EPSC

European Planetary Science Congress

Discussion about the Physical Origin of the Venus Low Atmosphere Chemical Gradient

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Abstract

Venus shares many similarities with the Earth but, concomitantly, some of its features are extremely original. This is especially true for its atmosphere, where high pressures and temperatures are found at ground level. In these conditions, carbon dioxide, the main component of Venus atmosphere, is a supercritical fluid. Recent works have suggested the existence of a vertical gradient of nitrogen abundances, around 5 ppm per meter, in the deep atmosphere of Venus. An analogous chemical gradient is observed in terrestrial hydrocarbon reservoirs, but in that case, the fluids are trapped in a porous medium which efficiently impede fast large scale transport, leaving diffusion at work over long timescales. The venusian separation mechanism had to be faster than the mixing produced by atmospheric large scale circulation. Our goal was then to discuss which physical processes could lead to the establishment of a nitrogen gradient, around the expected value, in the deep atmosphere of Venus. Using an appropriate equation of state, we have explored the thermodynamic properties of the binary mixture CO_2-N_2, under supercritical conditions. We have particularly focused our attention on a possible pressure diffusion transport, caused by gravity.

1. Introduction

At ground level, the Venus air is under hellish conditions, where the temperature is close to 740 K and the pressure not too different than 90 bars. Since carbon dioxide dominates the atmospheric composition, with a mole fraction around 97%, at low altitude the venusian air is a supercritical fluid. The second most abundant atmospheric compound is molecular nitrogen, N_2, with a mole fraction of about 3%. Therefore, nitrogen is also in a supercritical state. In the phase diagram, plotted in Fig. 1, we have recalled the position of carbon dioxide and nitrogen
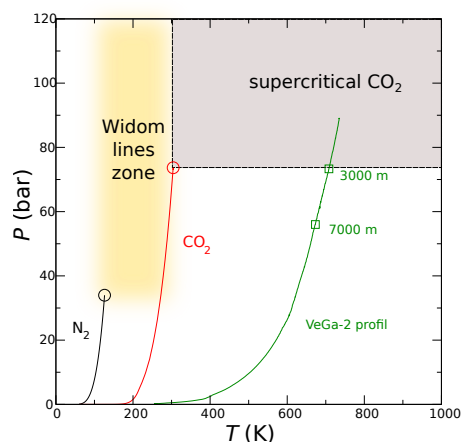

Figure 1: Simplified phase diagram of CO_2. The position of the critical point of pure CO_2 has been plotted, together with its position when a small fraction of nitrogen is added to the system. The introduction of N_2 shifts the position of the critical point by a few bars and a few kelvins (Goos et al. 2011). The green and the blue lines refer respectively to pressure-temperature of Venus atmosphere derived respectively from GCM simulations (Lebonnois & Schubert, 2017) and measurements performed by the VeGa-2 probe (Lorenz et al. 2018).

respective critical points, this, complemented by the pressure-temperature atmospheric profile measured during the descent of the VeGa-2 probe (Lorenz et al. 2018). Recently, the existence of a composition gradient in the Venus deep atmosphere, *i.e.* for layers below the altitude of $\sim$ 7000 m, has been suggested (Lebonnois & Schubert, 2017). The abundance of nitrogen seems to decreases from $\sim$ 3.5% at 7000 m, to zero at ground level; yielding to a gradient of about 5 ppm m^{-1}. As it can be seen in Fig. 1, this deep atmosphere is partially in CO_2 supercritical domain

and entirely in that of N_2. Then, we first checked that the apparent composition gradient could not be only an effect of compressibility properties of the CO_2-N_2 mixture. For this purpose, we have employed an equation of state (Duan et al. 1996), specifically developed for mixture like CO_2-N_2, under supercritical conditions. We found that the compressibility factor Z stays around 1 in the deep atmosphere of Venus. Actually, Z measures the deviation of real gases from ideal gases behavior, a value around the unity shows a compressibility behavior similar to what we have with an ideal gas. Then, this result, also supported by laboratory measurements (Mohagheghian et al. 2015), tends to confirm the existence of compositional variations.

2. The Effect of Molecular Diffusion

For almost a century, chemical composition variations are known among terrestrial reservoirs of hydrocarbons, *i.e.* containing gases or petroleum (Sage & Lacey, 1939), or both. These variations are horizontal, but also vertical: in that case, for a given well, the abundances of species evolves with depth. The emergence of such a gradient of composition is due to the effect of gravity and, also to thermodiffusion. In this context, the convection is not very efficient since the fluid is trapped in a porous medium. Here, we focus our attention on the physics of the vertical compositional grading. If the air mixing, due to atmospheric circulation, is slow or inefficient enough, deep atmosphere of Venus could be the subject of analogous physical processes, leading to the suspected gradient of nitrogen concentration.

Assuming a steady state, an ideal gas, and using the pressure and temperature gradient, provided by the VeGa-2 probe (Lorenz et al. 2018), the nitrogen mole fraction (x_1) gradient is given by

$$
\frac{\partial x_1}{\partial z} = -\frac{x_1}{P}\left(1 - \frac{M_1}{\bar{M}}\right)\left.\frac{\partial P}{\partial z}\right|_{\text{VeGa2}} \\
- \frac{\alpha_{T\,1,2}}{T}\,x_1(1 - x_1)\,\left.\frac{\partial T}{\partial z}\right|_{\text{VeGa2}}
\tag{1}
$$

Thanks to the kinetic theory of gases (Chapman & Cowling, 1970), the thermal diffusion coefficient $\alpha_{T\,1,2}$ may be estimated for the system N_2-CO_2. By integrating Eq. (1) from the top of the Venus deep atmosphere, *i.e.* from an altitude of 7000 m, down to

the surface, we obtained a nitrogen mole fraction gradient of ~ 0.6 ppm m^{-1}. This value is roughly one order of magnitude lower than the expected gradient (Lebonnois & Schubert, 2017) of ~ 5 ppm m^{-1}.

Now we can turn to a more realistic model, taking into account non-ideal effects, the relevant equation is then (Ghorayeb & Firoozabadi, 2000)

$$
\left.\frac{\partial \ln f_1}{\partial \ln x_1}\right|_{P,T}\frac{\partial x_1}{\partial z} + \frac{x_1}{RT}\left(\bar{V}_1 - \frac{M_1}{\rho}\right)\left.\frac{\partial P}{\partial z}\right|_{\text{VeGa2}} \\
- \frac{\alpha_{T\,1,2}}{T}\,x_1(1 - x_1)\,\left.\frac{\partial T}{\partial z}\right|_{\text{VeGa2}} = 0
\tag{2}
$$

where f_1 denotes the fugacity of compound (1) (here nitrogen), $\bar{V}_1$ is the nitrogen partial molar volume and the density of the mixture is called ρ. All these quantities are evaluated with the EoS published by Duan et al. (1996) and relevant for supercritical carbon dioxide. With this new equation, we may expect enhanced composition gradient $\partial x_1/\partial z$. Indeed, close to the critical point the derivative $\partial \ln f_1/\partial \ln x_1$ tends to zero. Unfortunately, even with this more realistic modeling, the computed gradient is not in agreement with the value suspected for Venus deep atmosphere. In addition, the estimated molecular diffusion coefficient of N_2 in supercritical CO_2 leads to relaxation time around 16 mega-years, largely incompatible with dynamic mixing timescale computed by Lebonnois & Schubert (2017).

3. Summary and Future Work

Even for a supercritical material, like the mixture of CO_2 and N_2 present at Venus, the diffusional properties cannot explain the compositional gradient of ~ 5 ppm m^{-1} proposed by Lebonnois & Schubert, (2017). We are now turning our attention to "exotic" properties of supercritical system, like those liked to the existence of the so-called "Frenkel line" (Bolmatov et al. 2013; Brazhkin et al. 2013; Bolmatov et al. 2014). We plan to perform molecular dynamics simulations in order to identify some, still unknown, physical processes which could lead to a kind of "phase transition" in the supercritical domain.

References

Lebonnois & Schubert, 2017; Mohagheghian et al. 2015, Sage & Lacey, 1939; Duan et al. 1996; Lorenz et al. 2018; Chapman & Cowling, 1970; Ghorayeb & Firoozabadi, 2000.