

Thermodynamic Features Governing the Atmospheric Composition on Venus. A. Pilchin^{1*}, ¹ Universal Geoscience & Environmental Consulting, 205 Hilda Ave., #1402, North York, Ontario, Canada, M2M 4B1. (*arkadypilchin@yahoo.ca).

Introduction: Previous researches conducted on Venus show that: the atmospheric pressure near its surface is now on average ~9.56 MPa [1]; the average surface temperature is about 740 K [1]; there is a thick cloud system (a global cloud layer at altitudes of ~45 to ~70 km) [2]; there is virtually no data on the chemical composition and thermal structure of the Venusian lower atmosphere below an altitude of ~22 km [1]; it reflects about 75% (spherical albedo) or ~0.84 (geometric albedo) of incidental solar radiation [3]; the shortage of direct measurements leaves no alternative but to use methods of infrared spectroscopy to analyze the atmospheric composition; the atmosphere is predominantly composed of CO₂ (96.5%) and N₂ (3.5%), with smaller amounts of SO₂, H₂O, H₂SO₄, CO, OCS, HCl, HF and traces of certain other compounds [1, 2]; lastly, thermodynamic conditions at their highest (Maxwell Montes) and lowest (deep depressions; -2 km) altitudes are about 650 K, 4.5 MPa and 755 K, 11.0 MPa, respectively [4].

Methods: Thermodynamic methods used to estimate and analyze the composition of the early Earth atmosphere [5, 6, 7] were applied to the atmosphere of Venus. The methods involve determining the densities of the primary atmospheric compounds under different P-T-conditions, comparing them, and determination the different layers and their positions within the atmosphere. For atmospheric composition, the main components of volcanic gases and fumaroles (H₂O, CO₂ and SO₂) were accepted. Experimental data of [8] was used to calculate the densities of H₂O and CO₂; and experimental data of [9] was used to calculate the density of SO₂, with calculations employing thermodynamic and fluid laws used for temperatures above 523 K.

Thermodynamic conditions in the atmosphere of Venus and main features of its composition: Thermodynamic analysis of conditions of the early Earth atmosphere shows [5, 6, 7] that: the content of carbon oxides was governed by the Boudouard reaction ($2\text{CO} = \text{CO}_2 + \text{C}$), the content of CO and CO₂ is equimolar respectively at 947 K and at 673 K with content of CO less than 1%; the content of sulfur oxides was constrained by the disproportionation reaction ($2\text{SO}_2 = \text{SO}_3 + \text{S}$), with SO₃ content of ~55% at 873 K, ~90% SO₃ at 773 K, and up to 100% at 673 K; sulfuric acid is the main compound containing sulfur oxides at temperatures below about 700-610 K depending on pressure. Elemental sulfur has a boiling point as high as 717.75 K [10]. A comparison of this data with the thermodynamic conditions within the atmosphere of

Venus shows that near the surface: the main carbon oxide is CO₂; the main sulfur compounds should be SO₃, H₂SO₄ and S⁰; and that water could not be in its liquid state.

Analysis of thermodynamic characteristics of the main components of the atmosphere of Venus shows that: under average atmospheric pressure and temperature near the surface such compounds as CO₂, CO, SO₂, SO₃, COS, HCl, HF, H₂S, Cl₂ and F₂ are in supercritical condition; H₂O is in critical condition by temperature; sulfuric acid is in critical condition by pressure; while elemental sulfur (S, S_n; n is from 2 to 8) is not in critical condition [5, 6, 7]. Comparing the critical pressure (P_C) and critical temperature (T_C) of most typical compounds with the actual distribution of pressure and temperature with altitude within the atmosphere of Venus shows that: CO₂ is in critical condition by temperature at altitudes of ~5-51 km and in its gas state at altitudes of ~60-70 km; both SO₂ and SO₃ are in critical condition by temperature at altitudes of ~5-30 km and in their gaseous states at the temperatures at ~40-70 km; H₂SO₄ is in critical condition by pressure at altitudes of up to ~10 km, and in its liquid state at ~10-60 km, as well as for concentrations of over 30% at ~70 km; H₂O is in critical condition by temperature at altitudes of up to ~10 km, vaporous until ~39 km, liquid until ~58 km and ice at ~58-70 km; elemental sulfur (S_n) should be in its vaporous state below an altitude of ~2-3 km, and liquid until ~44 km.

Results of calculating the densities of H₂O, CO₂ and SO₂ at different temperatures and pressures show that: the densities of these compounds are respectively about 32, 70 and 159 kg/m³ for a pressure of 10 MPa, and 16.5, 38.0 kg/m³ for 5 MPa (the density of SO₂ was not calculated for P=5 MPa, but is certainly greater than that of the other two compounds); under pressure of ~10 MPa H₂O is denser than CO₂ at temperatures below 550 K, and denser than SO₂ only within the range of about 473-573 K; under pressure of ~5 MPa H₂O is denser than CO₂ at temperatures below 600 K, and it is denser than SO₂ only within the range of about 450-600 K; while SO₂ is denser than CO₂ throughout the entire range of temperatures (273-823 K) and pressures (5 and 10 MPa) used for calculating their densities. The last fact is extremely important, because the primary sulfur compounds stable under the P-T-conditions at surface of Venus are SO₃, H₂SO₄ (at altitude 5 km and above) and S⁰, which have densities increasing in the order (from left to right) SO₂ → SO₃ → H₂SO₄ → S_n [10]. At the same time, SO₂ is unstable at

altitudes above ~12 km. This means that among the mentioned sulfur compounds, only SO_3 and S^0 could be present on the surface of Venus. If these compounds were not yet re-distributed into the crust, as happened with the early Earth atmosphere [5, 6, 7], they would be present only at and near the surface of Venus. The results also show that under the temperature conditions within the atmosphere of Venus, the CO_2 near the surface and at altitudes with a pressure of ~5 MPa (up to an altitude of about 30 km) is denser than H_2O and would take a position between the sulfur-layer and the water-layer. Within the interval of altitudes between ~30 km and ~39 km, the densities of CO_2 and H_2O are somewhat close and can exist as a mixture. However, at altitudes from ~38-39 km to ~58 km water should be in its liquid state, and from ~58 km to 70 km and up water (as ice) is clearly denser than CO_2 .

Composition of the atmosphere on Venus: During planetary accretion on Venus, the three main layers of the atmosphere (sulfur-, carbon- and water-layer) were formed similarly to that of the early Earth atmosphere [5, 6, 7]. The sulfur-layer (lowest in the atmosphere) by now was either completely or mostly re-distributed into solid rocks. The water-layer (upper) was open for Sun's UV-radiation ~4.6 billion years and lost most of its water through photodissociation and escape of hydrogen. The carbon-layer is still mostly unchanged, because of absence of water bodies on the surface required for the re-distribution of CO_2 , just as it was on Earth [5, 6, 7]. The main features governing the composition of the atmosphere on Venus are: water has no access to the surface and is likely not present below an altitude of ~30 km (density within the atmosphere between 9 and 10 km is ~39 kg/m^3 [11] and the density of water vapor is ~17 kg/m^3); H_2SO_4 can only be formed above ~30-38 km (due to necessity of H_2O); volatile sulfur compounds probably concentrate near the surface (estimated density near the surface is 64.79 kg/m^3 [11] and calculated density of SO_2 is ~150 kg/m^3); formed H_2SO_4 should move downward (by density) and decompose at a height of 5-10 km; near the surface sulfur compounds can be present only as supercritical fluids of SO_2 and SO_3 , and S_n vapor; CO is not stable within the atmosphere. Comparing these conditions with the atmospheric abundances of the main components derived by experimental measurements and estimated with infrared spectroscopy shows that: concentrations of SO_2 (main sulfur compound in volcanic fluids) of about 150-200 ppm at altitudes of 22-42 km [4] is explained by their ejection during volcanic activity; H_2O content of ~20 ppmv near the surface [1] and 20-200 ppm below 20 km [13] is explained by the release of water during the decomposition of H_2SO_4 ; the boundary line between the vapor and liquid state of water is ~39 km, but liquid water

droplets can fall below this line until they vaporize (they can fall for up to 12 km [13]) and vapor can rise above 39 km until it liquefies (raining out-vaporization is likely between ~30 and 50 km); a similar raining out-vaporization effect could take place between ~5 and ~20 km for H_2SO_4 ; it is possible that the presence of H_2SO_4 was the reason for the destruction of some devices on the Venera 11-14 and Vega 1-2 landers at altitudes below 12 km; and equipment failure on all four probes from Pioneer Venus at altitudes 12-14 km [13]; the high content of H_2O measured, at 2000 ppm by humidity sensors of Venera 13-14 [13], up to 0.519% by Pioneer Venus [14], 1000-10000 ppm by Venera 4-6 [13], ~1000 ppm by Vega 1-2 [15] can be explained by the presence of liquid water droplets.

Infrared spectroscopy and composition of the atmosphere: The content of different components within the atmosphere was determined by infrared radiation absorbing bands (for CO_2 they are centered at 2.7, 4.3 and 15 μm). Research shows that bands centered at 2.7 μm have: water vapor [17], water molecule [17], CO_2 in solid H_2O and $\text{H}_2\text{O}/\text{CO}_2$ as ice [18], H_2SO_4 at increased temperatures [19], some sulfates [20]; 2.74 μm have liquid water [21] and an OH band [18]. These facts suggest that the share of H_2O and H_2SO_4 may be higher and the share of CO_2 lower than presently accepted for the atmosphere.

References: [1] Fegley B. (2004) Treatise on Geochemistry, Vol. 1487-507. [2] Fegley B. (2009) Encyclopedia of Paleoclimatology and Ancient Environments, 5-83. [3] Moroz V. (1983) Venus, Vol. 1, 27-35. [4] Basilevsky A. T. & Head J. W. (2003). Reports on progress in physics, 66, 1699-1734. [5] Pilchin A. (2011) Magnetite: Structure, Properties and Applications. Ch. 1, 1-99. [6] Pilchin A. & Eppelbaum L.V. (2012). Encyclopedia of Earth Science Research, 1-93. [7] Eppelbaum L. et al. (2014) Applied Geothermics. [8] Clark S. P. (1966). Handbook of physical constants. [9] Ihmels E. C. et al. (2003) Fluid Phase Equilibria, 207, 111-130. [10] Lide D. R. (2004). Handbook of Chemistry and physics. [11] Marov M. Ya. & Grinspoon D. H. (1998) The Planet Venus. [12] Esposito L. W. et al. (1997) Venus II, Vol. 1, pp. 415-458. [13] Kondrat'ev K. Ya. et al. (1987) Planet Venus. (in Russian) [14] Oyama V. I. et al. (1979) Science, 203, 802-805. [15] Surkov Yu. A. et al. (1982) Let. to Astronom. Journ., 8(7), 411-413. [16] Gomasca M. A. (2009) Basics of Geomatics. [17] Menzel W. P. (2001). WMO Satellite reports, SAT-28. [18] Bernstein M. P. et al. (2005) Icarus, 179, 527-534. [19] Biermann U. M. et al. (2000) J. Phys. Chem. A, 104, 783-793. [20] Cloutis E. A. et al. (2006) Icarus, 184, 121-157. [21] Vennyaminov S. Yu. & Prendergast, F. G. (1997) Analytic. Biochem., 248, 234-245.