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**RESERVE THIS SPACE**

## **Chemistry and composition of planetary atmospheres**

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This chapter summarizes atmospheric chemistry and composition for the seven planets in our solar system that have significant atmospheres. The terrestrial planets (Venus, Earth, and Mars) have secondary atmospheres that originated by the outgassing of volatile-rich material during and/or after planetary accretion. The gas giant planets (Jupiter, Saturn, Uranus, and Neptune) have primary atmospheres that were captured from the solar nebula. Some of the important chemical cycles that presently operate in planetary atmospheres are illustrated. Thermochemistry controls the atmospheric composition on Venus and in the deep atmospheres of the gas giant planets. In contrast, photochemistry dominates atmospheric chemistry on Mars and in the upper atmospheres of the gas giants. Biochemistry is the key process on Earth, with photochemistry also playing an important role. Some speculations about atmospheric chemistry and composition on extrasolar Earth-like planets are also presented.

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## Introduction

The planets in our solar system display a range of atmospheric compositions. Earth's atmosphere is oxygen-rich, those of Venus and Mars are mainly carbon dioxide, and the gas giant planets have hydrogen-rich atmospheres. Titan, the largest satellite of Saturn has a dense N<sub>2</sub>-rich, CH<sub>4</sub>-bearing atmosphere with a surface pressure of about 1.5 bar (1). A variety of tenuous atmospheres exist on Mercury, Pluto, and several planetary satellites. Mercury's rarified atmosphere of monatomic H, He, O, alkalis and alkaline earths has a surface pressure less than 10<sup>-12</sup> bars and arises from the solar wind, surface sputtering, outgassing, and vaporization of impactors (2). Pluto has an atmosphere containing N<sub>2</sub>, CH<sub>4</sub>, and possibly other gases. Its 40 K surface temperature corresponds to an N<sub>2</sub> pressure of 5.8 × 10<sup>-5</sup> bar (3). Neptune's largest satellite Triton has an N<sub>2</sub>-rich, CH<sub>4</sub>-bearing atmosphere with a surface pressure of 1.6 × 10<sup>-5</sup> bar (4). Io, the innermost Galilean satellite of Jupiter has a volcanically produced SO<sub>2</sub>-rich atmosphere with an average pressure of about 10<sup>-8</sup> bars. The erupted volcanic gases also contain SO, S<sub>2</sub> vapor, S, NaCl, Na, and K. Theoretical models predict that O, O<sub>2</sub>, S<sub>2</sub>O are also present (5). The other three Galilean satellites have rarified atmospheres of O<sub>2</sub> (Europa), O<sub>2</sub> and CO<sub>2</sub> (Callisto), and monatomic O and H (Ganymede) arising from charged particle bombardment and solar UV light irradiation of their icy surfaces (5).

This chapter reviews atmospheric chemistry and composition for the seven planets having significant atmospheres and is organized as follows. We first present some basic data about the nature and structure of planetary atmospheres. Next we describe the atmospheres of the terrestrial planets Venus, Earth, and Mars. Then we discuss atmospheric chemistry for the gas giant planets Jupiter, Saturn, Uranus, and Neptune. We close with some speculations about atmospheric chemistry on extrasolar Earth-like planets. Throughout the chapter we summarize the different processes responsible for producing and destroying atmospheric gases on each planet.

### Basic Information and Definitions

Before discussing the compositions of planetary atmospheres, it is helpful to define the units in which they are described. The most common is the volume-mixing ratio (or simply mixing ratio), which is a dimensionless quantity given by the ratio of the gas partial pressure ( $P_i$ ) to the total pressure ( $P_T$ ). It is also commonly referred to as the mole (or volume) fraction of the gas. Mixing ratios are given in terms of percent (%), parts per million (ppmv), parts per billion (ppbv), and parts per trillion (pptv) by volume.

Gas abundances are frequently given in terms of number density and column density (or column abundance). The number density of gas  $i$  is written as  $[i]$  and has units of particles (atoms + molecules) per unit volume (particles  $\text{cm}^{-3}$ ). It is calculated via the ratio  $P_i N_A / RT$ , where  $N_A$  is Avogadro's number,  $R$  is the ideal gas constant, and  $T$  is temperature in Kelvin. The column density of a gas is the number of gas particles throughout an atmospheric column and is found using the integral of  $[i]dz$  from a given altitude  $z_0$  (e.g. planetary surface) to the top of the atmosphere. It has dimensions of particles per unit area (particles  $\text{cm}^{-2}$ ) and can be calculated from the ratio  $P_i N_A / gM$ , where  $M$  is the formula weight of the gas and  $g$  is the acceleration due to gravity as a function of altitude.

The pressure scale height  $H$  is defined as the altitude change over which the atmospheric pressure decreases by a factor of  $e$  and is calculated from the ratio  $RT/\mu g$ , where  $\mu$  is the mean molecular weight of the gas. The change in pressure with altitude can be expressed through the barometric equation:  $P = P_0 \exp(-z/H)$ , which is valid in isothermal regions. In areas where temperature varies, the change in pressure with altitude is written as  $P = P_0 (T/T_0)^{-\beta}$ , where  $\beta = \mu g / R\Gamma$  and  $\Gamma = (dT/dz)$ , the atmospheric temperature gradient (K/km).

Table I compares physical parameters of the planetary atmospheres discussed below. We separate these into two groups: (1) the terrestrial planets (Venus, Earth, and Mars), and (2) the gas giant planets (Jupiter, Saturn, Uranus, and Neptune). Properties for the terrestrial planets are given at the observed surface conditions. Properties for the gas giant planets, which do not have observable solid surfaces, are given at the 1 bar atmospheric level.

**Table I. Physical Properties of Planetary Atmospheres**

<i>Planet</i>	$T_{\text{surface}}$ (K)	$P_{\text{surface}}$ (bars)	$g$ ( $m\ s^{-2}$ )	$\bar{\mu}$ <sup>a</sup> ( $g\ mole^{-1}$ )	$H$ <sup>b</sup> (km)	$\sigma$ <sup>c</sup> ( $cm^{-2}$ )
Venus	740	95.6	8.870	43.45	15.90	$1.49 \times 10^{27}$
Earth	288	1.013	9.820	28.97	8.42	$2.15 \times 10^{25}$
Mars	214	$6.36 \times 10^{-3}$	3.727	43.34	11.07	$2.37 \times 10^{23}$
Jupiter <sup>d</sup>	165	1 <sup>e</sup>	25.376	2.28	24.35	$1.04 \times 10^{26}$
Saturn <sup>d</sup>	134	1 <sup>e</sup>	10.443	2.25	51.54	$2.56 \times 10^{26}$
Uranus <sup>d</sup>	76	1 <sup>e</sup>	8.85	2.64	27.05	$2.58 \times 10^{26}$
Neptune <sup>d</sup>	71.5	1 <sup>e</sup>	11.14	2.53 <sup>f</sup>	21.09 <sup>f</sup>	$2.14 \times 10^{26,f}$

<sup>a</sup>Mean molecular weight. <sup>b</sup>Pressure scale height. <sup>c</sup>Column density. <sup>d</sup>Properties given at the 1 bar pressure level. <sup>e</sup>Observed P-T profiles are adiabatic below the tropopause. <sup>f</sup>assuming  $X_{H_2}=0.80$ ,  $X_{He}=0.19$ , and  $X_{CH_4}=0.01$ .

## Atmospheres of the Terrestrial Planets

We discuss the atmospheres of the three terrestrial planets Venus, Earth, and Mars together. The atmospheres of these three planets are secondary in origin, i.e. volatiles outgassed from the interior of the planets during and/or after planetary accretion. Primary atmospheres captured from the solar nebula would be rich in H<sub>2</sub> and He, the two most abundant gases in solar composition material. Even after loss of these two gases, primary atmospheres would not show large relative depletions of the rare noble gases (Ne, Ar, Kr, Xe) with respect to chemically reactive volatiles; however, this is exactly what is observed. For instance, the Ne/N<sub>2</sub> molar ratios in the atmospheres of Venus, Earth, and Mars are  $9.1 \times 10^{-5}$ ,  $1.1 \times 10^{-5}$ ,  $4.2 \times 10^{-5}$  times smaller than the Ne/N<sub>2</sub> ratio in a primary atmosphere captured from the solar nebula, respectively. This indicates that any gas initially captured from the solar nebula was lost, and the current atmospheres are the result of planetary outgassing.

The Earth's bulk chemical composition is similar to that of the ordinary chondritic meteorites (6). Figure 1 shows the calculated composition of an outgassed atmosphere for an Earth-like planet composed of average ordinary chondritic material. High temperature volcanic outgassing of the volatile elements H, C, N, O, F, Cl, and S produces an atmosphere dominated by CH<sub>4</sub> + H<sub>2</sub> (7). Stanley Miller and Harold Urey proposed that a similar atmosphere on the early Earth would create large amounts of organic compounds (e.g., the prebiotic soup), leading to the genesis of life (8, 9). Subsequent modification of the outgassed atmospheres of the terrestrial planets by various processes (e.g. thermochemistry, photochemistry, biochemistry, atmospheric escape, etc.) has altered them to their current states. On Venus and Mars, photochemical oxidation of CH<sub>4</sub> to CO<sub>2</sub> and loss of hydrogen has led to CO<sub>2</sub>-rich atmospheres. On Earth, active tectonism and the presence of liquid water at the surface prevent a massive CO<sub>2</sub> build-up in the atmosphere because much of the carbon on the planet is sequestered in marine sediments, primarily carbonates. Photosynthetic life forms produce the O<sub>2</sub>-rich disequilibrium atmosphere of today (10). Below we discuss the important volatile cycles and processes for the atmospheres of Venus, Earth, and Mars in turn.

### Venus

Table II gives the chemical composition of Venus' atmosphere, which is dominantly CO<sub>2</sub> with 3.5% of N<sub>2</sub> and smaller amounts of SO<sub>2</sub>, H<sub>2</sub>O, CO, and many reactive trace gases. The probable major sources and sinks for each gas are given in Table II. The gas abundances are taken primarily from (11), with

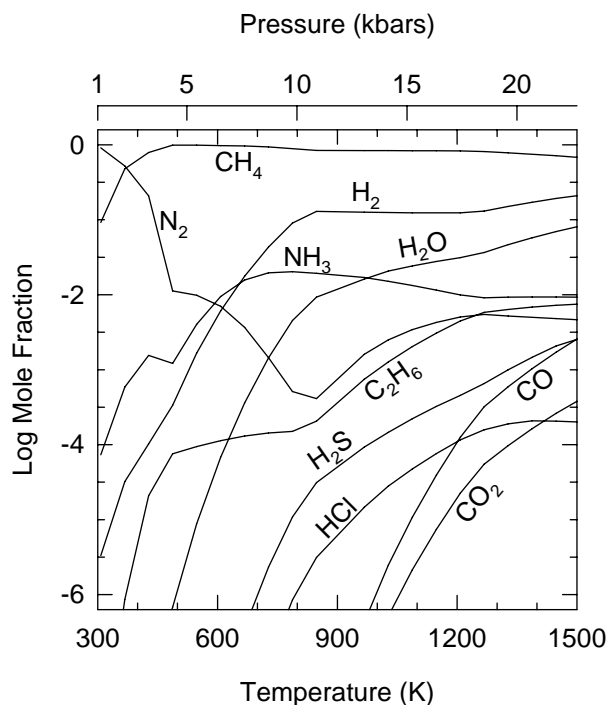
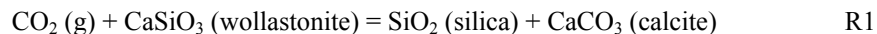


Figure 1. Chemical equilibrium composition of volatiles outgassed from average H-chondritic material as a function of temperature for the T-P profile of an Earth-like planet. Modified from (7).

new values for  $\text{H}_2\text{SO}_4$  (12) and  $\text{NO}$  (13). Chemistry in Venus' lower atmosphere is driven by high temperatures (740 K) and pressures (95 bars) generated by the massive  $\text{CO}_2$  greenhouse effect. Venus is shrouded by global sulfuric acid clouds, and less than ~11% of the incident sunlight reaches its surface, making photochemistry in the lower atmosphere negligible. Rather, the high temperatures and pressures at the surface force the rock-forming elements C, S, Cl, and F into the atmosphere where their abundances are controlled by reaction with minerals at the surface. For instance, the  $\text{CO}_2$  pressure on Venus is buffered by formation of carbonates on the surface through the reaction:



Carbon dioxide is only a minor gas in the Earth's atmosphere with a column abundance of  $5.32 \times 10^{21} \text{ cm}^{-2}$ , in comparison to Venus ( $1.40 \times 10^{27} \text{ cm}^{-2}$ ) and Mars ( $2.23 \times 10^{22} \text{ cm}^{-2}$ ). Most of Earth's surface carbon inventory is found in

**Table II. Chemical Composition of the Atmosphere of Venus**

<i>Gas</i>	<i>Abundance</i>	<i>Source(s)</i>	<i>Sink(s)</i>
CO <sub>2</sub>	96.5±0.8%	outgassing	UV photolysis, carbonate formation
N <sub>2</sub>	3.5±0.8%	outgassing	NO <sub>x</sub> formation by lightning
SO <sub>2</sub> <sup>a</sup>	150±30 ppm (22–42 km) 25–150 ppm (12–22 km)	outgassing & reduction of OCS, H <sub>2</sub> S	H <sub>2</sub> SO <sub>4</sub> formation, CaSO <sub>4</sub> formation
H <sub>2</sub> O <sup>a</sup>	30±15 ppm (0–45 km)	Outgassing and cometary impacts	H escape, Fe <sup>2+</sup> oxidation
<sup>40</sup> Ar	31 <sup>+20</sup> <sub>-10</sub> ppm	outgassing ( <sup>40</sup> K)	—
<sup>36</sup> Ar	30 <sup>+20</sup> <sub>-10</sub> ppm	Primordial	—
CO <sup>a</sup>	28±7 ppm (36–42 km)	CO <sub>2</sub> photolysis	photooxidation to CO <sub>2</sub>
<sup>4</sup> He <sup>b</sup>	0.6–12 ppm	outgassing (U, Th)	escape
Ne	7±3 ppm	outgassing, primordial	—
<sup>38</sup> Ar	5.5 ppm	outgassing, primordial	—
OCS <sup>a</sup>	4.4±1 ppm (33 km)	outgassing, sulfide weathering	conversion to SO <sub>2</sub>
H <sub>2</sub> S <sup>a</sup>	3±2 ppm (<20 km)	outgassing, sulfide weathering	conversion to SO <sub>2</sub>
HDO <sup>a</sup>	1.3±0.2 ppm (sub-cloud)	outgassing	H escape
HCl	0.5 ppm (35–45 km)	outgassing	mineral formation
<sup>84</sup> Kr	25 <sup>+13</sup> <sub>-18</sub> ppb	outgassing, primordial	—
SO <sup>a</sup>	20±10 ppb (cloud top)	photochemistry	photochemistry
S <sub>1-8</sub> <sup>a</sup>	20 ppb (<50 km)	sulfide weathering	conversion to SO <sub>2</sub>
HF	4.5 ppb (35–45 km)	outgassing	mineral formation
NO	5.5±1.5 ppb (sub-cloud)	lightning	conversion to N <sub>2</sub>
H <sub>2</sub> SO <sub>4</sub>	0.1 – 10 ppm (35-50 km)	SO <sub>2</sub> photolysis	cloud formation
<sup>132</sup> Xe	<10 ppb	outgassing, primordial	—
<sup>129</sup> Xe	<9.5 ppb	outgassing ( <sup>129</sup> I)	—

<sup>a</sup>Abundances are altitude dependent. <sup>b</sup>The He abundance in Venus' upper atmosphere is 12<sup>+24</sup><sub>-6</sub> ppmv (14). The value listed above is a model-dependent extrapolation to lower altitudes.

the crust, primarily as carbonates, with a total carbon abundance similar to that of CO<sub>2</sub> in Venus' atmosphere ( $0.7 \times 10^{27} \text{ cm}^{-2}$ ). Despite this similarity, we do not know if all CO<sub>2</sub> on Venus has been degassed and resides in the atmosphere. However, geological evidence summarized by (11) suggests that carbonates are present on Venus and that CO<sub>2</sub> is not completely degassed.

Hydrogen chloride and HF are present in terrestrial volcanic gases, and volcanism is probably the source of atmospheric Cl and F on Venus. The HCl and HF abundances are regulated by reaction with minerals such as sodalite (Na<sub>4</sub>[AlSiO<sub>4</sub>]<sub>3</sub>Cl) and fluorophlogopite (KMg<sub>3</sub>AlSi<sub>3</sub>O<sub>10</sub>F<sub>2</sub>) at the surface of Venus. The HCl and HF abundances in Venus' atmosphere are present at concentrations significantly higher than in the terrestrial troposphere. Most of the Cl and F in Earth's atmosphere are present as synthetic chlorofluorocarbon (CFC) gases due to anthropogenic emissions. Most of the 1 ppbv HCl and 25 pptv HF in Earth's atmosphere are also anthropogenic. Some HCl originates from sea salt, and volcanic gases provide localized HCl and HF. The bulk of the Earth's surficial Cl content is found dissolved in the oceans, and essentially all F is found in the crust. The terrestrial crustal inventories of Cl and F are larger than the abundances of HCl and HF in Venus' atmosphere, indicating that these elements have been only partially degassed.

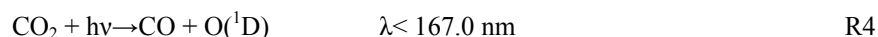
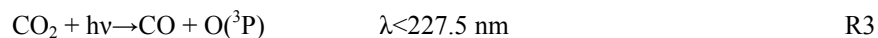
Sulfur dioxide is the third most abundant gas in Venus' atmosphere with an abundance of ~150 ppm in the middle atmosphere. It is produced primarily through volcanic outgassing and oxidation of volcanically outgassed reduced sulfur gases such as OCS and H<sub>2</sub>S. In contrast, all sulfur gases are much less abundant in the Earth's atmosphere. Carbonyl sulfide (OCS) is the most abundant sulfur gas in Earth's troposphere but is present at only a few hundred pptv. On Earth, the reduced sulfur gases (OCS, H<sub>2</sub>S, CS<sub>2</sub>, (CH<sub>3</sub>)<sub>2</sub>S, etc.) are mainly produced biologically. The volcanic sources of OCS and H<sub>2</sub>S are smaller than their biological sources. Most of the SO<sub>2</sub> in the terrestrial atmosphere is anthropogenic, with volcanic emissions being much less important.

The SO<sub>2</sub> abundance in Venus' atmosphere decreases at high altitudes due to the formation of the global sulfuric acid cloud layer (45-70 km), which is produced through SO<sub>2</sub> photolysis via the net photochemical reaction:



This reaction efficiently removes H<sub>2</sub>O and SO<sub>2</sub> from the upper atmosphere above the global cloud layer. At lower altitudes (<22 km), some SO<sub>2</sub> is thermochemically converted into OCS gas. Reaction of SO<sub>2</sub> with calcite (CaCO<sub>3</sub>) on the surface to form anhydrite (CaSO<sub>4</sub>) plus CO gas irreversibly removes SO<sub>2</sub> from the atmosphere. This net thermochemical reaction would completely remove SO<sub>2</sub> from Venus' atmosphere in ~1.9 Myr, unless it is replenished by volcanic outgassing.

The CO<sub>2</sub> in Venus' atmosphere is continually converted by UV sunlight (hν) to CO and O atoms in their ground (<sup>3</sup>P) and electronically excited (<sup>1</sup>D) states:



The direct recombination of oxygen atoms and CO is much slower than oxygen atom recombination to form O<sub>2</sub>. Therefore, photolysis would completely destroy all CO<sub>2</sub> in Venus' atmosphere in 5 Myr and would produce observable amounts of O<sub>2</sub> (which are not observed) in ~5 yr unless CO<sub>2</sub> is reformed by another route. Gas phase catalytic re-formation of CO<sub>2</sub> by H, Cl, or N gases has been proposed to solve this problem. For example, the reaction



is important at H<sub>2</sub> levels of tens of ppmv. At intermediate H<sub>2</sub> levels of ~0.1 ppmv, the reaction



precedes reaction R3, which then recycles CO to CO<sub>2</sub>.

At very low H<sub>2</sub> levels of ~0.1 ppbv, reaction R5 is no longer important and catalytic cycles such as that shown in Table III, made possible by the large HCl abundance in Venus' atmosphere, recycle CO to CO<sub>2</sub>. An analogous Cl cycle for O<sub>3</sub> destruction on Earth is made possible by anthropogenic emissions of CFCs.

## Earth

The composition of the Earth's atmosphere, given in Table IV, is controlled by biological processes, with additional influences from photochemistry and human activities. The abundances in Table IV are taken from (15), with updated abundances for the chlorofluorocarbons (CFCs), hydrofluorocarbons (HCFCs), hydrochlorocarbons (HCCs), and perfluorocarbons (PFCs) (16).

The major source of N<sub>2</sub> is the denitrifying bacteria in soils and oceans, which convert ammonium and nitrate compounds into N<sub>2</sub>. Major sinks for N<sub>2</sub> are nitrogen-fixing bacteria in soils and oceans, lightning, and combustion.



**Table III. Catalytic Chlorine Cycle in Venus' atmosphere**

$\text{CO} + \text{Cl} + \text{M} \rightarrow \text{COCl} + \text{M}^a$	R7
$\text{COCl} + \text{O}_2 + \text{M} \rightarrow \text{ClCO}_3 + \text{M}$	R8
$\text{ClCO}_3 + \text{O} \rightarrow \text{CO}_2 + \text{O}_2 + \text{Cl}$	R9
$\text{CO} + \text{O} \rightarrow \text{CO}_2$	Net Reaction R10

<sup>a</sup> M is any third body.

These sources and sinks result in an atmospheric lifetime of ~17 Myr for N<sub>2</sub> on Earth. In the absence of biological sinks, the atmospheric lifetime of N<sub>2</sub> would be a minimum of ~80 Myr, possibly as long as 1 Gyr in the absence of oxygen produced by photosynthesis.

The major oxygen-bearing species are O<sub>2</sub>, H<sub>2</sub>O, and CO<sub>2</sub>. The abundance of water vapor is controlled by evaporation-precipitation. Atmospheric O<sub>2</sub> and CO<sub>2</sub> are biologically controlled by photosynthesis and respiration/decay. Photosynthesis is represented by the net photochemical reaction:



where CH<sub>2</sub>O represents complex carbohydrates. The CO<sub>2</sub> destroyed by photosynthesis is restored by respiration and decay. However, the bulk of the carbon at the surface of the Earth is locked up in sedimentary rocks in the form of carbonates and organic carbon in roughly a 4:1 ratio (17). Photosynthetic production of O<sub>2</sub> began prior to 2.7 Gyr ago, but significant amounts of O<sub>2</sub> were not present in the atmosphere until ~2.3 Gyr ago (18). Build up of O<sub>2</sub> in the atmosphere may have been caused by gradual oxidation of the Earth's surface environment (crust and atmosphere) through H loss to space due to CH<sub>4</sub> photolysis (19). Most of the oxygen produced on Earth over time resides in Earth's crust and only a few percent is present as O<sub>2</sub> in the atmosphere.

Terrestrial stratospheric chemistry is closely linked to the ozone (O<sub>3</sub>) layer at 15-35 km, which shields the Earth's surface from harmful UV sunlight ( $\lambda < 300$  nm) and dissipates the absorbed solar energy as heat. The abundance of O<sub>3</sub> in the stratosphere is a balance between production, destruction, and lateral transport. Production and destruction of O<sub>3</sub> in the absence of other perturbing influences is described by the Chapman cycle given in Table V.

Reaction R15 in the Chapman cycle is kinetically slow, and several natural and anthropogenic trace gases in the earth's atmosphere catalyze ozone destruction more rapidly. Three important examples are the HO<sub>x</sub>, NO<sub>x</sub> and halogen (Cl, Br, I) oxide cycles, also shown in Table V. The HO<sub>x</sub> and NO<sub>x</sub>

**Table IV. Chemical Composition of the Terrestrial Troposphere**

<i>Gas</i>	<i>Abundance<sup>a</sup></i>	<i>Source(s)</i>	<i>Sink(s)</i>
N <sub>2</sub>	78.084%	denitrifying bacteria	nitrogen fixing bacteria
O <sub>2</sub>	20.946%	photosynthesis	respiration & decay
H <sub>2</sub> O	<4%, varies	evaporation, transpiration	condensation
Ar	9340 ppm	outgassing, <sup>40</sup> K decay	—
CO <sub>2</sub>	377 ppm	respiration, decay, combustion	photosynthesis, oceanic dissolution, weathering
Ne	18.18 ppm	outgassing	—
<sup>4</sup> He	5.24 ppm	outgassing (U, Th)	atmospheric escape
CH <sub>4</sub>	1.7 ppm	biological, agricultural	oxidation by OH
Kr	1.14 ppm	outgassing	—
H <sub>2</sub>	0.55 ppm	photochemistry, biology, combustion	uptake in soils, oxidation by OH
N <sub>2</sub> O	~320 ppb	anthropogenic & biological	stratospheric photolysis
CO	125 ppb	photochemistry	photochemistry
Xe	87 ppb	outgassing	—
O <sub>3</sub>	~10–100 ppb	photochemistry	photochemistry
HCl	~1 ppb	derived from sea salt	rainout
NMHCs <sup>b</sup>	≤ 80 ppb	foliar emissions, combustion, anthropogenic	photooxidation
H <sub>2</sub> O <sub>2</sub>	~0.3–3 ppb	photochemistry	photochemistry
NH <sub>3</sub>	0.1–3 ppb	biology	wet & dry deposition
HNO <sub>3</sub>	~0.04–4 ppb	photochemistry (NO <sub>x</sub> )	rainout
Reduced S-gases <sup>c</sup>	≤500 ppt	biology, anthropogenic	photodissociation, photooxidation
NO <sub>x</sub>	~30–300 ppt	combustion, biology	photooxidation
CFCs <sup>d</sup>	1013 ppt	anthropogenic	stratospheric photolysis
HCCs <sup>e</sup>	772.5 ppt	anthropogenic	reaction with OH
HCFCs <sup>f</sup>	133.6 ppt	anthropogenic	reaction with OH
PFCs <sup>g</sup>	73 ppt	anthropogenic	photolysis (upper atm.)
CH <sub>3</sub> Br	22 ppt	ocean, marine biota	reaction with OH
SO <sub>2</sub>	20–90 ppt	combustion	photooxidation
CH <sub>3</sub> I	~2 ppt	ocean, marine biota	photolysis (troposphere)
CClF <sub>2</sub> Br	3.8 ppt	anthropogenic	stratospheric photolysis

<sup>a</sup>Abundances by volume in dry air (non-urban troposphere). <sup>b</sup>Non-methane hydrocarbons: alkanes, alkenes, alkynes, aromatics, sterols. <sup>c</sup>OCS, H<sub>2</sub>S, CS<sub>2</sub>, (CH<sub>3</sub>)<sub>2</sub>S. <sup>d</sup>CF<sub>2</sub>Cl<sub>2</sub>, CFCl<sub>3</sub>, C<sub>2</sub>Cl<sub>3</sub>F<sub>3</sub>, C<sub>2</sub>Cl<sub>2</sub>F<sub>4</sub>, C<sub>2</sub>ClF<sub>5</sub>, CClF<sub>3</sub>, CCl<sub>4</sub>. <sup>e</sup>CH<sub>3</sub>Cl, CH<sub>3</sub>CCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>2</sub>ClCH<sub>2</sub>Cl, CHCl<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>Cl, CHCl<sub>2</sub>Cl. <sup>f</sup>CHClF<sub>2</sub>, CHCl<sub>2</sub>F. <sup>g</sup>CF<sub>4</sub>, C<sub>2</sub>F<sub>6</sub>.

**Table V. Cycles for Ozone Depletion in Earth's Atmosphere**

<i>Chapman Cycle</i>		
$O_2 + h\nu \rightarrow O + O$	$(\lambda = 180 - 240 \text{ nm})$	R12
$O + O_2 + M \rightarrow O_3 + M$		R13
$O_3 + h\nu \rightarrow O(^1D) + O_2$	$(\lambda = 200 - 300 \text{ nm})$	R14
$O + O_3 \rightarrow O_2 + O_2$		R15
$O_3 \rightarrow O + O_2$	Net Reaction	R16
<i>Catalytic Cycle (<math>X = H, OH, NO, Cl</math>)</i>		
$X + O_3 \rightarrow XO + O_2$		R17
$XO + O \rightarrow X + O_2$		R18
$O + O_3 \rightarrow O_2 + O_2$	Net Reaction	R15

cycles involve naturally occurring species: OH radicals produced by reaction of electronically excited oxygen ( $^1D$ ) with water vapor, and  $NO_x$  gases produced from nitrous oxide ( $N_2O$ ) transported upward from the troposphere. However, the halogen oxide cycle involves halogens and halogen oxide radicals produced primarily through solar UV photolysis of anthropogenically emitted halocarbons (including CFCs, HCFCs, HCCs, PFCs), many of which are used as refrigerants, e.g. freon-12 ( $CF_2Cl_2$ ). Modeling of stratospheric chemistry shows that the  $NO_x$ ,  $HO_x$ ,  $ClO_x$ , and Chapman cycles account for 31-34%, 16-29%, 19-20%, and 20-25% respectively of  $O_3$  destruction. The relative importance of the Chapman reactions and the various catalytic cycles varies with altitude and with the concentration of  $NO_x$ ,  $HO_x$ , and halogen oxide gases.

## Mars

The chemical composition of the Martian atmosphere is given in Table VI, along with plausible sources and sinks. The abundances are taken primarily from (15), with new abundances for He (20),  $H_2$  and HD (21),  $H_2O_2$  (22, 23), and  $CH_4$  (24). The Martian atmosphere is dominantly  $CO_2$ , which is continually converted to  $O_2$  and CO by solar UV light. However, as on Venus, the observed abundances of  $CO_2$ ,  $O_2$ , and CO cannot be explained simply by the direct recombination of CO and O atoms to  $CO_2$  because this reaction is too slow to maintain the high  $CO_2$  and low CO and  $O_2$  abundances. Instead, OH radicals produced from atmospheric water vapor by UV photolysis or by reaction with electronically excited O atoms enter into catalytic cycles such as that shown in

**Table VI. Chemical Composition of the Atmosphere of Mars**

<i>Gas</i>	<i>Abundance<sup>a</sup></i>	<i>Source(s)</i>	<i>Sink(s)</i>
CO <sub>2</sub>	95.32%	outgassing & sublimation	condensation
N <sub>2</sub>	2.7%	outgassing	escape as N
Ar	1.6%	outgassing ( <sup>40</sup> K), primordial	—
O <sub>2</sub>	0.13%	CO <sub>2</sub> photolysis	photoreduction
CO	0.08%	CO <sub>2</sub> photolysis	photooxidation
H <sub>2</sub> O*	0.03%	evaporation & desorption	condensation & adsorption
NO	~100 ppm (at 120 km)	photochemistry (N <sub>2</sub> , CO <sub>2</sub> )	photochemistry
Ne	2.5 ppm	outgassing, primordial	—
HDO	0.85±0.02 ppm	evaporation & desorption	condensation & adsorption
Kr	0.3 ppm	outgassing, primordial	—
Xe	0.08 ppm	outgassing, primordial	—
O <sub>3</sub> <sup>b</sup>	~(0.04–0.2) ppm	photochemistry (CO <sub>2</sub> )	photochemistry
He	10±6 ppm	solar wind, outgassing,	escape
H <sub>2</sub>	15±5 ppm	H <sub>2</sub> O photolysis	escape
H <sub>2</sub> O <sub>2</sub>	20–50 ppb	H <sub>2</sub> O photolysis	photochemistry
HD	11 ± 4 ppb	H <sub>2</sub> O photolysis	escape
CH <sub>4</sub>	10 ± 3 ppb	outgassing	photochemistry

<sup>a</sup>The mixing ratios, but not the column densities, of noncondensable gases are seasonally variable as a result of the annual condensation and sublimation of CO<sub>2</sub>.

<sup>b</sup>Spatially and temporally variable

Table VII, which recombine CO and O atoms to CO<sub>2</sub>. Another catalytic cycle involves photolysis of hydrogen peroxide:



The HO<sub>x</sub> radicals also regulate the O<sub>3</sub> level in the Martian atmosphere via catalytic cycles analogous to those in the terrestrial stratosphere. However, on Venus catalytic cycles involving chlorine for the re-combination of CO<sub>2</sub> are required because the hydrogen abundance is too low for catalytic cycles involving OH to be as efficient as they are on Mars.

**Table VII. Catalytic CO<sub>2</sub> Cycle in the Martian Atmosphere**

OH + CO → CO <sub>2</sub> + H	R20
H + O <sub>2</sub> + M → HO <sub>2</sub> + M	R21
HO <sub>2</sub> + O → OH + O <sub>2</sub>	R22
CO + O → CO <sub>2</sub>	Net reaction R23

### Atmospheres of the Gas Giant Planets

The atmospheres of the gas giant planets Jupiter, Saturn, Uranus, and Neptune are primary atmospheres composed of gases captured from the solar nebula, mainly H<sub>2</sub> and He. We separate them into two groups based on composition. Jupiter and Saturn are closer to solar composition, although both planets are generally enriched in elements heavier than He. Jupiter is depleted in oxygen relative to solar composition (25), and Saturn is less enriched in oxygen than other heavy elements (26). Their atmospheric compositions are given in Table VIII (15, 27-34). Abundances of the minor species PH<sub>3</sub>, GeH<sub>4</sub>, AsH<sub>3</sub>, and CO in the upper atmospheres of Jupiter and Saturn are larger than predicted from thermochemical equilibrium in the regions where these gases are observed. This indicates that they are transported upward from deeper levels where they are more abundant (27). Photochemistry (discussed below) and the Shoemaker-Levy 9 (SL9) impact into Jupiter's upper atmosphere affect stratospheric chemistry. The observed CO<sub>2</sub> and H<sub>2</sub>O in Jupiter's stratosphere are believed to have formed from H<sub>2</sub>O and CO delivered by SL9 (31).

Uranus and Neptune are smaller and denser than Jupiter and Saturn due to much larger enrichments of elements heavier than He. Oxygen is highly enriched on these planets and the net thermochemical reaction



produces 1,000 times more CO than on Jupiter or Saturn in the deep atmospheres of Uranus and Neptune (35). The compositions of their observable atmospheres are shown in Table IX (15, 36) and are seen to be significantly enriched in methane and deuterium relative to Jupiter and Saturn. Water, NH<sub>3</sub>, H<sub>2</sub>S, and other condensable gases are not observed because they are removed by cloud condensation hundreds of kilometers below the observable atmospheric regions. Photochemistry plays a major role in the chemistry of the atmospheres of all four gas giant planets. In particular, methane and ammonia

**Table VIII. Chemical Composition of the Atmospheres of Jupiter and Saturn**

<i>Gas</i>	<i>Jupiter<sup>a</sup></i>	<i>Saturn</i>
H <sub>2</sub>	86.4 ± 0.3%	88 ± 2%
<sup>4</sup> He	13.6 ± 0.3%	12 ± 2%
CH <sub>4</sub>	(1.81 ± 0.34) × 10 <sup>-3</sup>	(3.8 ± 1.1) × 10 <sup>-4</sup>
NH <sub>3</sub>	(6.1 ± 2.8) × 10 <sup>-4</sup>	(1.6 ± 1.1) × 10 <sup>-4</sup>
H <sub>2</sub> O	520 <sup>+340</sup> <sub>-240</sub> ppm	2–20 ppb
HD	45 ± 12 ppm	110 ± 58 ppm
H <sub>2</sub> S	67 ± 4 ppm	<0.4 ppm
<sup>13</sup> CH <sub>4</sub>	19 ± 1 ppm	~51 ppm
C <sub>2</sub> H <sub>6</sub>	5.8 ± 1.5 ppm	7.0 ± 1.5 ppm
PH <sub>3</sub>	1.1 ± 0.4 ppm	4.5 ± 1.4 ppm
C <sub>2</sub> H <sub>2</sub>	0.11 ± 0.03 ppm	0.30 ± 0.10 ppm
CH <sub>3</sub> D	0.20 ± 0.04 ppm	0.39 ± 0.25 ppm
C <sub>2</sub> H <sub>4</sub>	7 ± 3 ppb	~0.2 ppb <sup>b</sup>
CH <sub>3</sub> C <sub>2</sub> H	2.5 <sup>+2</sup> <sub>-1</sub> ppb	0.6 ppb
HCN	60 ± 10 ppb	<4 ppb
CO	1.6 ± 0.3 ppb	1.4 ± 0.7 ppb
GeH <sub>4</sub>	0.7 <sup>+0.4</sup> <sub>-0.2</sub> ppb	0.4 ± 0.4 ppb
C <sub>4</sub> H <sub>2</sub>	0.3 ± 0.2 ppb	0.09 ppb
AsH <sub>3</sub>	0.22 ± 0.11 ppb	2.1 ± 1.3 ppb
CO <sub>2</sub>	5-35 ppb	0.3 ppb

<sup>a</sup> <sup>3</sup>He 22.6±0.7 ppm, Ne 21±3 ppm, Ar 16±3 ppm, Kr 8±1 ppb, Xe 0.8±0.1 ppb. <sup>b</sup> assuming stratospheric column density of 1.54×10<sup>25</sup> cm<sup>-2</sup>

**Table IX. Chemical Composition of the Atmospheres of Uranus and Neptune**

<i>Gas</i>	<i>Uranus</i>	<i>Neptune</i>
H <sub>2</sub>	~82.5 ± 3.3%	~80 ± 3.2 %
He	15.2 ± 3.3 %	19.0 ± 3.2 %
CH <sub>4</sub>	~2.3 %	~1-2 %
HD	~148 ppm	~192 ppm
CH <sub>3</sub> D	~8.3 ppm	~12 ppm
C <sub>2</sub> H <sub>6</sub>	10 ± 1 ppb	1.5 <sup>+2.5</sup> <sub>-0.5</sub> ppm
C <sub>2</sub> H <sub>2</sub>	~10 ppb	60 <sup>+140</sup> <sub>-40</sub> ppb
H <sub>2</sub> S <sup>a</sup>	<0.8 ppm	<3 ppm
NH <sub>3</sub> <sup>a</sup>	<100 ppb	<600 ppb
CO	<40 ppb	0.65 ± 0.35 ppm
CH <sub>3</sub> CN	--	<5 ppb
HCN	<15 ppb	0.3 ± 0.15 ppb
HC <sub>3</sub> N	<0.8 ppb	<0.4 ppb
C <sub>4</sub> H <sub>2</sub>	0.16 ± 0.02 ppb	--
CH <sub>3</sub> C <sub>2</sub> H	0.25 ± 0.03 ppb	--
CO <sub>2</sub>	40 ± 5 ppt	--

<sup>a</sup>Converted to a mixing ratio using a H<sub>2</sub> column abundance of 400 km amagat. (1 km amagat = 2.69 × 10<sup>24</sup> cm<sup>-2</sup>)

photochemistry produce many of the minor species observed in the stratospheres of these four planets, as discussed below.

#### **Methane Photochemistry – Jupiter, Saturn, Uranus, and Neptune**

Methane is photolyzed by UV sunlight with wavelengths  $\lambda < 160$  nm to <sup>3</sup>CH<sub>2</sub> + 2H (51%), <sup>1</sup>CH<sub>2</sub> + H<sub>2</sub> (41%), and CH + H + H<sub>2</sub> (8%). <sup>3</sup>CH<sub>2</sub> is the triplet

**Table X. Ethane Formation from Methane**

$2(\text{CH}_4 + h\nu \rightarrow {}^1\text{CH}_2 + \text{H}_2)$	R25
$2({}^1\text{CH}_2 + \text{H}_2 \rightarrow \text{CH}_3 + \text{H})$	R26
$\text{CH}_3 + \text{CH}_3 + \text{M} \rightarrow \text{C}_2\text{H}_6 + \text{M}$	R27
$\text{H} + \text{H} + \text{M} \rightarrow \text{H}_2 + \text{M}$	R28
$2\text{CH}_4 \rightarrow \text{C}_2\text{H}_6 + \text{H}_2$	Net Reaction R29

(electronic ground) state of methylene, and  ${}^1\text{CH}_2$  is the singlet (electronic excited) state of methylene. Many higher hydrocarbons are formed from the products of methane photolysis. As an example, Table X shows the series of elementary reactions for the formation of ethane ( $\text{C}_2\text{H}_6$ ) from methane. The methyl radical, which is important in ethane formation, has been observed in the stratospheres of Saturn and Neptune at column abundances of  $(1.5 - 7.5) \times 10^{13} \text{ cm}^{-2}$  (37) and  $1.6_{-0.9}^{+1.2} \times 10^{13} \text{ cm}^{-2}$  (38), respectively. It has also been observed in the atmosphere of Jupiter (39) although its abundance has not been determined (40). There has been no detection of the methyl radical in Uranus' atmosphere, but an upper limit of .05 ppbv has been set (40).

Similar formation schemes can be written for the other observed hydrocarbons. Ethylene ( $\text{C}_2\text{H}_4$ ) is formed by reaction of a methyl radical ( $\text{CH}_3$ ) and a methylene triplet, or by reaction of CH radicals with methane. Acetylene ( $\text{C}_2\text{H}_2$ ) forms through reaction of 2 methylene triplets. All of these  $\text{C}_2$  hydrocarbons undergo further photochemical reactions to a greater ( $\text{C}_2\text{H}_4$ ) or lesser ( $\text{C}_2\text{H}_6$ ) extent depending on the UV shielding provided to them by methane. Only a minor fraction of  $\text{C}_2\text{H}_6$  is photolyzed via



and most  $\text{C}_2\text{H}_6$  is removed by vertical transport into the hot, lower atmospheres of the gas giant planets where  $\text{CH}_4$  reforms via the net thermochemical reaction



Ultimately, downward mixing into the hot, lower atmospheres of the Jovian planets reconverts all higher hydrocarbons back to  $\text{CH}_4$  via hydrogenation reactions.

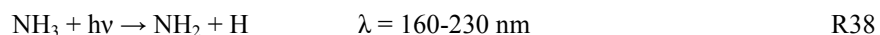


**Table XI. Reaction Cycle for N<sub>2</sub> Formation in Gas Giants**

$4(\text{NH}_3 + h\nu \rightarrow \text{NH}_2 + \text{H})$	R32
$2(\text{NH}_2 + \text{NH}_2 + \text{M} \rightarrow \text{N}_2\text{H}_4)$	R33
$2(\text{N}_2\text{H}_4 + h\nu \rightarrow \text{N}_2\text{H}_3 + \text{H})$	R34
$\text{N}_2\text{H}_3 + \text{N}_2\text{H}_3 \rightarrow 2\text{NH}_3 + \text{N}_2$	R35
$3(\text{H} + \text{H} + \text{M} \rightarrow \text{H}_2 + \text{M})$	R36
$2\text{NH}_3 = \text{N}_2 + 3\text{H}_2$	Net Reaction R37

### NH<sub>3</sub> Photolysis on Jupiter, Saturn, Uranus, and Neptune

Ammonia condenses out of Jupiter's atmosphere forming a cloud of NH<sub>3</sub> ice particles at 138 K and 0.46-0.53 bars pressure (41). It is photolyzed by UV sunlight in the 160 – 230 nm region in Jupiter's upper troposphere. Shorter wavelength light is absorbed at higher altitudes by H<sub>2</sub>, CH<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub> while longer wavelength light does not destroy NH<sub>3</sub>. Almost all NH<sub>3</sub> photolyzes via the reaction:



Most of the NH<sub>2</sub> radicals form N<sub>2</sub> via the pathway given in Table XI. Some of the N<sub>2</sub>H<sub>4</sub> (hydrazine) formed in reaction R32 condenses out of the upper atmospheres of the gas giants forming thin haze layers. However, most of the photolyzed NH<sub>3</sub> is recycled via photochemical reactions such as R34 and by



Ultimately the N<sub>2</sub> and N<sub>2</sub>H<sub>4</sub> produced by NH<sub>3</sub> photolysis are reconverted back to NH<sub>3</sub> via thermochemical reactions exemplified by



in the hot, deep atmospheres of the gas giant planets.

## Extrasolar Earth-like Planets

To date, 215 extrasolar planets have been detected. Of these, two recent detections seem to be terrestrial-sized extrasolar planets, Gliese 876d ( $7.5M_{\text{Earth}}$ ) (42) and OGLE-2005-BLG-390Lb ( $5.5M_{\text{Earth}}$ ) (43). This begs the question: what kind of atmospheres should we expect to find around such planets. These planetary atmospheres will be affected by a myriad number of variables including: the stellar environment (type of parent star, orbital location, tidal locking, planetary companions, etc.), the planet's size (tectonically active or not), its composition (wet or dry, volatile inventory), stage of evolution, presence of a biosphere, etc. Given the number of possible variables, the atmospheric compositions of extrasolar terrestrial-type planets will surely be more varied than we can possibly predict.

Spacecraft missions are being planned by both NASA (the Terrestrial Planet Finder) and ESA (Darwin) to search for Earth-like planets around other stars and to take spectra of their atmospheres and surfaces (44, 45). These missions are designed to detect planets located in the habitable zones (HZ) of other stars. The HZ is defined as the orbital area around a star where a planet can sustain liquid water at the surface. Several studies have attempted to define the HZ as a function of stellar type (e.g. F, G, K, M dwarf stars) and time (see e.g. 46, 47, and references therein). The HZ is of interest because it is widely believed that liquid water is necessary for the genesis of (recognizable) life. The particular emphasis of the planned space missions is to search for signs of life on extrasolar Earth-like planets via spectroscopy. Atmospheric compounds such as  $\text{O}_2$ ,  $\text{O}_3$ ,  $\text{N}_2\text{O}$ ,  $\text{CH}_4$ , and  $\text{CH}_3\text{Cl}$  are considered biomarkers, and their spectroscopic detection in a terrestrial-type atmosphere, particularly  $\text{O}_2$  or  $\text{O}_3$  found together with a reduced gas such as  $\text{CH}_4$ , would indicate life (48, 49). Detection of  $\text{CO}_2$  would indicate that the planet is indeed a terrestrial-type planet (50).

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