CHEMISTRY
In Venus’ Atmosphere
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\[ \begin{align*}
O_3 + O & \rightarrow O_2 + O_2 \\
H + O_3 & \rightarrow OH + O_2 \\
H_2 + O & \rightarrow OH + H \\
H_2 + O(1^D) & \rightarrow OH + H \\
H_2O + O(1^D) & \rightarrow OH + OH \\
OH + CO & \rightarrow CO_2 + H \\
OH + O & \rightarrow O_2 + H \\
OH + H_2 & \rightarrow H_2O + H \\
OH + OH & \rightarrow H_2O + O \\
OH + O_3 & \rightarrow O_2 + HO_2 \\
HO_2 + O & \rightarrow OH + O_2 \\
HO_2 + O_3 & \rightarrow O_2 + O_2 + OH \\
HO_2 + H & \rightarrow OH + OH + H_2 \\
H_2O_2 + OH & \rightarrow H_2O + HO_2 \\
O(1^D) + CO_2 & \rightarrow O + CO_2 \\
S + CO_2 & \rightarrow SO + CO \\
S + O_2 & \rightarrow SO + O \\
S + OH & \rightarrow SO + H \\
S + HO_2 & \rightarrow SO + OH \\
S_2 + O & \rightarrow SO + S \\
SO + O_2 & \rightarrow SO_2 + O \\
\end{align*} \]
Why do we care?

- How the atmosphere got to its current state
  - Outgassing from volcanoes? (lots of CO2 and sulfur)
  - Runaway greenhouse effect?

- How it maintains its state: Chemistry!
  - Main cycles: CO2 cycle, sulfur cycle
  - Active volcanoes?

- Application: Exoplanets
**Venusian Atmosphere Schematic**

- **Upper atmosphere**: (ion-ion, ion-neutral, photodissociation) at 110 km
- **Middle atmosphere**: (UV from Sun, photochemistry) at 90 km
- **Lower atmosphere**: (thermochemistry) at 60 km
- **Main cloud layer**: 70 km
- **Clouds and haze**: 45 km
- **30 km**
Big Picture

Carbon dioxide cycle goes here

Sulfur cycle (below):

1. S
2. SO
3. O
4. SO₂
5. δ
6. H₂O
7. O₂
8. ε
9. φ
10. γ
11. m
12. SO₃
13. μ
14. SO₂
15. κ
16. Sₓ
17. S
18. CO
19. OCS
Fast Atmospheric Sulfur Cycle

- **SO₂**
  - **upward transport**
  - **oxidation**
  - **H₂SO₄ (Sulfuric Acid)**
  - **H₂SO₄ Cloud**
  - **H₂SO₄ and H₂O Droplets**

- **H₂O, light, etc.**

**Cloud layer**

**Lower atmosphere**
More Detail

oxidation

Net: \( CO + O_2 + SO_2 + H_2O \rightarrow CO_2 + H_2SO_4 \) \hspace{1cm} (H)

Net: \( O_2 + 2SO_2 + 2H_2O \rightarrow 2H_2SO_4 \) \hspace{1cm} (J)

 thermochemistry ("The details [...] still are largely unknown")

\[ H_2SO_4 \rightarrow H_2O + SO_3 \] \hspace{1cm} (11)

Net: \( SO_3 + CO \rightarrow SO_2 + CO_2 \) \hspace{1cm} (12)

\[ Net: H_2SO_4 + CO \rightarrow H_2O + SO_2 + CO_2 \] \hspace{1cm} (A)
Mystery 1: Light/Dark Patches in UV

Pioneer

Esposito, L. W. Ultraviolet contrasts and the absorbers near the Venus cloud tops.

False-colour image of Venus taken by VMC from a distance of ~30,000 km in the ultraviolet filter.

Possible Explanation

At the right mixing ratio, H2O and/or SO2 can completely deplete the other

see: deep leftward dips ->

C.D Parkinson et al. (2015)
Mystery 2:
Spikes in global SO2 with time

Pioneer

Venus Express

\[SO_2\text{ abundance at 70 km (ppbv)}\]

Year


doi:10.1038/ngeo1650
Possible Explanations

1. Active volcanoes
2. Atmospheric circulation
   a. More eddy diffusion could yield more SO2 and less H2O...

see: red lines ->
Extra Slide: Active Volcanoes?

IR hotspots at Ganiki Chasma: caught in the act!

Carbon Dioxide Cycle ↔ Sulfur Cycle
The CO$_2$ Cycle

- CO$_2$ comprises ~96% of Venus’ atmosphere, and must be central in the chemistry and dynamics.
- What reactions take place in our steady-state system?
The CO$_2$ Cycle

- CO$_2$ is constantly dissociated in Venus’ upper atmosphere.

\[
\begin{align*}
2(\text{CO}_2 + \text{hv} & \rightarrow \text{CO} + \text{O}) \\
\text{O} + \text{O} + \text{M} & \rightarrow \text{O}_2 + \text{M}
\end{align*}
\]

\[
\text{Net: } 2\text{CO}_2 \rightarrow 2\text{CO} + \text{O}_2
\]

- And this creates a large, measurable production rate of O$_2$\(^{1\Delta}\)

Intensity Scale: 0-15 MR  
Crisp et al., 1996
The CO$_2$ Cycle

- The production of O$_2$(^1\Delta) matches the expected CO$_2$ dissociation rate.

- And almost 50% of this production occurs on the nightside.

Gerard et al., 2008

McElroy et al., 1973

Fig. 1. Dissociation rates for H$_2$O, HCl and CO$_2$ as a function of height above the Venus cloud deck.
The CO$_2$ Cycle

- O$_2$(^1A) production rate is large, yet measured O$_2$ has yet to be observed. Upper limit on mixing ratio of 3 ppm (Mills, 1999a)

- Venus Express only able to provide upper limit with limb scans.

- This quantity would be passed in just a few years given our current level of CO$_2$ dissociation.

- To account for the stability of CO$_2$ yet lack of O$_2$/CO, additional steps are required.
Chlorine Chemistry

- Several species could provide a chemical pathway, but high concentrations of HCl make Chlorine a likely source.

\[
\begin{align*}
O + O_2 + M &\rightarrow O_3 + M \\
Cl + O_3 &\rightarrow ClO + O_2 \\
ClO + O &\rightarrow Cl + O_2 \\
\text{Net: } 2O &\rightarrow O_2
\end{align*}
\]
Chlorine Chemistry

- What about CO? And the reforming of $\text{CO}_2$?

Reproduced observables well, but used incorrect lab results

None of these work on their own, but combining them into one model can produce close to our observed steady state
Lab experiments have validated all the involved pathways.

But equilibrium rates for Venus’ Atmosphere are uncertain.

Don’t have lab tests of the ways in which CLC(O)OO reacts with other atmospheric components.

No direct observations of these chlorine radicals as of yet.
Unsolved Questions

UV absorption at wavelengths >320nm

Candidates:
- Cl₂
- S₈
- FeCl₃
- C₅O₅H₂
- NOHSO₄
- S₂O

SO₂ and SO

Pollack et al., 1980
Unsolved Questions -- Lightning?

- Ground-based observations find ~7 flashes per 4 hours.
- Specifics of where/why are relatively unknown

Hansell et al., 1995
Unsolved Questions - Spatial/Vertical Variations

Water Vapor

CO

Large-scale ground based observations would help constrain models

Ignatiev et al., 1999

Krasnopolsky, 2006
Questions?
References

- Parkinson et al PSS 113:226 (doi:10.1016/j.pss.2015.02.015)
- Emmanuel Marcq1*, Jean-Loup Bertaux1*, Franck Montmessin1 and Denis Belyaev2, *Variations of sulphur dioxide at the cloud top of Venus’s dynamic atmosphere* DOI: 10.1038/NGEO1650