

Atmospheric Chemistry of Venus-like Exoplanets

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Abstract: We use thermodynamic calculations to model atmospheric chemistry on terrestrial exoplanets that are hot enough for chemical equilibria between the atmosphere and lithosphere, as on Venus. The results of our calculations place constraints on abundances of spectroscopically observable gases, the surface temperature and pressure, and the mineralogy of the planetary surface. These results will be useful in planning future observations of the atmospheres of terrestrial-sized exoplanets by current and proposed space observatories such as the *Hubble Space Telescope* (HST), *Spitzer*, *James Webb Space Telescope* (JWST), *Terrestrial Planet Finder*, and *Darwin*.

Subject keywords: astrochemistry; atmospheric effects; planets and satellites: atmospheres.

1. Introduction

The search for exoplanets in general and Earth-sized exoplanets in particular has been heating up in recent months. Results from the Kepler mission, which is designed to determine the frequency of Earth-sized exoplanets, are beginning to be published (e.g., Borucki et al. 2010) with much more data yet to be analyzed. The COROT space telescope has already returned results, including the discovery of one of the smallest and hottest exoplanets so far discovered (CoRoT-7b, Léger et al. 2009). Even ground-based methods are now capable of finding super-Earth exoplanets (Charbonneau et al. 2009). Current and future space observatories such as the Hubble Space Telescope (HST), the Spitzer Space Telescope, the James Webb Space Telescope (JWST) or the proposed missions Terrestrial Planet Finder (TPF) and Darwin will also be able to characterize the atmospheres of these exoplanets. As more discoveries of Earth-sized exoplanets are made and characterization of their atmospheres becomes more possible, it is important to model the nature of their atmospheres. What will their main components be? Will they look like the Earth's atmosphere? Or perhaps like the atmospheres of the other terrestrial planets in our own solar system?

Techniques for discovering exoplanets are initially biased towards planets with either short-periods or intermediate periods with high orbital eccentricities (Kane et al. 2009). This is particularly true for transits, in which a planet passes in front of its star and which allow atmospheric observations. As observations for a particular star increase, there is a greater chance of observing longer period planets, but initial discoveries are likely to be of large short period planets (e.g. Borucki et al. 2010). Short-period super-Earth planets like CoRot-7b ($a = 0.0172$ AU, Léger et al. 2009) should be hot and

depleted in volatiles. We have previously modeled such exoplanets, under the assumption that they have been completely stripped of their volatiles (Schaefer & Fegley 2009).

Models by others have considered the range of possible compositions we may expect to find for volatile-rich super-Earth exoplanets (e.g., Kaltenegger et al. 2007; Elkins-Tanton & Seager 2008).

In this paper we consider planets that more closely resemble Venus. These are planets that have shorter periods than the star's habitable zone (HZ), and therefore have lost, or never accreted, significant amounts of water. As on Venus, we expect the surface temperature and pressure of these planets to be hot enough to allow surface-atmosphere interaction. Therefore the bulk atmospheric composition will be controlled by the mineralogy of the surface. Models for Venus show that the observed partial pressures of CO₂, H₂O, HCl, and HF are in chemical equilibrium at a pressure and temperature very close to that observed at the surface of Venus (Fegley 2004; Lewis 1970). In this paper, we apply techniques used to model Venus' atmosphere to models for several hypothetical Venus-like exoplanets.

2. Venus Surface-Atmosphere Equilibrium Model

We model atmosphere-lithosphere chemical interactions on exoplanets with surface conditions similar to Venus. We do this by using mineral buffer reactions for minerals that may be plausibly found together in natural rock systems. The intersections of these mineral buffers on a pressure-temperature plot define a set of pressure and temperature conditions for the planet, which also allows us to determine within a reasonable range the allowable abundances of CO₂, H₂O, HCl, and HF that would be present in the atmosphere. This procedure was developed by Lewis (1970) to predict the

surface pressure and temperature for Venus. The abundances of CO₂, H₂O, HCl, and HF measured in the lower Venusian atmosphere allowed Lewis to describe a small suite of possible compatible mineral buffer systems for the surface of Venus. The calculations use plausible mineral buffers – that is buffers involving minerals that are found in the same rock types: felsic rocks with free silica (e.g., like Earth’s continental crust), or mafic rocks without free silica (e.g., like Earth’s basaltic oceanic crust). We used all buffers considered by Lewis (1970), Fegley and Treiman (1992), and the phyllosilicate buffers considered by Zolotov et al. (1997) in our model.

Figure 1a shows results for this method applied to Venus. The point on the graph shows the measured CO₂ pressure (taken as the total pressure), and the surface temperature. The lines in Fig. 1a represent the mineral buffers which provide the closest fit to the measured conditions for Venus (T , P_{CO_2} , $X_{\text{H}_2\text{O}}$, X_{HCl} , and X_{HF} , where X_i is the mole fraction of gas i defined as the partial pressure divided by the total pressure). The model parameters are listed in Table 1, and the mineral buffers used are listed in Table 2. The temperature of the planet is initially defined by the intersections of the CO₂ and H₂O buffers. The total pressure of the planet is assumed to be dominated by CO₂, so $P_T = P_{\text{CO}_2}$. The CO₂ pressure of Venus (92.1 bars) is most closely matched by the calcite-quartz-wollastonite buffer (reaction C1 in Table 2). Our model explicitly assumes that this buffer (C1) controls the CO₂ pressure in the lower Venusian atmosphere. The H₂O mixing ratio is defined by observations. In the case of Venus, we use $X_{\text{H}_2\text{O}} = 30 \pm 15$ ppm, based on the accepted value (Fegley 2004). We considered 53 water buffers given by Lewis (1970), Fegley & Treiman (1992), and Zolotov et al. (1997). The water buffer that intersects the CO₂ buffer most closely to the observed T and P conditions (740 K, 92.1 bars) is chosen.

This reaction is the eastonite buffer (W1 in Table 2). The C1 and W1 buffers intersect at 758 K and 122 bars, which is close to the observed surface conditions of Venus.

Figure 2 illustrates how the H₂O abundance affects the model results. The dark line is the C1 buffer, and the point shows Venus surface conditions. The thinner lines show the change in total pressure with the assumed H₂O mole fraction, from 0.1 ppm to 1%. Between 10 and 100 ppm, results are shown for 10 ppm steps. The temperature and pressure for Venus are matched exactly with an H₂O abundance of 24 ppm. This is somewhat lower than the observed value of 30 ppm, but well within the ± 15 ppm uncertainty (Fegley 2004).

The abundances of HCl and HF depend on both the total pressure and surface temperature, as well as on the H₂O mole fraction. Using the 10 HCl buffers from Lewis (1970) and Fegley & Treiman (1992), we find a range of HCl abundances from 42 ppb – 29 ppm. The best fit for the HCl abundance is given by the albite – halite – andalusite – quartz buffer (C11), which gives an HCl abundance of 0.76 ppm. For comparison, the accepted abundance of HCl in Venus' atmosphere is 0.5 ppm (Fegley, 2004). Similarly for the HF abundance, we find a range of values from 0.2 ppb – 25.7 ppm. The best fit to the HF abundance is given by the fluor-phlogopite buffer (F1) which gives an HF abundance of 4.6 ppb. This is very close to the observed value of 4.5 ppb (Fegley 2004).

3. Models of Venus-like Exoplanets.

Figure 1b-1d shows results from our models for 3 hypothetical exo-Venus planets. The initial parameters of these models were chosen from intersections of different CO₂ buffers and H₂O buffers. These intersections determine the total pressure of CO₂ and the

temperature. The parameters (T , P , $X_{\text{H}_2\text{O}}$, X_{HCl} , X_{HF}) for each model and the buffers used are listed in Table 1. The mineral buffer reactions are listed in Table 2.

We explored the necessary conditions to form planets hotter (740 – 1000 K) and colder (450 – 740 K) than Venus for both felsic and mafic mineral suites. We found that in order to create a planet hotter than Venus, the H_2O abundance had to increase significantly. For Venus-like exoplanets with felsic (SiO_2 -bearing) crusts like Earth's continental crust, abundances greater than ~ 100 ppm H_2O were necessary. All hot felsic planets had larger total pressures than Venus. Mafic planets required even larger H_2O abundances (≥ 1000 ppm) for all water buffers other than eastonite, which produced hotter temperatures than Venus for H_2O abundances > 30 ppm (see Figure 2). In general, therefore, higher water vapor abundances should correspond to higher surface temperatures and more mafic surface mineralogies. Mafic planets also produced a much wider range of pressures, some less than and some greater than that of Venus.

The first exoplanet model shown in Fig. 1b (model B in Table 1) is a high-temperature exo-Venus with a basaltic (mafic) crust suite. The CO_2 and H_2O buffers that define the temperature and pressure are reactions C2 (magnesite-enstatite-forsterite) and W2 (phlogopite-forsterite-leucite-kalsilite) in Table 2. Using our mafic HCl and HF buffers, we found a range of abundances for HCl (446-544 ppb) and HF (7.4 ppb – 4.34 ppm). In the figure, we show our chosen results for the C12 (wollastonite-sodalite-halite-anorthite-albite) and F2 (orthoclase-forsterite-fluorophlogopite-enstatite) buffers, which give 446 ppb HCl and 7.4 ppb HF, respectively. Although we do not show a high temperature felsic planet here, we found that they generally have lower HCl abundances and higher HF abundances than mafic planets. However, the ranges between the two

suites overlap significantly, so it is not possible to distinguish between a mafic and felsic mineral suite on this basis alone.

For planets colder than Venus, we found that nearly all mafic exoplanets had lower total surface pressures than Venus, whereas the felsic exoplanets could have pressures both significantly larger and smaller than Venus. As temperature and water vapor abundance increase for the mafic exoplanets, the total pressure increases. Wide ranges of water vapor abundance produced planets colder than Venus for both the felsic and mafic mineral suites. To compare the possible HCl and HF abundances, we chose a cold felsic (model C) and a cold mafic planet (model D) with similar temperatures, pressures, and H₂O abundances. The temperature and pressure of model C are defined by the intersection of the C3 (diopside-quartz-calcite-forsterite) and W3 (tremolite-enstatite-dolomite-quartz) buffers. The temperature and pressure of model D are defined by the C4 (diopside-enstatite-forsterite-dolomite) and W2 (phlogopite-forsterite-leucite-kalsilite) buffers. Both planets have an H₂O abundance of 100 ppm. The felsic planet (C) has a slightly higher range of HCl (32 ppb–10.98 ppm) and HF (0.1 ppb–12.5 ppm) abundances compared to the mafic exoplanet (4.04–37.2 ppb HCl, 0.12–382 ppb HF). We show representative values in Fig. 1c and 1d. Unfortunately, however, the range of abundances given by possible HCl and HF buffers are not significantly different enough to permit observations to constrain whether an exo-planet's surface is felsic or mafic.

4. Photochemical Effects and the Abundances of Other Gases.

As discussed earlier, chemical equilibria involving mineral assemblages that are characteristically found in mafic rocks (i.e., similar to basaltic crust on Venus and Earth's oceanic crust) or felsic rocks (similar to Earth's continental crust) may control the

abundances of CO₂, H₂O, HCl, and HF in the atmospheres of Venus-like exoplanets. However, the abundances of CO and SO₂, which are also important constituents of Venus' atmosphere, are plausibly controlled by photochemical processes. For example, on Venus (and Mars) CO is produced by photolysis of CO₂ and its abundance depends on catalytic cycles for reforming CO₂ from CO + O₂ with the reaction



playing an important role in the Martian atmosphere. This reaction or others involving Cl oxides are responsible for regulating the CO abundance and reforming CO₂ from CO + O₂ on Venus (Yung & DeMore 1999). Carbon monoxide is also destroyed in Venus' lower atmosphere by reaction with elemental sulfur vapor



Thus by analogy with Venus we expect that the CO abundances in the atmospheres of Venus-like exoplanets are not simply regulated by mineral buffers, but are instead affected by photochemical production and loss via gas phase catalytic cycles in the stratomesospheres and by thermochemical loss in the near surface tropospheres.

Likewise, the abundances of SO₂, H₂S, OCS, and S₂ are probably due to a balance of volcanic outgassing, mineral buffer reactions and photochemical reactions. By analogy with Venus we expect that SO₂, which is produced volcanically and/or by mineral buffer reactions, will be photochemically oxidized to SO₃ and thence to H₂SO₄ cloud droplets. The H₂SO₄ cloud layer on Venus covers the entire planet and makes observations of the lower atmosphere difficult. Hydrogen sulfide, OCS, and S₂ - if present in the upper atmospheres - should be photolyzed on fairly short timescales (see Table 3). However, it is more likely that H₂S, OCS, and S₂ will be regulated by gas phase and gas-solid

chemical equilibria in the lower atmospheres of Venus-like exoplanets as is the case on Venus (e.g., see Fegley 2004). Kaltenegger & Sasselov (2010) studied sulfur cycles on Earth-like exoplanets and suggest that abundances of greater than a few ppm of SO₂ may be observable. For comparison, Venus' upper atmosphere contains ~1-500 ppb SO₂, and the lower atmosphere contains ~20-150 ppm SO₂ (de Bergh et al. 2006, Fegley 2004).

5. Application to Exoplanets

We believe that this work is timely because several on-going space missions are searching for Earth-like planets (e.g., Spitzer, HST, COROT, Kepler). However, short-period planets are highly favored by current detection methods (Kane et al. 2009). Transits, which allow observation of planetary atmospheres, are observed far more frequently for short period planets than long-period planets, and so initial planet detections from these missions should be for short-period planets. Short-period planets are likely to be hot from proximity to their stars and tidal heating (e.g., Jackson et al. 2008a,b). These planets, if similar in size to the terrestrial planets in our own solar system, are more likely to have atmospheres resembling Venus than Earth. These planets will be depleted in water, either from having accreted less of it due to their orbital location, or because they have lost water over time, as Venus is suspected to have done (Fegley, 2004).

Observation of lower atmospheric abundances by transmission spectroscopy of Venus-like exoplanets is likely to be difficult. Ehrenreich et al. (2006) have shown that a cloud layer such as the H₂SO₄ clouds of Venus is optically thick, which effectively blocks the lower atmosphere and increases the planetary radius observed in transits. Only the atmosphere above the cloud tops would be probed by transmission spectroscopy. As

with Venus, emission spectroscopy would be necessary to probe the lower atmosphere (i.e., below the cloud deck), which is in equilibrium with the surface. The night-side of Venus has several spectral windows between 1.5 and 2.5 μm that emit thermal radiation from the lower atmosphere and allow Earth-based observations of different levels of the lower atmosphere. These observations have been used to determine the abundances of H_2O , HF, HCl, OCS, and CO in Venus' lower atmosphere (e.g., Allen & Crawford 1984; Bézard et al. 1990; de Bergh et al. 1995). Thermal emissions from exoplanets have already been observed for several gas giant planets by both Spitzer in the mid-IR and HST in the near-IR using the secondary eclipse technique (Deming et al. 2005; Charbonneau et al. 2005; Grillmair et al. 2007; Richardson et al. 2007; Swain et al. 2008, 2009a,b). These observations have identified a number of molecular species including H_2O , CO_2 , CO, and CH_4 . The JWST, which will have a greater aperture than Spitzer, will be able to conduct more sensitive observations, which should allow spectroscopic observations of Earth-sized exoplanets, particularly around smaller M-class stars (Clampin et al. 2009). Additionally, several proposed missions (e.g., Terrestrial Planet Finder, Darwin) will use a nulling interferometer, which would block the light of the parent star and image the planet directly (Lawson, 2009; Cockell et al. 2009). Such an instrument would allow better detection of infrared emission from the night-side of a planet, where spectral windows such as those found at Venus may be seen. Therefore, we believe that observations of the lower atmospheres of a super-Venus may be possible in the near future.

As a broad generalization, we can say that planets similar to Venus (i.e., thick CO_2 atmospheres with only trace water) are more likely to be colder than Venus rather

than hotter. Hotter planets should have significantly more water in their atmospheres, and generally will have higher total pressures. Hot felsic planets will have relatively large pressures and HF abundances, with less water and HCl than a similar mafic planet.

Planets colder than Venus are more geochemically plausible. These planets will generally have lower total pressures than Venus and may have water vapor abundances similar or larger than Venus. Cold felsic planets will have higher total pressures, HCl, and HF abundances, but lower H₂O abundances than similar mafic planets.

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Table 1. Model Parameters and Gas Abundances

Model	T (K)	P _{CO2} (bars)	X _{H2O} (ppm)	X _{HCl} (ppb)	X _{HF} (ppb)	buffers
A (Venus)	740	92.1	24	760	4.6	C1,W1,C11,F1
B (hot mafic)	790	439.4	1000	446	7.4	C2,W2,C12,F2
C (cold felsic)	647	43.3	100	87	1.87	C3,W3,C13,F3
D (cold mafic)	653	41.33	100	4.04	0.13	C4,W2,C14,F2

Table 2. Mineral Buffer Reactions used in Exoplanet Models

Buffer	Reaction
<i>CO₂ buffers</i>	
C1	$\text{CaCO}_3 + \text{SiO}_2 = \text{CaSiO}_3 + \text{CO}_2$
C2	$\text{MgCO}_3 + \text{MgSiO}_3 = \text{Mg}_2\text{SiO}_3 + \text{CO}_2$
C3	$2\text{CaMg}(\text{CO}_3)_2 + \text{SiO}_2 = 2\text{CaCO}_3 + \text{Mg}_2\text{SiO}_4 + 2\text{CO}_2$
C4	$\text{CaMg}(\text{CO}_3)_2 + 4\text{MgSiO}_3 = 2\text{Mg}_2\text{SiO}_4 + \text{CaMgSi}_2\text{O}_6 + 2\text{CO}_2$
<i>H₂O buffers</i>	
W1	$\text{KMg}_2\text{Al}_3\text{Si}_2\text{O}_{10}(\text{OH})_2 = \text{MgAl}_3\text{O}_4 + \text{MgSiO}_3 + \text{KAlSiO}_4 + \text{H}_2\text{O}$
W2	$2\text{KMg}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2 = 3\text{MgSi}_2\text{O}_4 + \text{KAlSi}_2\text{O}_6 + \text{KAlSiO}_4 + 2\text{H}_2\text{O}$
W3	$\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2 = 3\text{MgSiO}_3 + 2\text{CaMgSi}_2\text{O}_6 + \text{SiO}_2 + \text{H}_2\text{O}$
<i>HCl buffers</i>	
Cl1	$2\text{HCl} + 2\text{NaAlSi}_2\text{O}_6 = 2\text{NaCl} + \text{Al}_2\text{SiO}_5 + 3\text{SiO}_2 + \text{H}_2\text{O}$
Cl2	$12\text{HCl} + 6\text{CaSiO}_3 + 5\text{Na}_4[\text{AlSiO}_4]_3\text{Cl} = 17\text{NaCl} + 6\text{CaAl}_2\text{Si}_2\text{O}_8 + 3\text{NaAlSi}_3\text{O}_8 + 6\text{H}_2\text{O}$
Cl3	$2\text{HCl} + 8\text{NaAlSi}_3\text{O}_8 = 2\text{Na}_4[\text{AlSi}_3\text{O}_8]_3\text{Cl} + \text{Al}_2\text{SiO}_5 + 5\text{SiO}_2 + \text{H}_2\text{O}$
Cl4	$2\text{HCl} + 9\text{NaAlSiO}_4 = \text{Al}_2\text{O}_3 + \text{NaAlSi}_3\text{O}_8 + 2\text{Na}_4[\text{AlSiO}_4]_3\text{Cl} + \text{H}_2\text{O}$
<i>HF buffers</i>	
F1	$2\text{HF} + \text{KAlSi}_2\text{O}_6 + 2\text{Mg}_2\text{SiO}_4 = \text{KMg}_3\text{AlSi}_3\text{O}_{10}\text{F}_2 + \text{MgSiO}_3 + \text{H}_2\text{O}$
F2	$2\text{HF} + \text{KAlSi}_3\text{O}_8 + 3\text{Mg}_2\text{SiO}_4 = \text{KMg}_3\text{AlSi}_3\text{O}_{10}\text{F}_2 + 3\text{MgSiO}_3 + \text{H}_2\text{O}$
F3	$2\text{HF} + \text{NaAlSiO}_4 + 2\text{CaMgSi}_2\text{O}_6 + 3\text{MgSiO}_3 = \text{NaCa}_2\text{Mg}_5\text{Si}_7\text{AlO}_{22}\text{F}_2 + \text{SiO}_2 + \text{H}_2\text{O}$

Table 3. Photochemical lifetimes at zero optical depth (top of atmosphere) for major atmospheric gases assuming solar flux at 1 AU

Species	J_1 (s^{-1})	t_{chem} (s)
CO ₂	2.02×10^{-6}	4.95×10^5
CO	6.459×10^{-7}	1.548×10^6
SO ₂	2.491×10^{-4}	4.014×10^3
OCS	6.493×10^{-4}	1.54×10^3
HCl	7.2×10^{-6}	1.39×10^5
HF	1.8×10^{-6}	5.56×10^5
H ₂ O	11.8038×10^{-6}	8.47×10^4

Sources: Levine (1985)

Figure Captions

Figure 1. (a) Best fit of mineral buffer systems to the observed conditions and atmospheric abundances of Venus. The mineral buffer model is then applied to several theoretical exoplanets: (b) hot mafic exo-Venus, (c) cold felsic exo-Venus, (d) cold mafic exo-Venus. The point represents the surface conditions of Venus. Buffer reactions are listed in Table 2.

Figure 2. Effect of H₂O abundance on total pressure, temperature and CO₂ abundance, using the C1 buffer (dark line), and the W1 buffer (thin lines). Lines for the W1 buffer between 10 ppm and 100 ppm are in 10 ppm increments. The point shows the observed surface pressure and temperature of Venus.

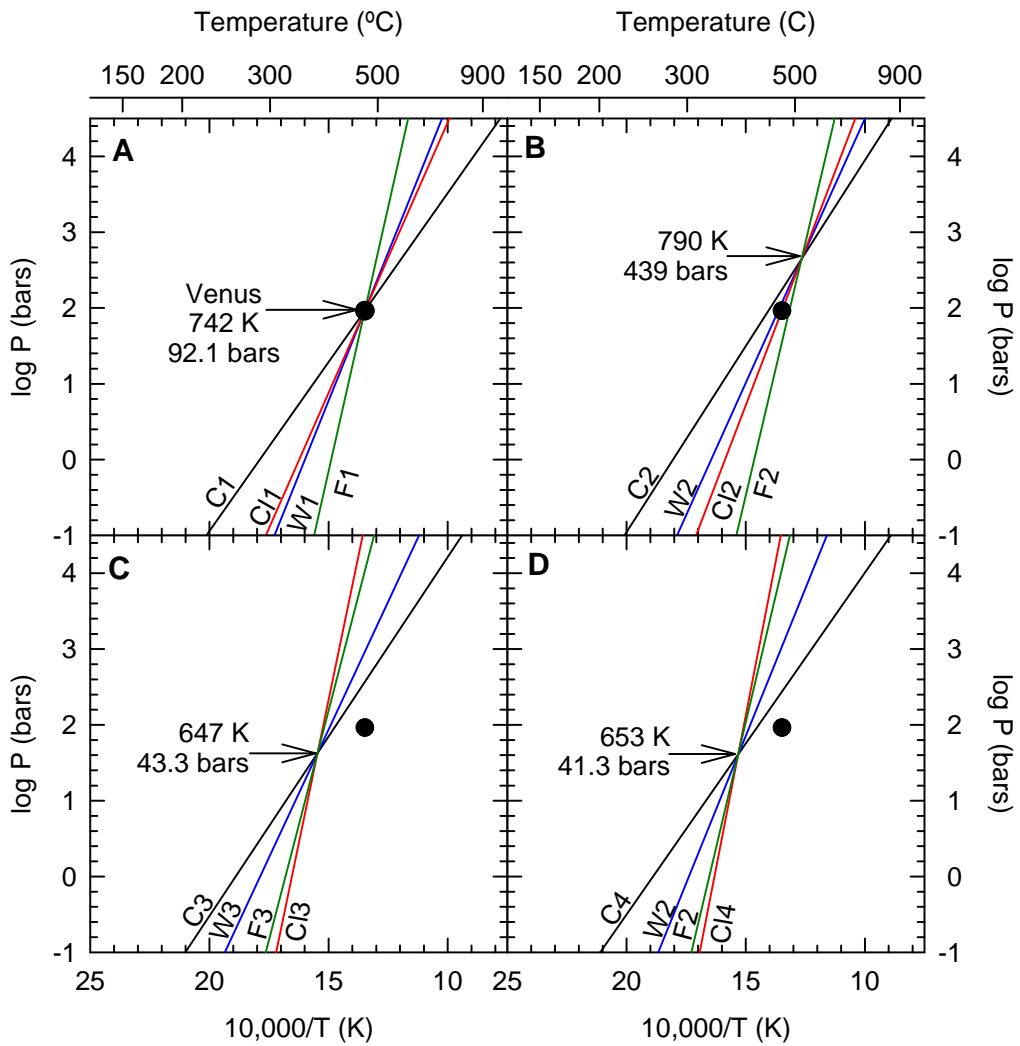


Figure 1.

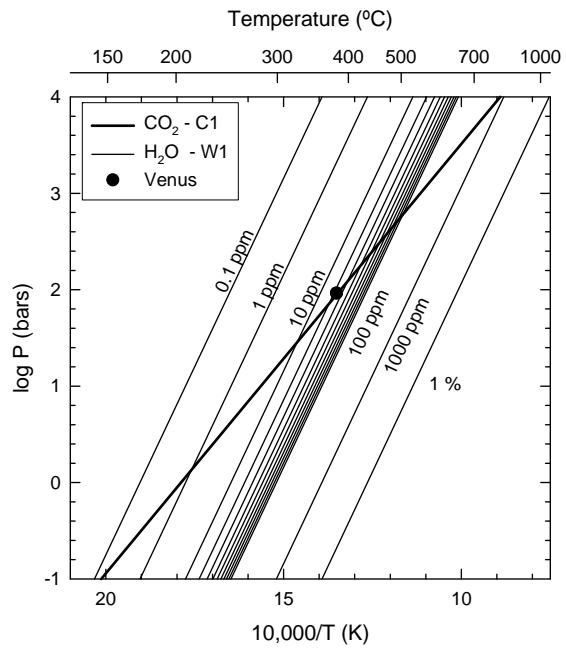


Figure 2.