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

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Venus's atmosphere: CO_2 / N_2 / SO_2

- 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*).
- For computation purposes, the profile $T(h)$ by VEGA is correlated using polynomials:

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

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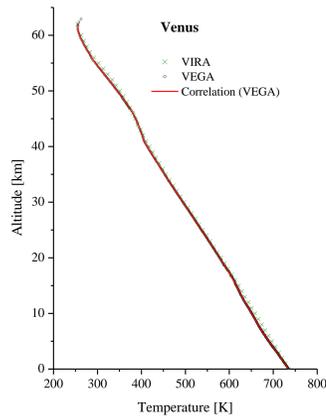
i	Altitudes	
	0 – 41 km	**41 – 62 km**
0	734.863249	406.773623
1	−7.642702	−6.755073
2	−0.71474	2.42324
3	0.12952	−0.931572
4	−0.009494	0.15933
5	3.553979E-4	−0.015415
6	−7.160138E-6	8.545841E-4
7	7.310104E-8	−2.511086E-5
8	−2.897589E-10	3.027652E-7

- Total composition of $CO_2/N_2/SO_2$ in the atmosphere: {96.45%, 3.54% , 0.014%} is assumed at the altitude of 41 km. The mole fraction of N_2 is from *Oyama et al.* (*JGR 1980, 85, 7891*), and SO_2 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):

$$g(h) = 8.8691 - 0.00289\, h \quad [m/s^2]$$

Thermo-gravitational effects

- In a stable phase α that is subject to gravity and thermo-diffusion:

$$d\mu_i^\alpha = M_i g\, dh - \frac{Q_i}{T} dT \qquad i = 1, ..., N$$

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 ($\Sigma z_i = 1$)
$\bar{U}_i^R$ – 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 SO_2: binary CO_2/N_2

- Due to the tiny mole fraction of SO_2, it is of modeling interest to see the effect of the inclusion of SO_2.
- For the binary, the composition is 3.54% N_2 with CO_2 as the balance (96.46%).

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 CO_2 and SO_2 decrease while N_2 increases with altitudes, which implies the dominance of gravitational effects over the thermal diffusion counterpart as N_2 is the lightest component.
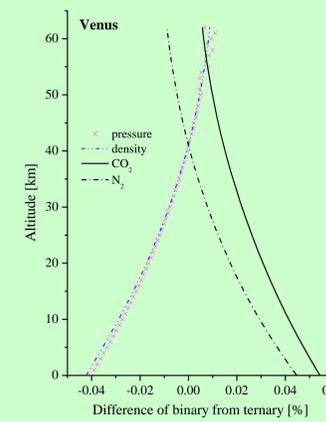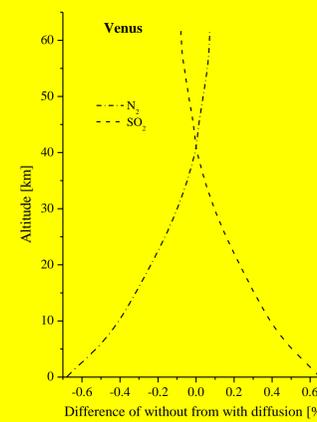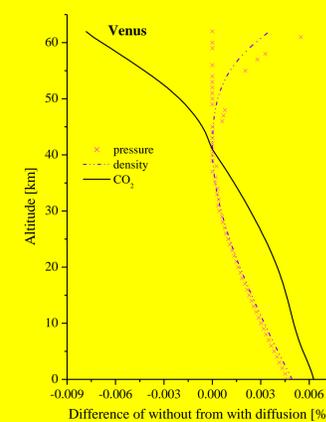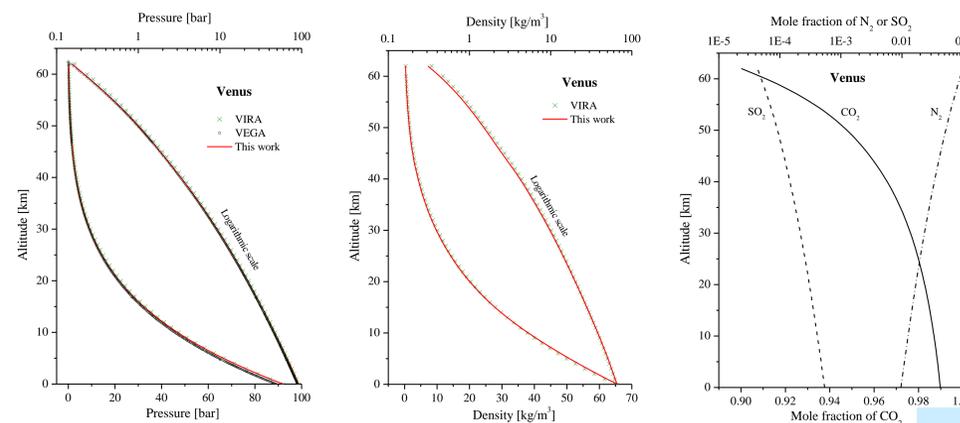

The omission of thermal diffusion makes:
- The pressure and density to overestimate by 0.005% on the surface.
- CO_2 to underestimate by 0.008% at the altitude of 62 km and overestimate by 0.006% on the surface.
- N_2 and SO_2 to underestimate and overestimate by about 0.65% on the surface, respectively.

The use of binary CO_2/N_2 instead of ternary $CO_2/N_2/SO_2$ makes:
- The pressure and density to underestimate by 0.04% on the surface.
- CO_2 and N_2 to overestimate by 0.054% and 0.045% on the surface, respectively.
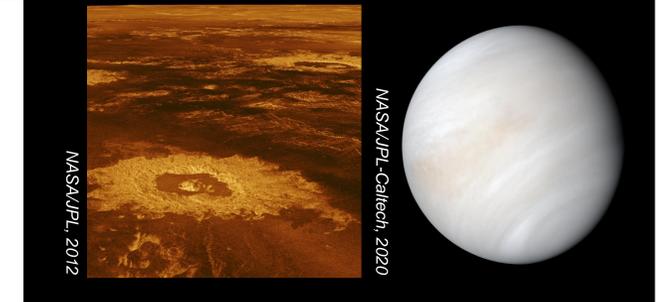
- The atmospheric properties at the surface and the altitudes of 41 km and 62 km are tabulated below.

	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/m³]	65.75	3.81	0.31

Supercriticality
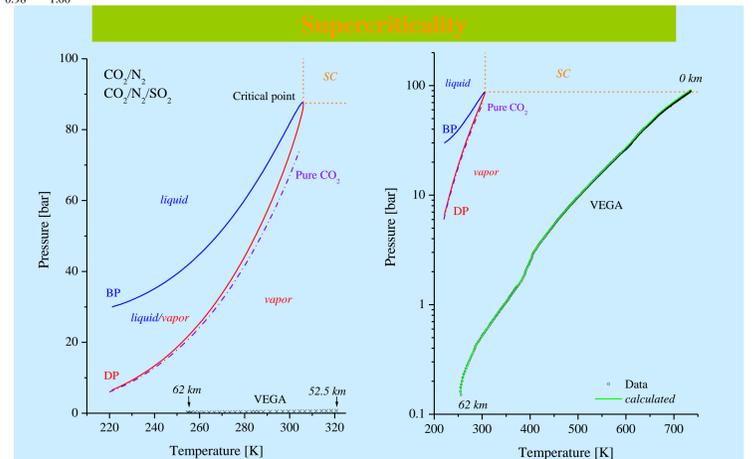
- Vapor (low density) and liquid (high density) phases can only coexist between the dew-point curve (DP) and bubble-point curve (BP) on the *P-T* phase diagram forming the so-called phase envelope.
- The phase envelop of ternary $CO_2/N_2/SO_2$ with the total composition of {96.45%, 3.54% , 0.014%} is indistinguishable from that of binary CO_2/N_2 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.