forming elements Ge, P, and As should be present as GeH_4, PH_3, and AsH_3, while SiH_4, formed from more refractory Si, should be absent from the observable atmosphere (Barshay & Lewis 1978; Fegley & Lodders 1994). In fact, GeH_4, PH_3, and AsH_3 are observed on Jupiter (Bjoraker, Larson, & Kunde 1986; Noll, Larson, & Geballe 1990), while SiH_4 is not seen, and the upper limit of $<2.5 \times 10^{-9}$ on the SiH_4/H_2 mixing ratio (Treffers et al. 1978) is ~29,000 times smaller than the solar Si/H_2 ratio.

The lines labeled C/CO, CO/CH_4, O/H_2O, and N_2/NH_3 are boundaries along which these carbon, oxygen, and nitrogen gases have equal abundances. Taking the CO/CH_4 boundary as an example, the net thermochemical reaction

$$CO(g) + 3H_2(g) = CH_4(g) + H_2O(g), \qquad (1)$$

controls the equilibrium distribution of carbon between CO and CH_4 as a function of temperature and pressure. Methane is more abundant than CO to the right of the CO/CH_4 phase boundary and is less abundant than CO to the left of the boundary. Graphite is thermodynamically unstable, and CO_2 is less abundant than C(g), CO, or CH_4 in the P-T region shown in Figure 1 (Lewis, Barshay, & Noyes 1979). Likewise, the net thermochemical reaction

$$N_2(g) + 3H_2(g) = 2NH_3(g), \qquad (2)$$

determines the equilibrium partitioning of nitrogen between N_2 and NH_3. At much higher temperatures between the C/CO and O/H_2O boundaries, N_2 dissociates to atomic N(g). Thermochemical equilibria analogous to reactions (1) and (2) can be written for the N/N_2, C/CO, and O/H_2O boundaries, but they are not relevant to the present discussion.

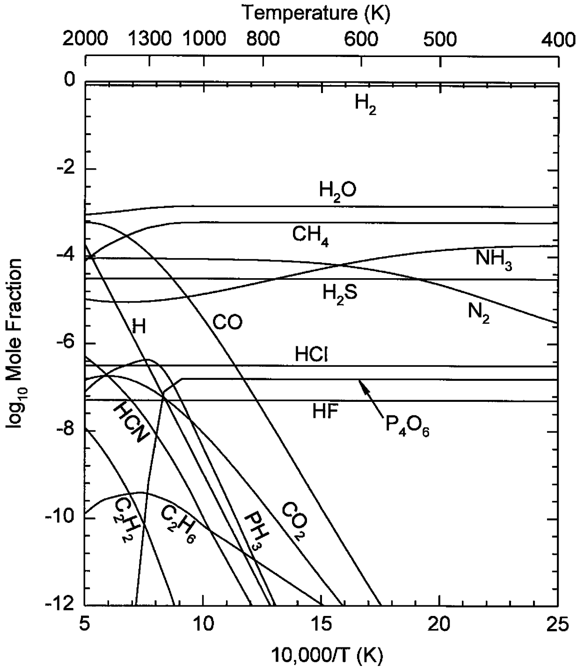

FIG. 2.—Thermochemical equilibrium abundances of the major H, O, C, N, S, P, Cl, and F gases along the adopted P-T profile for the atmosphere of Gl 229B. The mole fractions of the different gases are equal to the partial pressure of a gas divided by the total pressure. These calculations assume solar elemental abundances (Anders & Grevesse 1989).

Although several similarities exist, Figure 1 shows that in some respects the atmospheric chemistry of Gl 229B is likely to be different than that of Jupiter. Methane is observed to be the dominant carbon-bearing gas in the Jovian atmosphere, with a CH_4/H_2 mixing ratio of $\sim 2 \times 10^{-3}$ (Niemann et al. 1996). The observed CO/H_2 mixing ratio on Jupiter is only $\sim 1 \times 10^{-9}$ (Bjoraker et al. 1986) and is due to rapid vertical mixing of CO from the deep atmosphere at a rate faster than the CO → CH_4 conversion in upwelling Jovian gas (Prinn & Barshay 1977; Fegley & Prinn 1988a). However, the CO/CH_4 ratio is still $\ll 1$ in the deep atmosphere of Jupiter (Fegley & Lodders 1994) because the Jovian P-T profile is well inside the CH_4 stability field (see Fig. 1).

In contrast, the adopted P-T profile for the atmosphere of Gl 229B is closer to the CO/CH_4 phase boundary and intersects the CO/CH_4 boundary at ~1470 K. As a consequence, CO should be the dominant carbon-bearing gas at temperatures greater than 1470 K in the atmosphere of Gl 229B. Although Figure 2 shows that CO is less abundant than CH_4 at lower temperatures, the predicted CO/CH_4 ratio on Gl 229B is larger than on Jupiter at the same temperature levels in the two atmospheres.

Sufficiently rapid vertical mixing in the atmosphere of Gl 229B is expected to yield detectable quantities of CO in the atmosphere of this brown dwarf. As an example, the observed CO abundance of 1×10^{-9} on Jupiter corresponds to rapid vertical transport from about the 1065 K temperature level (Fegley & Lodders 1994). The CO abundance on Gl 229B at the same temperature is $\sim 1 \times 10^{-5}$, or ~10,000 times larger. Further modeling to take into account the rate of vertical mixing and the deeper radiative-convective boundary for Gl 229B than on Jupiter (e.g., Marley et al. 1996) could constrain further the expected abundance of CO and other high-temperature species in the observable atmosphere of Gl 229B.

Finally, Figure 2 shows that CO_2, C_2H_6, and C_2H_2 are less abundant than CO along the adopted thermal profile for Gl 229B. This is also true for C_2H_4, which overlaps C_2H_6 and C_2H_2. Other carbon gases included in the calculations have even lower abundances and are not shown.

Likewise, Figure 1 illustrates that N_2 should be much more abundant in the atmosphere of Gl 229B than in the Jovian atmosphere. Figures 1 and 2 show that N_2 should be more abundant than NH_3 at temperatures greater than 630 K in the atmosphere of Gl 229B. In contrast, NH_3 is observed to be the dominant nitrogen-bearing gas on Jupiter with a NH_3/H_2 mixing ratio of $\sim 2.6 \times 10^{-4}$ from IR spectroscopy (Bjoraker et al. 1986). Thermochemical modeling predicts that rapid vertical transport will yield $N_2/H_2 \sim (1\text{–}3) \times 10^{-5}$ in the Jovian troposphere (Fegley & Prinn 1988b; Fegley & Lodders 1994), but as yet no N_2 has been reported by the *Galileo* probe mass spectrometer experiment. Although N_2 is infrared inactive, observations of the NH_3/CH_4 ratio in the atmosphere of Gl 229B could provide important information about nitrogen chemistry.

On Jupiter, the observed NH_3/CH_4 ratio of $\sim$0.13 is apparently half the solar photospheric N/C ratio of $\sim$0.26 (Grevesse & Noels 1993). The difference may indicate a greater enrichment of carbon than nitrogen on Jupiter or may be due to NH_3 condensation in water clouds and solid NH_3 clouds in the Jovian atmosphere. This question may be resolved if an NH_3 abundance in the deep Jovian atmosphere can be determined from the *Galileo* probe mass spectrometer data.

On Gl 229B, NH_3/CH_4 ratios significantly lower than solar (assumed here to be representative for the bulk N/C atomic ratio in Gl 229A and Gl 229B) could indicate either high-temperature quenching of the $N_2 \rightarrow NH_3$ conversion in upwelling gas parcels or that the thermal profile for Gl 229B crosses the N_2/NH_3 phase boundary at lower temperatures than indicated by the adopted thermal profile. Observations of HCN, whose abundance is also a sensitive function of temperature (Fig. 2), could help to distinguish between these two possibilities.

Using numerical models provided to us by M. Marley, we studied the sensitivity of nitrogen and carbon chemistry to different thermal profiles. A cooler thermal profile ($T_{\rm eff} = 880$ K and $g = 1000$ m s^{-2}) intersects the N_2/NH_3 boundary at 680 K, while a hotter thermal profile ($T_{\rm eff} = 1030$ K and $g = 600$ m s^{-2}) intersects the N_2/NH_3 boundary at 550 K. Likewise, these two profiles intersect the CO/CH_4 boundary at different temperatures of 1585 K and 1305 K, respectively, for the cooler and hotter profiles.

Finally, Figure 2 illustrates also the chemistry of oxygen, sulfur, phosphorus, chlorine, and fluorine gases. Water vapor is the major oxygen gas below 2000 K. Its abundance may be depleted by H_2O-NH_3 aqueous solution or water ice cloud condensation at temperatures below 300 K. Hydrogen sulfide is the major sulfur gas throughout the 400–2000 K range. Phosphine (PH_3) is an important phosphorus gas at high temperatures ($T > 1155$ K), but if equilibrium is maintained it is converted to P_4O_6(g) with decreasing temperature. By analogy with Jupiter and Saturn, where rapid vertical mixing quenches PH_3 destruction (Barshay & Lewis 1978; Fegley & Lodders 1994), we expect that PH_3 should be observable in the atmosphere of Gl 229B. Lastly, our calculations show that the hydrogen halides HCl and HF are the dominant chlorine and fluorine gases over the 400–2000 K temperature range.

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