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Venusian Atmospheric Equilibrium Chemistry at the Pioneer Venus Anomalous Event Altitude

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Introduction

No convincing explanation for the anomalous behavior of the Atmospheric Structure Experiment temperature sensors at ~13km altitude has been found. It occured on all of the widely-spaced probes, in a similar fashion. This suggests an interaction between the probe and some property of the 13km atmospheric conditions. Could -the probes have provided local condensation sites for a metallic vapor? Could the probes have picked up static charges from the descent through the cloud layer, and a chemical reaction at 13km result in spallation and loss of charge? Several questions of this nature have been raised. Additional knowledge of the probe environment would surely suggest other possible scenarios, and perhaps offer a basis for evaluation.

A preliminary effort has been made to determine atmospheric chemical species which might be present at 13 km. The purpose of this effort is to initiate suggestions of possible chemical interactions and to explore the effects of the presence of possible metal reactants including condensation. Equilibrium fractions of chemical species were calculated at a variety of conditions. Baseline calculations were made for the altitudes near 13 km. For comparison calculations were also made at 13km but with the introduction of plausible metal atoms.

Assumptions

As a start, chemical equilibrium in the lower portion of the atmosphere is assumed. The high temperatures and pressures of Venus' lower atmosphere makes this reasonable. This assumption, however, does not hold with all species. For example the PVGC measurements indicate higher levels of CO, and lower levels of COS, than the calculated equilibrated amounts. For our purposes the gross, chemically reactive atmospheric constituents were assumed to be reasonably represented by the species

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mole fractions given in the table below. These values are similar to those recommended and discussed by von Zahn[1].

Table 1

species	mole fraction
CO_2	.965
N_2	.035
CO	20ppm
H_2O	140ppm
SO_2	150ppm
H_2S	3ppm
HCl	0.4ppm
HF	5ppb

The atmospheric equilibrium was determined from the composition defined by this mixture and the local conditions of temperatures and pressures

Results

Baseline Atmosphere

A calculation of the equilibrium species mixture for a baseline atmosphere (i. e., one without the addition of metallic compounds) was determined by calculations[2] of mole fractions as at four altitudes- ground level, the altitude of the anomaly, and the altitudes characterized by ±100K around the anomaly altitude. The conditions used were are shown below.

Table 2

altitude	temperature	pressure
0 km	740K	93atm
3.8km	700K	8atm
13km	640K	40atm
17km	600K	29.5atm

The resulting species mole fractions are given in figure 1. Carbon dioxide and N_2 are not plotted. The computation considered many more species than shown in the figure but only those whose fractions were greater than

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1 von Zahn et. al., chapter 13 of VENUS, Hunten et. al., editors, page 325, U. of Ariz. Press, 1983

2 The program used was developed by Gordon and McBride and is described in NASA SP 273, 1971.

1ppb are plotted. The list of species considered but whose fractions were estimated to be less than 1 ppb is given in appendix A.

From this figure it is reasonable to assume, from an equilibrium viewpoint, that there is no unusual chemical dependence on altitude in the region of the anomaly. Additionally no highly reactive, "surprise" species are formed from consideration of equilibrium of the species in appendix A.

The main hydrogen bearing species is H_2O and, in equilibrium, is nominally in the recommended amount in table 1. Other hydrogen bearing species are formed but only in trace. The measurements of HCl and HF, discussed by von Zahn[3], are the values shown in table 1, and are basically the equilibrated values. The only other hydrogen bearing species above 1ppb are H_2S and H_2. The former is less tenuous in equilibrium at 13km than the recommended amount of (0.6ppm vs 3ppm) but is consistent with the upper limit of 2 ppb suggested by the PVGC results. The former is only present in the ppb range and than only at the lower altitudes.

The main sulphur bearing species is SO_2 and, as H_2O, is present in equilibrium at the recommended levels. Other sulphur bearing species are formed, i. e., COS, H_2S, S_2 and S_2O. Although COS has not been measured in the Venusian atmosphere, the PVGC placed an upper limit of a few ppm above 22km. This value is somewhat less than the calculated amount of 8ppb at 17km, but similar enough be consistent with the assumption of equilibrium. H_2S has been discussed. Measurements of the sulphur allotrope S_3 have been made and resulting equilibrium calculations[4] yielded about the same level of S_2 calculated herein. Elemental sulphur should exist mainly as the allotrope S_2 at these lower altitudes. The last sulphur species shown, S_2O, is present in amounts greater than SO and SO_3 but only at about 10ppb.

Addition of Metallic Vapors

The metals chosen for consideration were titanium, the material of which the Atmospheric Structure Experiment temperature sensors were constructed, and metals from the composition measurements by Veneras 13 and 14[5] , viz., Mg, Al, Si, K, Ca, Ti, Mn, and Fe. The species chosen for

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[3] von Zahn et. al., chapter 13 of VENUS, Hunten et. al., editors, page 401, U. of Ariz. Press, 1983
[4] von Zahn et. al., chapter 13 of VENUS, Hunten et. al., editors, page 394, U. of Ariz. Press, 1983
[5] Moroz, Chapter 5 of VENUS, Hunten et. al., editors, page 67, U. of Ariz. Press, 1983

initial examination were Ti, Mg, Fe, and K. These species were chosen partly because of the ready availability of thermodynamic data, and the likelihood of forming volatile compounds or aerosols which could reach the probe.

Figures 2-5 are the equilibrium mole fractions calculated for the conditions at 13km. The independent variable is the mole fraction of the volatilized atom. The notion of mole fractions of gas phase metal atoms at 13km over Venus might be not realizable, but the condition of chemical equilibrium does not involve consideration of the specific compounds being used as the reactions. Rather the atomic inventory and the possible compounds being equilibrated define the system.

Perusal of the figures indicates a marked influence on the balance of the trace species. No gas phase metallic compounds are formed. However an assortment of solid phase species are seen. As with the baseline calculations, more species were considered in the calculations. Appendices B through E list the species considered for each metal in addition to those species given in appendix A.

With the additions of the metals the levels of H_2O and HF are unaffected. In each case the levels of SO_2 decrease and CO and H_2 are increased. COS and H_2S are increased with Ti, K and Mg, but decreased slightly with Fe. HCl is unaffected with Ti, Fe and Mg, but with K added eventually exchanges with KCl as the chlorine compound. Graphite occur with Ti and Fe Ti and Fe and trace amounts of CH_4 occur with Ti, Fe and Mg.

The condensed species formed with each metal considered are given in the table below.

	Titanium	Iron	Potassium	Magnesium
metal fraction				
small	TiO_2	Fe_3O_4 FeS_2	K_2SO_4	K_2CO_3
large	TiO_2	Fe_3O_4 FeS	K_2CO_3 K_2SO_4 KCl	K_2CO_3

Appendix A

Species considered in the calculation of equilibrium composition of the baseline Venus atmosphere, but whose fractions were estimated to be less than 1 ppm.

C	CCL	CCLF3	CCL2
CCL2F2	CCL3	CCL3F	CCL4
CF	CF2	CF3	CF4
CH	CHCL	CHCLF2	CHCL2F
CHCL3	CHF3	CH2	CH2CLF
CH2CL2	CH2F2	CH3	CH3CL
CH3OH	CN	CNN	COCL
COCLF	COCL2	COF	COF2
COOH	CS	CS2	C2
C2CL2	C2CL4	C2CL6	C2F2
C2F4	C2H	C2HCL	C2HF
CHCO,ketyl	C2H2,acetylene	C2H2,vinylidene	
CH2CO,ketene	C2H3,vinyl	CH3CN	
CH3CO,acetyl	C2H4		
C2H4O,ethylen o	CH3CHO,ethanal	CH3COOH	(HCOOH)2
C2H5	C2H6	CH3N2CH3	CH3OCH3
C2H5OH	CCN	CNC	C2N2
C2O	C3	C3H3,propargyl	C3H4,allene
C3H4,propyne	C3H4,cyclo-	C3H5,allyl	
C3H6,propylene	C3H6,cyclo-	C3H6O	
C3H7,n-propyl	C3H7,i-propyl		
C3H8	C3H8O,1propanol	C3H8O,2propanol	C3O2
C4	C4H2	C4H4,1,3-cyclo-	
C4H6,butadiene			
C4H6,2-butyne	C4H6,cyclo-	C4H8,1-butene	
C4H8,cis2-buten	C4H8,tr2-butene	C4H8,isobutene	C4H8,cyclo-
(CH3COOH)2	C4H9,n-butyl	C4H9,i-butyl	C4H9,s-butyl
C4H9,t-butyl	C4H10,isobutane	C4H10,n-butane	C4N2
C5	C5H6,1,3cyclo-	C5H8,cyclo-	C5H10,1-
pentene	C5H10,cyclo-	C5H11,pentyl	C5H11,t-
pentyl	C5H12,n-pentane	C5H12,i-pentane	
CH3C(CH3)2CH3	C6H2	C6H5,phenyl	
C6H5O,phenoxy	C6H6	CL	CLCN
CLF	CLF3	CLO	CLO2
CL2	CL2O		
F	FCN	FO	FO2

F2	F2O	FS2F,fluorodisu	H
HCN	HCO	HCCN	HNC
HNCO	HNO	HNO2	HNO3
HOCL	HOF	HO2	HSO3F
HCHO,formaldehy	HCOOH	H2F2	H2O2
H2SO4	H3F3	(HCOOH)2	H4F4
H5F5	H6F6	H7F7	N
NCO	NF	NF2	NF3
NH	NHF	NHF2	
NH2	NH2F	NH3	NH2OH
NO	NOCL	NOF	NOF3
NO2	NO2CL	NO2F	NO3
NO3F	NCN	N2F2	N2F4
N2H2	NH2NO2	N2H4	N2O
N2O3	N2O4	N2O5	N3
N3H	O	OH	O2
O3	S	SCL	SCL2
SF	SF2	SF3	SF4
SF5	SF6	SH	SN
SO	SOF2	SO2CLF	SO2CL2
SO2F2	SO3	S2CL	S2CL2
S2F2,thiothiony	S8	C(gr)	H2O(s)
H2O(L)	H2SO4(L)	NH4CL(a)	NH4CL(b)
S(cr1)	S(cr2)	S(L)	SCL2(L)
S2CL2(L)			

Appendix B
Addition of Metallic Iron

Species considered in addition to those of Appendix A in the calculation of equilibrium composition of the Venus atmosphere with addition of metallic iron, but whose fractions were estimated to be less than 1 ppm.

Fe	FeC5O5	FeCL	FeCL2
FeCL3	FeO	Fe(OH)2	Fe2CL4
Fe2CL6	Fe(a)	Fe(a)	Fe(c)
Fe(d)	Fe(L)	FeC5O5(L)	FeCL2(s)
FeCL2(L)	FeCL3(s)	FeCL3(L)	FeO(s)
FeO(L)	Fe(OH)2(s)	Fe(OH)3(s)	FeS(a)
FeS(b)	FeS(c)	FeS(L)	FeSO4(s)
Fe2O3(s)	Fe2S3O12(s)	Fe(a)	Fe(c)
Fe(d)	Fe(L)	FeC5O5(L)	FeCL2(s)
FeCL2(L)	FeCL3(s)	FeCL3(L)	FeO(s)
FeO(L)	Fe(OH)2(s)	Fe(OH)3(s)	FeS(a)
FeS(b)	FeS(c)	FeS(L)	FeSO4(s)
Fe2O3(s)	Fe2S3O12(s)		

Appendix C
Addition of Metallic Titanium

Species considered in addition to those of Appendix A in the calculation of equilibrium composition of the Venus atmosphere with addition of metallic titanium, but whose fractions were estimated to be less than 1 ppm.

Ti	TiCL	TiCL2	TiCL3
TiCL4	TiO	TiOCL	TiOCL2
TiO2	Ti(a)	Ti(b)	Ti(L)
TiC(s)	TiC(L)	TiCL2(s)	TiCL3(s)
TiCL4(L)	TiN(s)	TiN(L)	TiO(a)
TiO(b)	TiO(L)	TiO2(L)	Ti2O3(1)
Ti2O3(2)	Ti2O3(L)	Ti3O5(a)	Ti3O5(b)
Ti3O5(L)	Ti4O7(s)	Ti4O7(L)	

Appendix D
Addition of Metallic Potassium

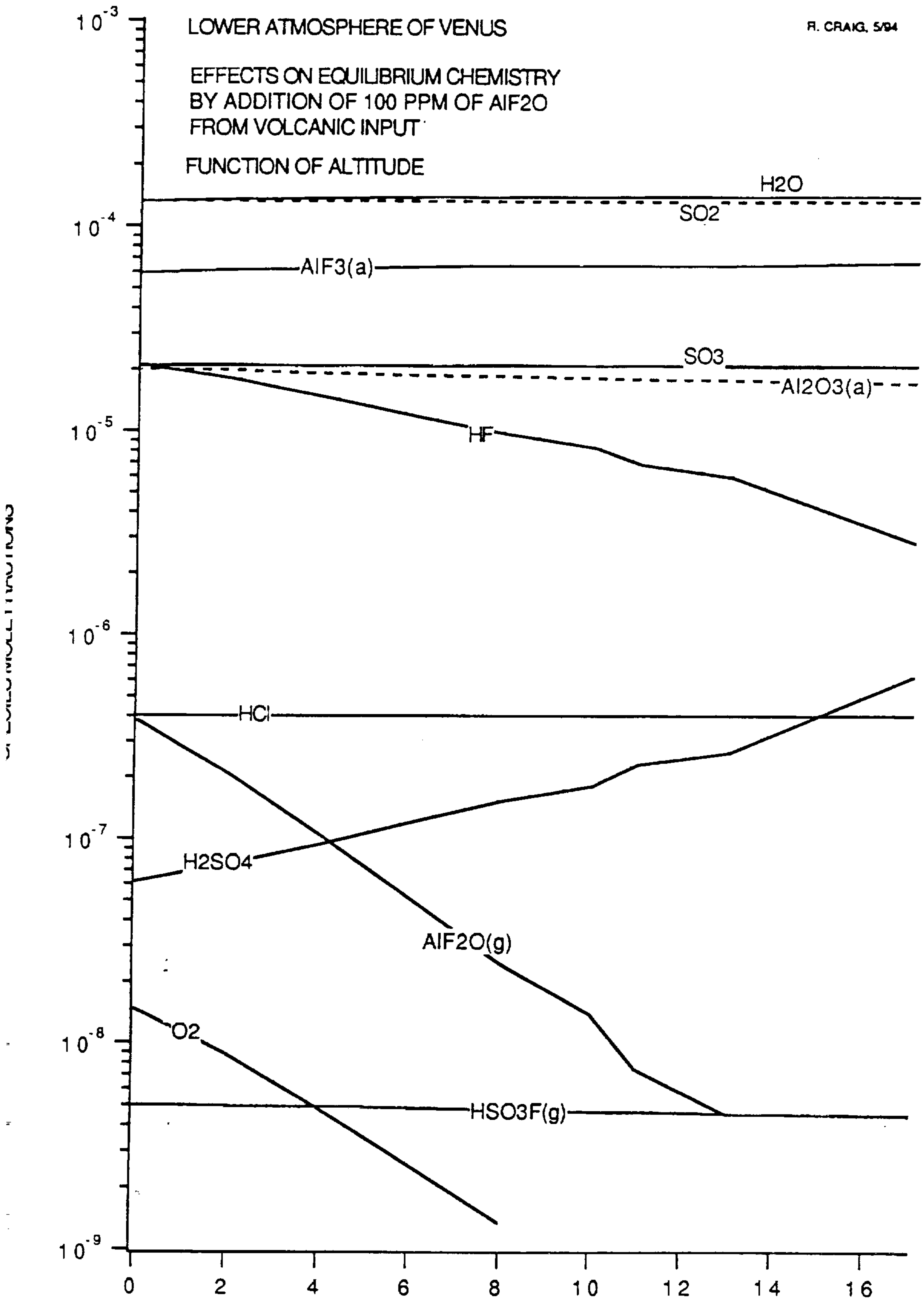
Species considered in addition to those of Appendix A in the calculation of equilibrium composition of the Venus atmosphere with addition of metallic potassium, but whose fractions were estimated to be less than 1 ppm.

K	KCN	KCL	KF
KH	KO	KOH	K2
K2C2N2	K2CL2	K2F2	K2O2H2
K2SO4	K(cr)	K(L)	KCN(s)
KCN(L)	KCL(s)	KCL(L)	KF(s)
KF(L)	KHF2(a)	KHF2(b)	KHF2(L)
KOH(a)	KOH(b)	KOH(L)	KO2(s)
K2CO3(s)	K2CO3(L)	K2O(s)	K2O2(s)
K2S(1)	K2S(2)	K2S(3)	K2S(L)
K2SO4(b)	K2SO4(L)		

Appendix E
Addition of Metallic Magnesium

Species considered in addition to those of Appendix A in the calculation of equilibrium composition of the Venus atmosphere with addition of metallic magnesium, but whose fractions were estimated to be less than 1 ppm.

Mg	MgCL	MgCLF	MgCL2
MgF	MgF2	MgH	MgN
MgO	MgOH	MgO2H2	MgS
Mg2	Mg2F4	Mg(cr)	Mg(L)
MgCL2(s)	MgCL2(L)	MgF2(s)	MgF2(L)
MgO(s)	MgO(L)	MgO2H2(s)	MgS(s)
MgSO4(s)	MgSO4(L)		



LOWER ATMOSPHERE OF VENUS
R. CRAIG, 5/94
EFFECTS ON EQUILIBRIUM CHEMISTRY
BY ADDITION OF 100 PPM OF AlF2O
FROM VOLCANIC INPUT
FUNCTION OF ALTITUDE
H2O
SO2
AlF3(a)
SO3
Al2O3(a)
HF
HCl
H2SO4
AlF2O(g)
O2
HSO3F(g)
10^-3
10^-4
10^-5
10^-6
10^-7
10^-8
10^-9
0
2
4
6
8
10
12
14
16
ALTITUDE, KM