



High-Pressure and High-Temperature Behavior of Venus's Atmosphere Near the Surface: A Thermo-Gravitational Study

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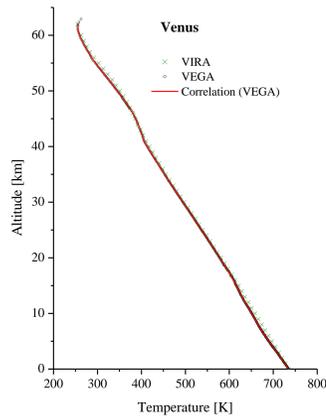
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Venus's atmosphere: CO₂ / N₂ / SO₂

- The temperature profile of the atmosphere at low latitudes was measured by VEGA (Linkin et al., *Kosmich. Issled.* 1987, 25, 659) and modeled by VIRA (Seiff et al., *Adv. Space. Res.* 1985, 5, 3).
- The temperature profile $T(h)$ by VEGA is correlated using polynomials:

$$T(h) = \sum_{i=0}^8 c_i (h - h_0)^i \quad [\text{K}]$$

in two parts corresponding to the altitude ranges of $h = 0-41$ km ($h_0 = 0$) and $41-62$ km ($h_0 = 41$) as seen in the figure. The correlation has an accuracy of 0.08%. The constants c_i is tabulated below the figure.



i	Altitudes	
	0 – 41 km	41 – 62 km
0	734.863249	406.773623
1	-7.642702	-6.755073
2	-0.71474	2.42324
3	0.12952	-0.931572
4	-0.009494	0.15933
5	3.553979E-4	-0.015415
6	-7.160138E-6	8.545841E-4
7	7.310104E-8	-2.511086E-5
8	-2.897589E-10	3.027652E-7

- Total composition of CO₂/N₂/SO₂ in the atmosphere: {96.45%, 3.54%, 0.014%} is assumed at the altitude of 41 km. The mole fraction of N₂ is from Oyama et al. (*JGR* 1980, 85, 7891), and SO₂ is from Arney et al. (*JGR Planets* 2014, 119, 1860).
- Calculations were started from the altitude of 41 km down to the surface as well as up to the altitude of 62 km (near tropopause).
- The gravity of Venus is from VIRA as a linear function of the altitude (h in km):
 $g(h) = 8.8691 - 0.00289 h \quad [\text{m/s}^2]$

Thermo-gravitational effects

- In a stable phase α that is subject to gravity and thermo-diffusion:
 $d\mu_i^\alpha = M_i g dh - \frac{Q_i}{T} dT \quad i = 1, \dots, N$
where:
 μ_i – chemical potential of component i
 N – the number of components
 T – absolute temperature
 M_i – molar mass of component i
 g – gravity
 h – altitude
 Q_i – heat due to diffusion of component i (Firoozabadi et al. *AICHE J.* 2000, 46, 892):
$$\frac{Q_i}{RT} = -\frac{\bar{U}_i^R}{4RT} + \frac{1}{4RT} \frac{\bar{v}_i}{\sum_j z_j \bar{v}_j} \sum_j z_j \bar{U}_j^R$$

 R – gas constant
 $\mathbf{z} = \{z_i\}$ – composition ($\sum z_i = 1$)
 \bar{U}_i^R – partial molar residual internal energy of component i
 \bar{v}_i – partial molar volume of comp i
- For calculations on the vertical profiles of fluid properties, the applied algorithm is the same as that in the AGU Fall Meeting 2020 with the application for Titan's subsurface liquid (Tan & Kargel, paper # P067-0002).

Without thermal diffusion

- To see whether the thermal diffusion is significant, Q_i is set to zero ($Q_i = 0$). This is called the zeroth-order approximation or the passive thermal diffusion.

Without SO₂: binary CO₂/N₂

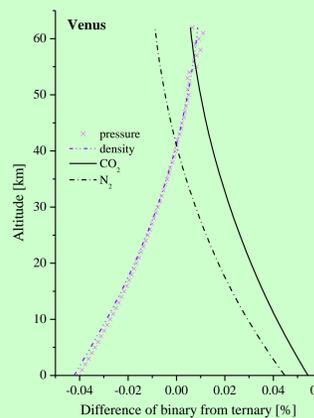
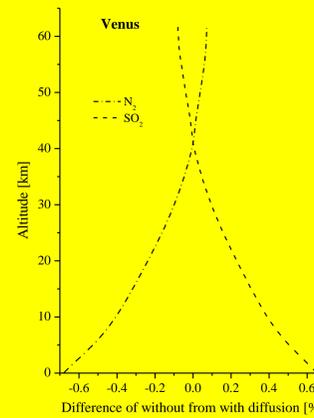
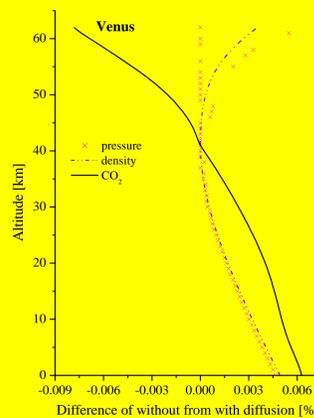
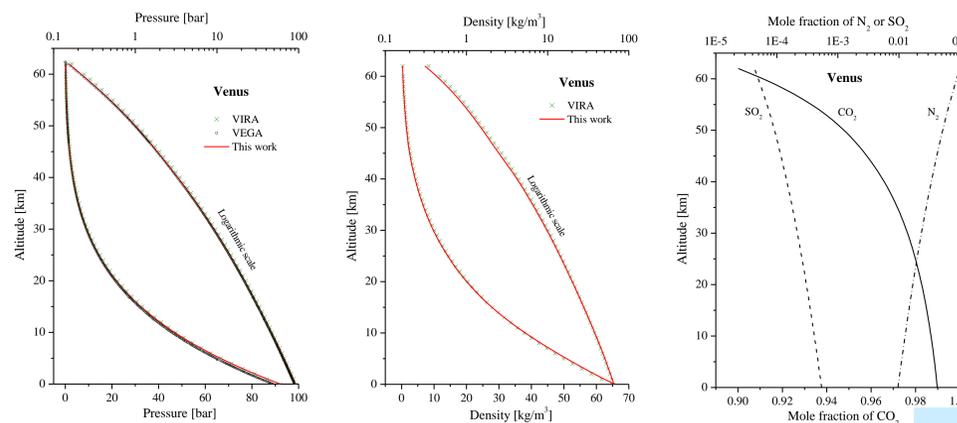
- Due to the tiny mole fraction of SO₂, it is of modeling interest to see the effect of the inclusion of SO₂.

Equation of state

- The equation of state (EOS) used in the calculation is the PC-SAFT (Gross & Sadowski, 2001, *Ind. Eng. Chem. Res.*, 40, 1244).

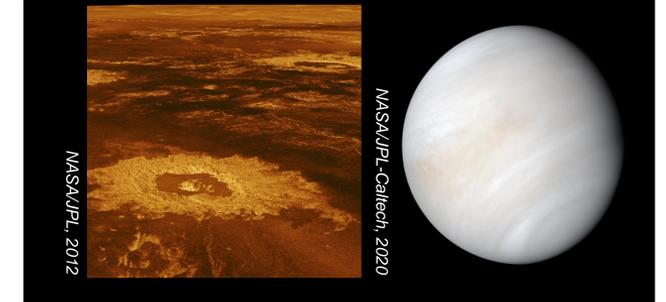
Results and Discussion

- The resulting pressure profile agrees well with both VEGA and VIRA, particularly in the higher altitudes with VEGA and lower latitudes with VIRA.
- The resulting density profile agrees well with VIRA.
- The resulting compositional grading due to the thermo-gravitational effects reveals that CO₂ and SO₂ decrease while N₂ increases with altitudes, which implies the dominance of gravitational effects over the thermal diffusion counterpart as N₂ is the lightest component.



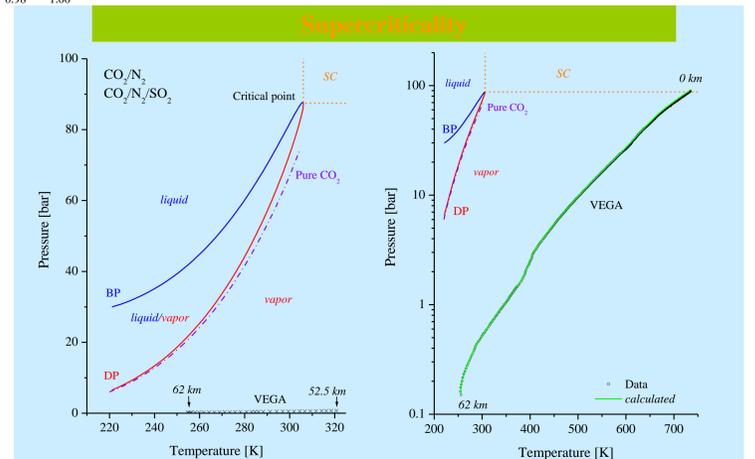
- The omission of thermal diffusion makes:
- The pressure and density to overestimate by 0.005% on the surface.
 - CO₂ to underestimate by 0.008% at the altitude of 62 km and overestimate by 0.006% on the surface.
 - N₂ and SO₂ to underestimate and overestimate by about 0.65% on the surface, respectively.

- The use of binary CO₂/N₂ instead of ternary CO₂/N₂/SO₂ makes:
- The pressure and density to underestimate by 0.04% on the surface.
 - CO₂ and N₂ to overestimate by 0.054% and 0.045% on the surface, respectively.



- The atmospheric properties at the surface and the altitudes of 41 km and 62 km are tabulated below.

	Altitudes		
	0 km	41 km	62 km
Temperature [K]	734.86	405.60	255.44
Pressure [bar]	92.12	2.94	0.1534
CO ₂ [mole fraction]	0.9898	0.9645	0.9001
N ₂ [mole fraction]	0.0096	0.0354	0.0999
SO ₂ [mole fraction]	5.42E-4	1.40E-4	0.43E-4
Density [kg/m ³]	65.75	3.81	0.31



- Vapor (low density) and liquid (high density) phases can only coexist between the dew-point curve (DP) and bubble-point curve (BP) on the P - T phase diagram forming the so-called phase envelope.
- The phase envelop of ternary CO₂/N₂/SO₂ with the total composition of {96.45%, 3.54%, 0.014%} is indistinguishable from that of binary CO₂/N₂ with a total composition of {96.46%, 3.54%} on the diagram.
- The supercritical region of the atmosphere (SC) is located above the critical point (where DP meets BP) on the phase diagram.
- The P - T relationship of the atmosphere (green curve) is mostly in the vapor phase, except for that in the lowest of 6-7 km, where the atmosphere becomes supercritical.
- There is no indication of "gas-gas" equilibrium along the P - T function of the atmosphere as it must be above the phase envelope.