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Hot stuff: Chemistry on Venus

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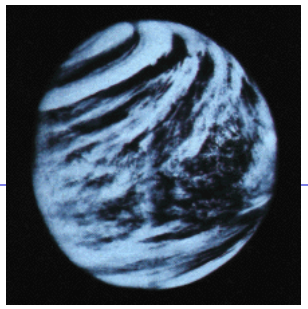

The planet Venus

The dark and light areas show differences in UV absorbance in the atmosphere

Special points of interest:

- Cytherean chemistry
- Triton Fun stuff
- Superfluous questions

The planet Venus is a hot, hellish world with a dense atmosphere and temperatures at its surface that could melt lead (~900 F). Venus has been visited by many spacecraft sent to study it by the United States, Russia and now Europe. The atmosphere has been observed and measured by flybys, orbiters and landers since the first mission to the planet, Mariner 2, flew by in 1962. There is a general understanding of the atmospheric chemistry in some regions of the atmosphere but not all portions are understood to the same degree. The troposphere near the surface is probably the least understood. However, studies of the sulfur chemistry in the Venus atmosphere has been done by a number of observers and modelers.

A veritable fleet of spacecraft have visited Venus*: Mariner 2, Mariner 4, Pioneer Venus* (orbiter and multiprobes), *Mariner 10, Venera 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, Magellan, Vega 1 and 2*, and *Venus Express*. The Venera and Vega were Russian, Pioneers and Mariners from the USA, and the most current mission still exploring Venus today is ESA's Venus Express. Other spacecraft did flybys to gain trajectory changes; they usually studied Venus while passing by, gathering new data. Some of the flyby spacecraft were *Galileo, Cassini* and *Messenger*.

Three of the missions that landed probes on the Venus surface had gas chromatographs: Pioneer Venus (Large probe), and Venera 11 and 12. Measurements of the upper atmosphere were done by the Pioneer Venus orbiter neutral mass spectrometer as well as some of the Venera missions.

In the atmosphere of Venus, carbon dioxide is the most abundant, but there is also *nitrogen, water, sulfur dioxide, hydrogen chloride, hydrogen fluoride, nitrous oxide, carbonyl sulfide, carbon monoxide* and *sulfuric acid*. There are smaller amounts of other species, including the noble gases.

Sulfur dioxide was found to be the most abundant sulfur species above 22 km, exceeding the concentrations of H_2S and OCS. The SO_2 reacts with water and eventually forms the sulfuric acid particles (via SO_3) from which the clouds at 48 km and above are comprised (von Zahn et al. 1983). These would be water droplets containing H_2SO_4. Venera 11 and 12 detected strong absorptions in the lower atmosphere (10-30 km) in the spectral region between 450 -600 nm. These were interpreted as originating from the sulfur allotropes, most notably S_3, which has an absorption at 450 nm. Since the atmosphere gets hotter as one goes toward the surface, the lighter allotropes predominate at lower altitudes (San'ko (1980) .

The sulfuric acid clouds are a very important component of the sulfur budget in the Venus atmosphere. As the water content varies in the altitude region between 20 and 70 km, the droplets can change their concentration of H_2SO_4 as they evaporate or condense water. Esposito et al (1983) report that, using their water profile, the concentration of H_2SO_4 in the cloud droplets should be around 85% +/- 5% at all cloud levels. However, they will vary according to altitude. Krasnopolsky (2007) reports that the concentration of sulfuric acid is 85% in the upper cloud deck, increasing to 98% at the lower cloud boundary near 48 km as the humidity changes. The droplets are *very* acidic. H_2O concentration is 1-2.5 ppm.

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Venus chemistry: *continued*

Photos/Info: NASA /Ames Research Center/Jet Propulsion Laboratory

The sulfur species thought to be present on Venus (in no particular order) are as follows: H_2S, SO_2, SO_3, $S_{2\text{-}8}$, COS, CS_2, H_2SO_4, H_2S_2, HSO_3, SO, HS, and S in the atmosphere, and sulfur-containing rocks and minerals such as FeS_2 (*pyrite*), Fe_7S_8 (*pyrrhotite*) and $CaSO_4$ (*anhydrite*) on the surface. There is interaction between the gases and the cloud droplets which contain some water. The sulfuric acid is in concentrated solutions in the droplets whose strength varies with altitude according to the local humidity. The decomposition of *pyrite* is thought to be the source of elemental sulfur vapor in the atmosphere and that the source for COS and H_2S is the oxidation of *pyrrhotite*. Some of the sulfur dioxide goes to make *anhydrite* but the reaction is slow enough that SO_2 persists in the atmosphere. The sulfur-containing rocks are oxidized by the carbon dioxide in the atmosphere to form iron oxides:

$$FeS_2 + 2CO_2 \longrightarrow FeO + 2COS + \tfrac{1}{2} O_2$$

$$3Fe_7S_8 + 28CO_2 \longrightarrow 7Fe_3O_4 + 12S_2 + 28CO$$

$$Fe_9S_{10} + 12CO_2 \longrightarrow 3Fe_3O_4 + 5S_2 + 2CO$$

The mineral pyrite converts to pyrrhotite to produce S_2 :

$$7FeS_2 \longrightarrow Fe_7S_8 + 3S_2$$

The cycle starts off near the surface as S_2 coming from the minerals and then getting more and more oxidized, until the end product is sulfuric acid, H_2SO_4:

$$S_2 \longrightarrow H_2S + COS \longrightarrow SO_2 \longrightarrow H_2SO_4$$

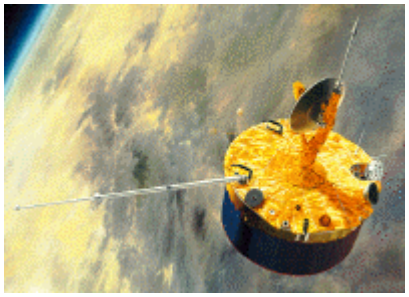
SO_2 is the most dominant *radiatively active* species at low altitudes (behind that of CO_2 and N_2). As one goes up in altitude, SO_2 drops off as it gets used up in the H_2SO_4 clouds and CO become more dominant in the region above 60 km.

The spectral dependence of the albedo of Venus is dependent on composition. In the wavelength range of 0.1 – 4.0 microns, SO_2 is a strong absorber of radiation. Absorption by CO_2 and H_2SO_4 are also significant in this region. The spectrum includes the band from the "unknown UV absorber" which has its peak between 0.3-0.4 microns; the identity of the molecule responsible for this peak has stymied observers of Venus for over 40 years. However, the best candidate materials for this absorber are most likely S_3 and S_4 which have absorptions in this ultraviolet region (Mills et al. 2007).

In 2007, Krasnopolsky published the first self-consistent chemical kinetic model for the Venus atmosphere in the range of 0-47 km. The most important (and most abundant) sulfur species in the model are SO_2, OCS, H_2SO_4, and S_x. Other species that play a role in the sulfur chemistry are H_2S, SO, SO_2Cl_2 and SH though their mixing ratios are much lower as compared to the first set of molecules.

S_3 was detected by the Venera 11-14 spacecraft and this model calculates the abundance of S_3 at the surface correctly. However, there is a large dropoff of S_3 from the surface to 20 km in the model which is not expected from the observations.

The hot surface and atmosphere of Venus provides a laboratory for exotic chemistry that happens nowhere else in the solar system, with the possible exception of the insides of volcanoes. The study of Venus can help us understand the alien geology of other worlds.



Pioneer Venus

An extraordinary American mission to Venus in the 1970's, it was outfitted with 4 probes that landed on the hot surface and used instruments to sample the gases in the atmosphere

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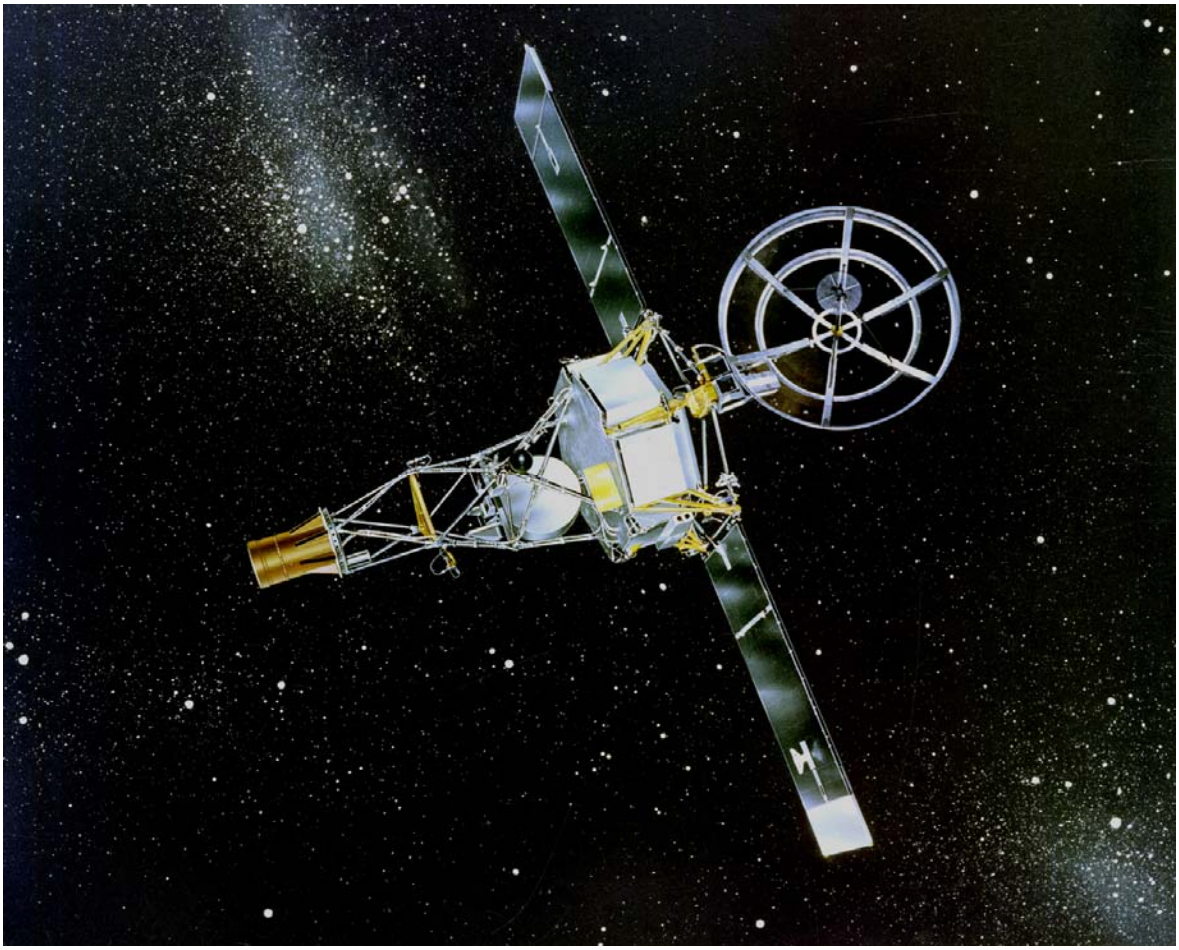

First spacecraft to the planets

Mariner 2 was launched on August 27, 1962 and was the first spacecraft to leave the vicinity of Earth and visit a planet. It had a slow data rate of around 8 bits per second, but sent back the first information about Venus showing that the surface temperature was very hot. The Mariner spacecraft carried a number of instruments: solar plasma sensor, charged particle sensor, fluxgate magnetometer, micrometeorite detector, cosmic ray detector, microwave radiometer and an infrared radiometer. No camera was onboard because of the thick, opaque nature of the atmosphere that precluded seeing any surface details. The spacecraft instruments studied the temperature of the planet and its atmosphere and found that the surface was radiating profusely in the infrared meaning that the surface was very hot, around 500 C (~ 900 F). The atmosphere was shown to be very dense, about 90 times the density of Earth's atmosphere at its surface. It also detected a weak magnetic field.

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Superfluous Questions:

1) On the TV show *Star Trek*, the robot *Nomad* thought Capt Kirk was its creator; whose name was *what* ?

a) Sam Kirk b) Jim Seakirk c) Jackson Roykirk d) John Kirkovich

2) Nix and Hydra are two moons circling *what* planet ?

a) Saturn b) Jupiter c) Uranus d) Pluto

3 Limahl is the name of a British pop singer whose real name is *what* ?

a) Eden Kane b) Tom Fletcher c) Jack Rubinacci d) Chris Hamill

4) The cochlea is a part of *what* organ in the human body ?

a) heart b) kidney c) spleen d) ear

—> ANSWERS in next months issue of the Science Newsletter ! <——-

** ANSWERS to April's Superfluous Questions: 1. c) Alpha Centauri 2. b) Sagittarius 3. d) Thalassa 4. a) Eastern bluebird