

## REDOX CONDITIONS OF THE NEARSURFACE ATMOSPHERE OF VENUS. II. Equilibrium and disequilibrium models. M. Yu. Zolotov, Vernadsky Institute USSR Academy of Sciences, Moscow, USSR.

The estimation of redox conditions near the surface of Venus results in relative wide range of  $\log P(O_2)$  value:  $(-22.67) - (-20.53)$  at the temperatures 735-745 K [1]. Possible reasons of the disagreement of  $\log P(O_2)$  values estimated from various instrumental data are discussed below.

**EQUILIBRIUM MODEL FOR THE LOWLANDS.** The estimated range of the  $\log P(O_2)$  value seems to be not wide enough for the absolute exclusion the assumption about the gaseous chemical equilibrium near the surface. In the case of the equilibrium the estimated redox interval should be considered as uncertainty range being a result of incorrect measurements of gas contents. Indeed the instrumental data of atmospheric chemical composition (especially for  $H_2O$ ,  $H_2S$ ,  $CO_2$  and  $S_2$ ) are not enough accurate. In case of equilibrium it is possible to estimate the content of chemically active gases within the estimated range of redox conditions (Table 1). These calculations show that the concentrations of atmospheric gases are extremely sensitive to variations of  $\log P(O_2)$  within the estimated interval.

**DISEQUILIBRIUM MODELS FOR THE LOWLANDS AND HIGHLANDS.** The obtained incomplete agreement of  $\log P(O_2)$  values calculated from different gaseous equilibria also could be interpreted as a lacking of complete equilibrium in respect to all active gases. Indeed if the contents of gases are correctly measured it means the existence of disequilibrium. In this case the calculations of equilibrium oxygen partial pressures for various gas reactions [1] show the redox capability for the separated gases. For instance, at 740 K the interaction of  $H_2S$  along with  $SO_2$  and  $H_2O$  with some Fe-bearing mineral could result in pyrite formation, while the interaction of  $CO_2$  along with  $SO_2$  and  $CO$  could result in hematite formation (see Fig. 1. in [1] and [7]). The real directions of the competing natural chemical processes seems to be governed by the reactions rates.

The gaseous equilibrium for the highland conditions are hardly expected even in the case of an equilibrium within thin nearsurface atmospheric layer (e.g. 3,5,8). Unequilibrium between gases is considered as the obstacle for the correct estimation of atmospheric oxidation state in terms of chemical thermodynamics because the atmosphere could contain relatively high content of oxidized ( $CO_2$ ,  $SO_2$ ,  $H_2O$ , and  $O_2$ ) and reduced gases ( $CO$ ,  $CO_2$ ,  $H_2S$ ,  $S_2$ ,  $H_2$ ). The atmospheric oxidation state above the nearsurface formally could be governed by several factors:

A. If to assume the existence of 'frozen' chemical tropospheric composition up to about 12km [2-5], the  $O_2$  content on the highlands would be considered as equal to the  $O_2$  content on the lowlands [9]. In this case the nearsurface tropospheric layer seems to be characterized by the most reduced conditions in the troposphere [9] in contrast to equilibrium distribution shown at Fig. 1 in [1]. But taking into account the participation of really existing gases in redox reactions rather than free oxygen [1] this approach now seems to be oversimplified.

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B. Taking into account the the detection of free oxygen higher than 35 km[5,10] the traces of free O<sub>2</sub> penetrated from the 30-40 km atmospheric level should not be excluded. And so it seems likely to expect the some increasing of PO<sub>2</sub> value up to the mean planetary radius that also (as for point A) results in hematite stability at the highlands.

C. If to exclude the incorporation of O<sub>2</sub> to the surface the redox conditions should be governed by really existing gases that results in more reduced conditions for the highlands than for the lowlands for the all measured atmospheric gases (see Fig.1, in [1]).

The last possibility seems to be more real. In this case the estimation of possibility of redox reactions could be realized by the comparison of results of equilibrium calculations with the participation of various gases with the real partial pressures of these gases in the atmosphere. But it should be born in mind that the estimated stability of a mineral in relation to various gases will be different as a result of disequilibrium in the atmosphere.

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Table 1. Chemical composition of the near-surface tropospheric layer at various redox conditions (calculated values, mixing ratio). Redox conditions are corresponding to: 1 - CO<sub>2</sub>-CO equilibrium (eq. 1 in [1]), 2 - magnetite-pyrite equilibrium (eq.7 in [1]), 3 - SO<sub>2</sub>-S<sub>2</sub> equilibrium (eq. 3 in [1]), 4 - hematite-magnetite equilibrium (eq. 6 in [1]). Starting mixing ratios for CO<sub>2</sub>, CO, SO<sub>2</sub> and S<sub>2</sub> were taken according to instrumental data (0.965; 1.7E-5; 1.5E-4; 2E-8; ( ref. see in [1])). For H<sub>2</sub>S and H<sub>2</sub> the range is given correspondingly to uncertainties of H<sub>2</sub>O content (2-10)E-5. Temperature 735 K corresponds to 91.8 bar, planetary radius 6052.05 km, 745 K - 99.2 bar, 6050.75 km in the atmosphere of Venus [11].

Gas	T, K	1	2	3	4
log	735	-21.61	-21.46	-20.89	-20.48
P(O <sub>2</sub> )	745	-21.07	-21.16	-20.53	-20.00
CO	735		1.4E-5	7.4E-6	4.6E-6
	745	1.7E-5	1.9E-5	9.2E-6	5.0E-6
COS	735	4.8E-5	2.9E-5	4.1E-6	9.9E-7
	745	2.7E-5	3.7E-5	7.8E-6	6.8E-7
S <sub>2</sub>	735	5.4E-7	2.8E-7		3.0E-9
	745	2.4E-7	3.6E-7	2.0E-8	1.8E-9
H <sub>2</sub> S	735	(1.3-6.3)E-7	(0.8-3.8)E-7	(1.1-5.3)E-8	(0.3-1.3)E-8
	745	(0.7-3.3)E-7	(0.9-4.4)E-7	(1.0-5.1)E-8	(1.7-8.3)E-9
H <sub>2</sub>	735	(0.3-1.2)E-8	(0.2-1.1)E-8	(1.1-5.4)E-9	(0.7-3.4)E-9
	745	(0.2-1.1)E-8	(0.3-1.3)E-8	(1.2-6.2)E-9	(0.7-3.4)E-9