Properties and Composition of the Terrestrial Oceans and of the Atmospheres of the Earth and Other Planets

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1. PHYSICAL PROPERTIES AND COMPOSITION OF THE TERRESTRIAL OCEANS

Geographical data on the areas, volumes, and depths of the major ocean basins are summarized by Turekian [209]. Many physical properties of seawater are summarized by Cox [49] and Riley [182]. The major element composition of seawater is reviewed by Wilson [216]. A comprehensive discussion of the chemistry of the atmosphere-ocean system, of continental weathering, riverine inputs to the oceans, and the composition of sea water over geologic time is given in two books by Holland [105,106]. Many in depth reviews of different aspects of the chemistry of seawater are given in the multivolume series *Chemical Oceanography,* most recently edited by Riley and Chester.

The temperature of ocean surface waters depends on the geographic location and season of the year. It is also affected by the presence of oceanic currents which transport waters from northern or southern latitudes. Thus, surface waters in the Gulf Stream still have relatively high temperatures at northern latitudes. The deeper regions of the oceans, below about 1 km depth, have a nearly constant temperature of 275-277 K due to their origins in high latitudes around Greenland and the Antarctic continent. Between about 100 meters depth, the bottom of the well mixed layer, and 1 km depth, the temperature of sea water decreases nearly monotonically to the low values typical for the deeper regions of the oceans. This transition region is known as the thermocline.

The salinity of ocean water is about 35 parts per thousand by mass (35 ‰); variations from about 33 ‰ to 38 ‰ are observed in the open oceans. As illustrated in Table 1, the composition of sea water is dominated by the six elements Cl, Na, S, Mg, Ca, and K. Despite the observed variations in salinity, their concentrations relative to one another are essentially constant. These elements and the other elements in sea water which behave similarly are conservative elements. Variations in their concentrations can be explained solely by either the addition or subtraction of pure water to the oceans. Because of this conservative behavior the salinity of sea water can be determined by measuring the content of chloride, the most abundant anion in sea water. The salinity (S) is related to the chlorinity (Cl) by the approximate equation S(‰) ~ 1.805 Cl(‰) + 0.030, where both S and Cl are in g/kg of sea water. Cox [49] describes several methods, including conductivity measurements, for more accurate and precise measurements of the salinity of sea water.

Other elements display variable concentrations relative to local salinity and are nonconservative. Several of these elements such as C, N (as nitrate), Si, and P are nutrients, and are generally depleted in surface waters and are enriched in deeper regions. Many other elements (e.g., Cr, Mn, Fe, Co, Ni, Cu, Zn, Sr, Cd) have vertical concentration profiles similar to those of the nutrient elements. However, it is not always clear if this similarity is due to passive processes (e.g., coprecipitation, adsorption on dead sinking organisms) or to active biochemical processes. For example, growth of phytoplankton is apparently limited by the availability of Fe. On the other hand, Al also displays nutrient-like profiles but this is probably due to surface inputs by

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Global Earth Physics
A Handbook of Physical Constants
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TABLE 1. Chemical Composition of Seawater[a,b]

At. No.	Element	Dissolved Form	Mean Concentration	Notes & References
1	H	H_2		biogenic or hydrothermal origin
2	He	Dissolved He	1.9 nmole/kg	non-nutrient dissolved gas
3	Li		178 μg/kg	conservative
4	Be		0.2 ng/kg	increases with depth
5	B	Inorganic boron	4.4 mg/kg	conservative
6	C	Total CO_2	2200 μmole/kg	nutrient
7	N	N_2	590 μmole/kg	non-nutrient dissolved gas
		NO_3	30 μmole/kg	nutrient
8	O	Dissolved O_2	150 μmole/kg	biologically controlled profile
9	F	Fluoride	1.3 mg/kg	conservative
10	Ne	Dissolved Ne	8 nmole/kg	non-nutrient dissolved gas
11	Na		10.781 g/kg	conservative
12	Mg		1.28 g/kg	conservative
13	Al		1 μg/kg	nutrient-like profile
14	Si	Silicate	110 μmole/kg	nutrient
15	P	Reactive phosphate	2 μmole/kg	nutrient
16	S	Sulfate	2.712 g/kg	conservative
17	Cl	Chloride	19.353 g/kg	conservative
18	Ar	Dissolved Ar	15.6 μmole/kg	non-nutrient dissolved gas
19	K		399 mg/kg	conservative
20	Ca		415 mg/kg	conservative (1st. approx.)
21	Sc		<1 ng/kg	
22	Ti		<1 ng/kg	
23	V		<1 μg/kg	conservative
24	Cr		330 ng/kg	nutrient-like profile
25	Mn		10 ng/kg	nutrient-like profile
26	Fe		40 ng/kg	nutrient-like profile
27	Co		2 ng/kg	nutrient-like profile
28	Ni		480 ng/kg	nutrient-like profile
29	Cu		120 ng/kg	nutrient-like profile
30	Zn		390 ng/kg	nutrient-like profile
31	Ga		7-60 ng/kg	[164]
32	Ge		5 ng/kg	correlated with silicate
33	As	As(V)	2 μg/kg	nutrient-like profile
34	Se	Total Se	170 ng/kg	correlated with phosphate

TABLE 1. (continued).

At. No.	Element	Dissolved Form	Mean Concentration	Notes & References
35	Br	Bromide	67 mg/kg	conservative
36	Kr	Dissolved Kr	3.7 nmole/kg	non-nutrient dissolved gas
37	Rb		124 µg/kg	conservative
38	Sr		7.8 mg/kg	correlated with phosphate
39	Y		13 ng/kg	conservative (1st approx.)
40	Zr		<1 µg/kg	
41	Nb		1 ng/kg	
42	Mo		11 µg/kg	conservative
44	Ru		~1 ng/kg	[14]
45	Rh			
46	Pd		0.2-0.7 pmole/kg	[132]
47	Ag		3 ng/kg	
48	Cd		70 ng/kg	correlated with phosphate
49	In		0.2 ng/kg	
50	Sn		0.5 ng/kg	anthropogenic
51	Sb		0.2 µg/kg	conservative
52	Te	Total Te	0.6-1.3 pmole/kg	[133]
53	I		59 µg/kg	correlated with phosphate
54	Xe		0.5 nmole/kg	non-nutrient dissolved gas
55	Cs		0.3 ng/kg	conservative
56	Ba		11.7 µg/kg	nutrient-like profile
57	La		4 ng/kg	nutrient-like profile
58	Ce		4 ng/kg	nutrient-like profile
59	Pr		0.6 ng/kg	nutrient-like profile
60	Nd		4 ng/kg	nutrient-like profile
62	Sm		0.6 ng/kg	nutrient-like profile
63	Eu		0.1 ng/kg	nutrient-like profile
64	Gd		0.8 ng/kg	nutrient-like profile
65	Tb		0.1 ng/kg	nutrient-like profile
66	Dy		1 ng/kg	nutrient-like profile
67	Ho		0.2 ng/kg	nutrient-like profile
68	Er		0.9 ng/kg	nutrient-like profile
69	Tm		0.2 ng/kg	nutrient-like profile
70	Yb		0.9 ng/kg	nutrient-like profile
71	Lu		0.2 ng/kg	nutrient-like profile

TABLE 1. (continued).

At. No.	Element	Dissolved Form	Mean Concentration	Notes & References
72	Hf		<8 ng/kg	
73	Ta		<2.5 ng/kg	
74	W		<1 ng/kg	
75	Re		7.2-7.4 ng/kg	conservative, [1]
76	Os			
77	Ir			
78	Pt			
79	Au		50-150 fmole/liter	[75]
80	Hg		6 ng/kg	correlated with silicate
81	Tl		12 ng/kg	conservative
82	Pb		1 ng/kg	anthropogenic
83	Bi		10 ng/kg	
90	Th		<0.7 ng/kg	
92	U		3.2 μg/kg	conservative

[a]Modified from [179]

[b]Abbreviations: mg/kg = 10^{-3}g/kg, μg/kg = 10^{-6}g/kg, ng/kg = 10^{-9}g/kg, pmole/kg = 10^{-12}mole/kg, fmole/l = 10^{-15}mole/liter

dust and decreases at depth as a result of scavenging by organic particulates and by sedimentation of mineral grains.

Dissolved gases generally have abundance patterns that are initially controlled by their solubility in surface waters at the ambient temperature and gas partial pressure. The mixing produced by waves can also lead to trapping of air bubbles, which will introduce a deviation from the solubility controlled abundance. The exceptions to this behavior are gases such as O_2, CO_2, CO, H_2S, H_2, N_2O, and N_2 which are involved in biological processes. For example, the O_2 concentration is higher in surface waters where it is produced by photosynthesis and is lower in deeper regions where it is consumed by respiring organisms.

Quinby-Hunt and Turekian [179] discuss several other factors which also affect the vertical profiles of some elements in sea water. Radionuclides produced from fission and fusion bombs (e.g., tritium (T), the bomb component of ^{14}C, ^{90}Sr, ^{137}Cs, Pu) are supplied to the ocean from the atmosphere and coastal sources. As a consequence their concentrations decrease with increasing depth in the oceans. Likewise, the concentration of Pb, which is an anthropogenic input to the oceans, displays similar behavior. On the other hand, the major source for ^3He is at oceanic spreading centers; infalling cosmic dust and meteorites are estimated to contribute <25% of the ^3He in the oceans [140]. Removal processes at the sea floor also influence the distribution of some trace elements and nuclides.

To a first approximation, chemical equilibria between atmospheric CO_2, dissolved carbonate and bicarbonate, and $CaCO_3(s)$ are responsible for controlling the pH of the oceans. The relevant equilibria and equilibrium constants at 298 K are

$$CO_2(g) = CO_2(aq)$$
$$K_{eq} = 10^{-1.43}$$
$$CO_2(aq) + H_2O = H^+(aq) + HCO_3^-(aq)$$
$$K_{eq} = 10^{-6.35}$$
$$HCO_3^-(aq) = H^+(aq) + CO_3^{2-}(aq)$$
$$K_{eq} = 10^{-10.33}$$
$$CaCO_3(s) = Ca^{2+}(aq) + CO_3^{2-}(aq)$$
$$K_{eq} = 10^{-8.34}$$

If this system of equations is solved using the constraints of mass balance, chemical equilibrium, and charge balance, the derived pH for the observed CO_2 partial pressure

TABLE 2. Physical Properties of Planetary Atmospheres[k]

Planet/Satellite	Surface Temperature (K)	Surface Pressure (Bars)	Surface Gravity (cm s^{-2})	Mean Mol. Wt. (g $mole^{-1}$)	Pressure Scale Height (km)[h]
Mercury[a]	590-725[i]	$<10^{-12}$	372	species dependent	species dependent
Venus[b]	737	95	887	43.45	15.9
Earth[c]	288	1.01	978	28.97	8.5
Mars[d]	215	~6.36 mbars	372	43.34	11.1
Jupiter[e]	165±5(1 bar)	adiabat P>1 bar	2312	2.22	27
Saturn[e]	134±4 (1 bar)	adiabat P>1 bar	896	2.07	59.5
Uranus[e]	76±2 (1 bar)	adiabat P>1 bar	869	2.64	27.7
Neptune[e]	71.5±2 (1 bar)	adiabat P>1 bar	1100	2.53-2.69	19.1-20.3
Pluto[f]	~50(?)	~3 μbars(?)	40(?)	~16-25(?)	~60
Titan[g]	94	1.5	135	~28.6	~20.2
Triton[j]	38±4	16±3μbars	78	~28(?)	~14.4(?)

[a]Values from [212].

[b]Values from [186].

[c]Values from [214].

[d]Values from [7]. The CO_2 pressure varies by about 37% due to the annual condensation into & sublimation out of the polar caps.

[e]Values for the temperatures at 1 bar and the equatorial surface gravity for the Jovian planets are from [135]. The Jovian planets do not have a solid surface. The observed P,T profiles are adiabatic below the tropopauses and the necessity to transport the observed heat fluxes out of the planets (except Uranus) requires adiabatic P,T profiles at lower levels below those directly probed by spacecraft. An adiabatic profile is also assumed in theoretical models of Uranus [175].

[f]Values from [108]. The lower value for the mean mol. wt. corresponds to a pure CH_4 atmosphere, the upper value is that chosen by [108].

[g]Values from [109].

[h]The pressure scale height values are either at the planetary surface or at the 1 bar level.

[i]Temperature of the sunward side of Mercury.

[j]Data from [29,95,211].

[k](?) indicates that the value is uncertain

(~ 0.34 mbars) is about 8.4. This is close to the value of ~ 8 observed in sea water.

The concentrations of the major conservative elements in sea water are controlled by a balance between riverine inputs and various loss processes For example, most Na and Cl are removed from the oceans in pore waters in ocean sediments, as sea spray, and as evaporites. Magnesium is mainly removed by hydrothermal exchange. Sulfur is depleted by the deposition of biogenic sediments (which also depletes Ca) and by hydrothermal exchange. Potassium is apparently removed by ion exchange with clay minerals to form illite and by some reactions with basalt, but its mass balance is not well understood.

2. COMPOSITION OF THE ATMOSPHERES OF THE EARTH AND OTHER PLANETS

This section presents physical and chemical data on the at-

mospheres of the Earth, the other planets, Titan, the largest satellite of Saturn, and Triton, the largest satellite of Neptune. The physical properties of the different planetary atmospheres are summarized in Table 2; their chemical and isotopic compositions are summarized in Tables 3-13. The data in these tables come from various sources. Compositional data on the terrestrial atmosphere are obtained from direct measurements at ground level, from balloons and high flying aircraft, ground-based spectroscopy, and satellite measurements. Earth-based remote sensing and *in situ* spacecraft measurements provide the data for the other planets, Titan, and Triton (e.g., see Hanel et al [98] for a review of infrared remote sensing techniques). Schematic P,T profiles for Venus, Earth, Mars, and Titan are illustrated in Figure 1 and those for the four Jovian planets are displayed in Figure 2. The properties of the different planetary atmospheres are discussed below in order of increasing radial distance from the Sun.

2.1 Mercury

The planet Mercury has a very tenuous atmosphere composed of atomic H, He, O, Na and K. Dayside number densities are 100 to 40,000 atoms cm^{-3} , about two orders of magnitude lower than the Mariner 10 radio occultation upper limit of $P < 10^{-12}$ bars. The atoms in the Mercurian atmosphere come from the solar wind (H, He) and from evaporation of meteoritic material (O, Na, K) impacting the surface. Recent descriptions of the properties of the Mercurian atmosphere are given in Vilas et al [212] and Sprague [192].

2.2 Venus

The chemical composition of the Venusian atmosphere and the probable sources and sinks for the gases in it are listed in Table 3. The isotopic composition of the Venusian atmosphere is summarized in Table 4. A comprehensive review of the chemistry and spectroscopy of the atmosphere of Venus is given by Von Zahn et al [213]. This has recently been updated by Fegley and Treiman [77].

The abundance of SO_2 (Table 3) decreases with increasing altitude above 48 km (the main cloud base) due to its photochemical conversion to H_2SO_4 droplets which make up the global cloud layer. At cloud top levels (~70 km) the SO_2 abundance is 100 ppb or less, and has been decreasing with time during the 1978-1992 period [154]. The water vapor abundance also decreases above the cloud base to typical values of a few ppm at cloud top levels [213]. As indicated in Table 3, the H_2O abundance is also altitude dependent in the sub-cloud atmosphere. It decreases from values of about 150 ppm at 42 km to values of about 20 ppm at the surface [60,153]. The cause(s) for this profile is/are controversial; formation of another hydrogen bearing gas or atmosphere-surface reactions may be involved. The ongoing controversy about the abundance and vertical profile of water vapor on Venus is discussed by Fegley and Treiman [77]. Data from the Pioneer Venus (PV) and Venera 11/12 spacecraft [87,149,172] also show an apparent decrease in the CO abundance with decreasing altitude. The Kr abundance given in Table 3 is also a subject of debate. Inconsistent Kr abundances were obtained by the PV Large Probe neutral mass spectrometer and the Venera

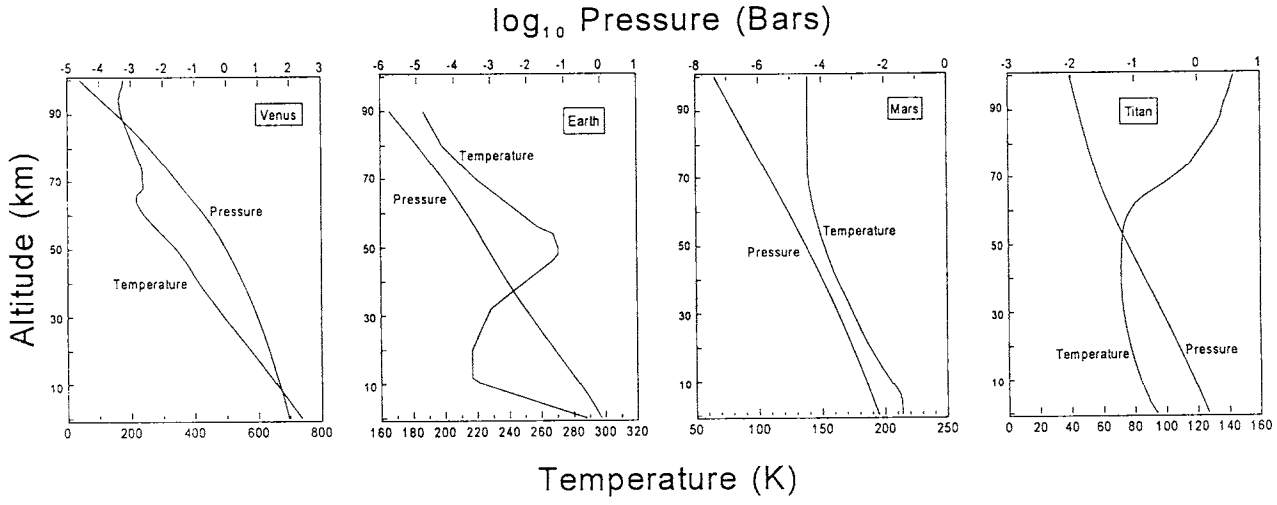

Fig. 1. Schematic P,T profiles for the atmospheres of Venus, Earth, Mars, and Titan. Data from Seiff (1983), Warneck (1988), Barth (1985), and Lindal et al (1983).

11/12 mass spectrometers [213]. The values given in Table 3 reflect Donahue's analysis of the PV data [59].

The isotopic ratios in Table 4 for C, N, O, Cl, and $^{36}Ar/^{38}Ar$ are identical to the terrestrial values within the uncertainties of the measurements. However, the isotopic ratios for D/H, $^{20}Ne/^{22}Ne$, and $^{40}Ar/^{36}Ar$ are not identical. The D/H ratio on Venus is about 100-120 times larger than the D/H ratio of the Earth as defined by standard mean ocean water (SMOW, see Table 6). The $^{20}Ne/^{22}Ne$ ratio is also larger and is closer to the assumed solar value [174]. The $^{40}Ar/^{36}Ar$ ratio is about 300 times smaller than the terrestrial value. No information is available on the $^{3}He/^{4}He$ ratio. The implications of the isotopic data for the origin and evolution of the atmosphere of Venus have been extensively discussed [134,174].

2.3 Earth

Table 5 summarizes the chemical composition of important constituents in the non-urban terrestrial troposphere, Figure 3 displays vertical abundance profiles for important minor and trace gases in the terrestrial stratosphere, and Table 6 summarizes the isotopic composition of the noble gases in the terrestrial atmosphere and of terrestrial standards for isotopic analysis of H, C, N, O, and Cl for comparison with data for other planetary atmospheres. Chamberlain and Hunten [33] summarize atmospheric chemistry, dynamics, and spectroscopy. Terrestrial atmospheric chemistry is summarized by Warneck [214]. The different chemical compounds found in the terrestrial atmosphere are tabulated by Graedel [90].

The terrestrial atmosphere is divided into several regions, primarily on the basis of temperature. The troposphere is the region closest to the surface where temperature decreases with altitude. The gradient (lapse rate) is about 6.5 K/km up to the tropopause, at about 12 km, where the mean temperature is about 216 K (see Figure 1). The region immediately above the tropopause is the stratosphere. In contrast to the troposphere which contains about 1-4 % water vapor by volume, the stratosphere is extremely dry due to the cold trap at the tropopause. The stratosphere is also characterized by a temperature increase with increasing altitude up to the stratopause (at about 50 km) where the temperature peaks. The temperature rise is due to absorption of solar ultraviolet radiation by O_3. The mesosphere, where temperature again decreases with altitude, lies between 50-80 km. The thermosphere where strong heating occurs due to absorption of solar UV radiation, leading to extensive photodissociation and photoionization of N_2 and O_2, is at about 80-100 km.

Important aspects of tropospheric chemistry include biogeochemical cycles such as those involving carbon, water,

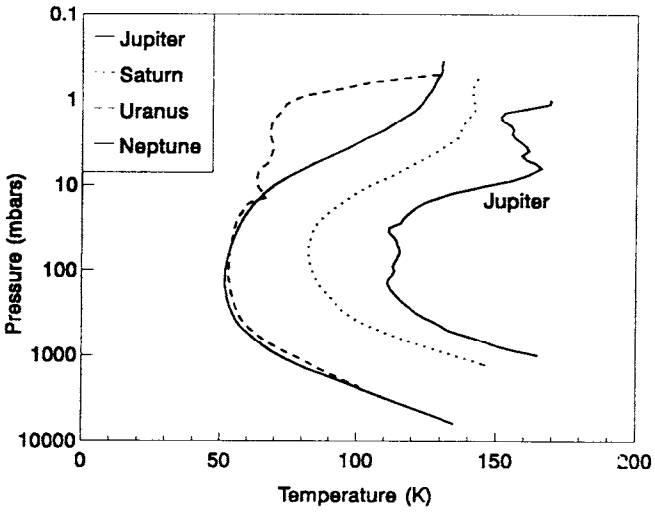

Fig. 2. Schematic P,T profiles based on Voyager radio occultation data for the atmospheres of the Jovian planets (Lindal 1992).

nitrogen, and sulfur and the production and destruction of various trace gases (e.g., CH_4, other hydrocarbons, SO_2, reduced sulfur gases, NO_x, O_3). Important greenhouse gases produced naturally or via human activity in the troposphere are CO_2, CH_4, N_2O, and the halocarbons. The OH radical plays an important role in the production and destruction of many trace gases as the major oxidizer in tropospheric chemistry. Hydroxyl radicals in the troposphere are produced from the photolysis of O_3 to produce electronically excited O atoms which subsequently react with H_2O to produce two OH radicals from each water molecule. The globally averaged mean OH concentration in the troposphere is about $10^{5.7}$ OH per cm^3.

Stratospheric chemistry is closely connected to the O_3 layer at 15-35 km, which both shields the Earth from biologically harmful solar UV radiation shorter than about 300 nm and also dissipates the absorbed radiation as heat. The O_3 distribution in the stratosphere is controlled by a balance between production and destruction and by the transport of O_3 from regions of net production to regions of net destruction. In the absence of other perturbing influences, the production and destruction of O_3 involves the four reactions of the Chapman cycle:

$$O_2 + h\nu(\lambda = 180 - 240nm) \rightarrow O +$$
$$O + O_2 + M \rightarrow O_3 + M$$
$$O_3 + h\nu(\lambda = 200 - 300nm) \rightarrow O_2 +$$
$$O + O_3 \rightarrow O_2 + O_2$$

This cycle is perturbed by the presence of other trace

TABLE 3. Chemical Composition of the Atmosphere of Venus

Gas	Abundance	Source(s)	Sink(s)	Notes & References
CO_2	96.5±0.8%	Outgassing	Carbonate formation	[213]
N_2	3.5±0.8%	Outgassing	---	[213]
SO_2[a]	185±43 ppm	Photochemistry &	H_2SO_4 formation &	22km, [172]
	130±35 ppm	Outgassing	$CaSO_4$ formation	<42 km, [87]
H_2O[a]	150 ppm	Outgassing	H escape &	42 km, [153]
	60 ppm		Fe^{2+} oxidation	22 km, [153]
	20 ppm			0 km, [153]
	40 ppm			35-45 km, [19]
Ar	70±25 ppm	Outgassing, primordial	---	[213]
CO[a]	45±10 ppm	CO_2 photolysis	Photooxidation	cloud top, [40]
	30±18 ppm			42 km, [172]
	20±3 ppm			22 km, [172]
	28±7 ppm			36-42 km, [87]
	17±1 ppm			12 km, [149]
	45 ppm			35-45 km, [19]
He	12^{+24}_{-8} ppm	Outgassing (U, Th)	---	[213]
Ne	7±3 ppm	Outgassing, primordial	---	[213]
H_2S[a]	3±2 ppm	Outgassing (FeS_2)	Conversion to SO_2	<20 km, [102]
HDO[a]	1.3±0.2 ppm	Outgassing	H escape	sub-cloud, [51]
HCl	0.6±0.12 ppm	Outgassing	Cl mineral formation	cloud top, [39]
	0.4 ppm			cloud top, [56]
	0.5 ppm			35-45 km, [19]
COS[a]	0.3 ppm	Outgassing (FeS_2)	Conversion to SO_2	35-45 km, [19]
Kr	~25 ppb	Outgassing, primordial	---	[61]
SO[a]	20±10 ppb	Photochemistry	Photochemistry	cloud top, [154]
S_{1-8}[a]	20 ppb	Outgassing	Conversion to SO_2	<50 km, [152]
HF	$5^{+5}_{-2.5}$ ppb	Outgassing	F mineral formation	cloud top, [39]
	4.5 ppb			35-45 km, [19]
Xe	~1.9 ppb	Outgassing, primordial	---	[59,174]

[a]Abundances of these species are altitude dependent. See [213] and [77] for detailed information.

TABLE 4. Isotopic Composition of the Atmosphere of Venus[a]

Isotopic Ratio	Observed Value	Notes & References
D/H	1.6±0.2 %	Pioneer Venus MS[b] [62]
	1.9±0.6 %	IR spectroscopy [51]
$^{12}C/^{13}C$	86±12	IR spectroscopy [18]
	88.3±1.6	Venera 11/12 MS [110]
$^{14}N/^{15}N$	273±56	Pioneer Venus MS [101]
$^{16}O/^{18}O$	500±25	Pioneer Venus MS [102]
	500±80	IR spectroscopy [18]
$^{20}Ne/^{22}Ne$	11.8±0.7	Pioneer Venus MS [59]
$^{35}Cl/^{37}Cl$	2.9±0.3	IR spectroscopy [39,219]
$^{36}Ar/^{38}Ar$	5.56±0.62	Pioneer Venus MS [59]
	5.08±0.05	Venera 11/12 MS [110]
$^{40}Ar/^{36}Ar$	1.03±0.04	Pioneer Venus MS [102]
	1.19±0.07	Venera 11/12 MS [110]

[a]No isotopic compositions are available for Kr and Xe on Venus.

[b]MS = Mass Spectrometer

gases, notably the oxides of Br, Cl, H, and N, which are involved in the gas phase catalytic destruction of O_3 in the stratosphere. These cycles are more rapid than the O_3 loss in the Chapman cycle and are the dominant O_3 loss processes. The gas phase catalytic cycles involving oxides of halogens are exemplified by the following reaction sequence:

$$Cl + O_3 \rightarrow ClO + O_2$$
$$\underline{ClO + O \rightarrow Cl + O_2}$$
$$O + O_3 \rightarrow 2O_2$$

The reactive halogens involved in these cycles come from photochemical destruction of halocarbon gases, such as CF_2Cl_2 and $CFCl_3$, which are anthropogenic emissions transported upward into the stratosphere. As shown in Table 5, the atmospheric concentrations of many halocarbon gases are increasing at the rate of several percent a year.

The HO_x and NO_x catalytic cycles for O_3 destruction are exemplified by the reaction sequences below:

$$OH + O_3 \rightarrow HO_2 + O_2$$
$$\underline{HO_2 + O_3 \rightarrow OH + 2O_2}$$
$$O_3 + O_3 \rightarrow 3O_2$$

$$O_3 + h\nu \rightarrow O + O_2$$
$$O + NO_2 \rightarrow O_2 + NO$$
$$\underline{NO + O_3 \rightarrow NO_2 + O_2}$$
$$O_3 + O_3 \rightarrow 3O_2$$

The major source of stratospheric OH is the reaction of $O(^1D)$ atoms with H_2O, which is either transported from the troposphere or produced via CH_4 oxidation in the stratosphere. At present, the major source of stratospheric NO_x is N_2O transported upward from the troposphere.

Recently (1985-1992) ozone depletions have been observed to occur in the Antarctic stratosphere during southern spring. These depletions are due to heterogeneous reactions on the surfaces of polar stratospheric clouds which convert relatively inert chlorine reservoir molecules such as $ClONO_2$ and HCl into highly reactive species such as HOCl, Cl_2, and $ClNO_2$, which release Cl-bearing radicals upon photolysis. These radicals then deplete ozone via gas phase catalytic cycles such as those illustrated above. The current status of ozone monitoring and of the apparent decreases at different geographic locations is reviewed by Stolarski et al [193].

The isotopic composition of the noble gases in the terrestrial atmosphere and of terrestrial standards for isotopic

TABLE 5. Chemical Composition of the Terrestrial Troposphere[a,b]

Gas	Abundance*	Source(s)	Sink(s)	Notes & References
N_2	78.084%	Denitrifying bacteria	Nitrogen fixing bacteria	[214]
O_2	20.946%	Photosynthesis	Respiration & decay	[214]
H_2O	<4%	Evaporation	Condensation	variable
Ar	9340 ppm	Outgassing (^{40}K)	---	[173]
CO_2	350 ppm	Combustion, biology	Biology	Keeling et al 1984
Ne	18.18 ppm	Outgassing	---	[173]
^4He	5.24 ppm	Outgassing (U, Th)	Escape	[173]
CH_4	1.7 ppm	Biology & agriculture	Reaction with OH	+1%/yr, [70]
Kr	1.14 ppm	Outgassing	---	[173]
H_2	0.55 ppm	H_2O Photolysis	H atom escape	[214]
N_2O	~320 ppb	Biology	Photolysis (stratosphere)	[214]
CO	125 ppb	Photochemistry	Photochemistry	[214]
Xe	87 ppb	Outgassing	---	[173]
O_3	~10-100 ppb	Photochemistry	Photochemistry	[214]
HCl	~1 ppb	Derived from sea salt	Rainout	[214]
Isoprene, etc.	~1-3 ppb	Foliar emissions	Photooxidation	[214]
C_2H_6, etc	~3-80 ppb	Combustion, biomass burning, grasslands	Photooxidation	[214]
H_2O_2	~0.3-3 ppb	Photochemistry	Photochemistry	[187]
C_2H_2, etc	~0.2-3 ppb	Combustion, biomass burning, oceans	Photooxidation	[214]
C_2H_4, etc	~0.1-6 ppb	Combustion, biomass burning, oceans	Photooxidation	[214]
C_6H_6 etc	~0.1-1 ppb	Anthropogenic	Photooxidation	[214]
NH_3	0.1-3 ppb	Biology	Wet & dry deposition	[214]
HNO_3	~0.04-4 ppb	Photochemistry (NO_x)	Rainout	[214]
CH_3Cl	612 ppt	Ocean, biomass burning	Reaction with OH	[176]
COS	500 ppt	Biology	Photodissociation	[214]
NO_x	~30-300 ppt	Combustion, biology	Photooxidation	[214]
CF_2Cl_2 (F12)	300 ppt	Anthropogenic	Photolysis (stratosphere)	+5.1%/yr, [176]
$CFCl_3$ (F11)	178 ppt	Anthropogenic	Photolysis (stratosphere)	+5.1%/yr, [176]
CH_3CCl_3	157 ppt	Anthropogenic	Reaction with OH	+4.4%/yr, [177]
CCl_4	121 ppt	Anthropogenic	Photolysis (stratosphere)	+1.3%/yr, [176]
CF_4 (F14)	69 ppt	Anthropogenic	Photolysis (upper atm.)	+2.0%/yr, [176]
$CHClF_2$ (F22)	59 ppt	Anthropogenic	Reaction with OH	+10.9%/yr, [176]
H_2S	30-100 ppt	Biology	Photooxidation	[214]
$C_2Cl_3F_3$ (F113)	30-40 ppt	Anthropogenic	Photolysis (stratosphere)	+11.5%/yr, [176]

TABLE 5. (continued).

Gas	Abundance*	Source(s)	Sink(s)	Notes & References
CH_2Cl_2	30 ppt	Anthropogenic	Reaction with OH	[214]
CH_2ClCH_2Cl	26 ppt	Anthropogenic	Reaction with OH	[214]
CH_3Br	22 ppt	Ocean, marine biota	Reaction with OH	[214]
SO_2	20-90 ppt	Combustion	Photooxidation	marine air, [214]
$CHCl_3$	16 ppt	Anthropogenic	Reaction with OH	[214]
CS_2	~15 ppt	Anthropogenic	Photooxidation	[214]
$C_2Cl_2F_4$ (F114)	14 ppt	Anthropogenic	Photolysis (stratosphere)	[214]
C_2H_5Cl	12 ppt	Anthropogenic	Reaction with OH	[214]
$CHClCCl_2$	7.5 ppt	Anthropogenic	Reaction with OH	[214]
$(CH_3)_2S$	5-60 ppt	Biology	Photooxidation	marine air, [214]
C_2ClF_5 (F115)	4 ppt	Anthropogenic	Photolysis (stratosphere)	[214]
C_2F_6 (F116)	4 ppt	Anthropogenic	Photolysis (upper atm)	[214]
$CClF_3$ (F13)	3.3 ppt	Anthropogenic	Photolysis (stratosphere)	[214]
CH_3I	~2 ppt	Ocean, marine biota	Photolysis (troposphere)	[214]
$CHCl_2F$ (F21)	1.6 ppt	Anthropogenic	Reaction with OH	[214]
$CClF_2Br$	1.2 ppt	Anthropogenic	Photolysis (stratosphere)	+20%/yr, [176]

[a]Abundances by volume in dry air

[b]Abbreviations: ppm = parts per million, ppb = parts per billion, ppt = parts per trillion

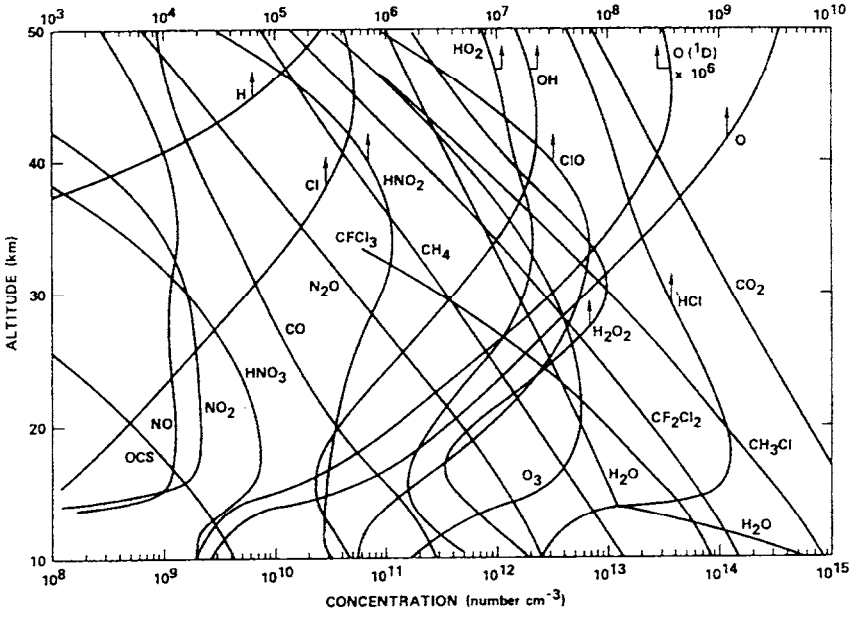

Fig. 3. Vertical concentration profiles for important minor and trace gases in the terrestrial stratosphere. Note the two different concentration scales. The total number density at 10 km altitude is $10^{18.9}$ and the total number density at 50 km altitude is $10^{16.3}$. From Turco (1985).

TABLE 6. Isotopic Composition of the Noble Gases in the Terrestrial Atmosphere and of Terrestrial Standards for Isotopic Analyses

Isotopic Ratio	Observed Value	Notes & References
D/H	$(1.5576\pm0.0005) \times 10^{-4}$	SMOW [96]
$^{3}He/^{4}He$	$(1.399\pm0.013) \times 10^{-6}$	[148]
$^{12}C/^{13}C$	89.01±0.38	[104]
$^{14}N/^{15}N$	272.0±0.3	air [113]
$^{16}O/^{17}O$	2681.80±1.72	SMOW [104]
$^{16}O/^{18}O$	498.71±0.25	SMOW [104]
$^{20}Ne/^{22}Ne$	9.800±0.080	[69]
$^{21}Ne/^{22}Ne$	$(2.899\pm0.025) \times 10^{-2}$	[69]
$^{35}Cl/^{37}Cl$	3.1273±0.1990	[104]
$^{36}Ar/^{38}Ar$	5.320±0.002	[155]
$^{40}Ar/^{36}Ar$	296.0±0.5	[155]
$^{78}Kr/^{84}Kr$	$(6.087\pm0.002) \times 10^{-3}$	[9]
$^{80}Kr/^{84}Kr$	3.960±0.002 %	[9]
$^{82}Kr/^{84}Kr$	20.217±0.021 %	[9]
$^{83}Kr/^{84}Kr$	20.136±0.021 %	[9]
$^{86}Kr/^{84}Kr$	30.524±0.025 %	[9]
$^{124}Xe/^{132}Xe$	$(3.537\pm0.0011) \times 10^{-3}$	[173]
$^{126}Xe/^{132}Xe$	$(3.300\pm0.017) \times 10^{-3}$	[173]
$^{128}Xe/^{132}Xe$	7.136±0.009 %	[173]
$^{129}Xe/^{132}Xe$	98.32±0.12 %	[173]
$^{130}Xe/^{132}Xe$	15.136±0.012 %	[173]
$^{131}Xe/^{132}Xe$	78.90±0.11 %	[173]
$^{134}Xe/^{132}Xe$	38.79±0.06 %	[173]
$^{136}Xe/^{132}Xe$	32.94±0.04 %	[173]

analysis are listed in Table 6. Atmospheric N_2 is the standard for nitrogen isotopes, but H, C, and O gases in the terrestrial atmosphere are isotopically fractionated relative to the standard isotopic ratios. Atmospheric O_2 is enriched in ^{18}O relative to SMOW, an effect which is believed to be due to biological activity. This is a mass fractionation effect. However, stratospheric O_3 is more enriched in $^{50}O_3$ than expected for mass fractionation. The exact nature of the enrichment (e.g., the symmetric or asymmetric form of $^{18}O^{16}O_2$) and its cause are currently debated [89,117]. The isotopic composition of the terrestrial atmosphere and possible mechanisms for explaining the observed fractionations are reviewed by Kaye [117]. The systematics of stable isotopes in precipitation are reviewed by Dansgaard [50].

2.4 Mars

Table 7 summarizes the chemical composition of the Martian atmosphere and the probable sources and sinks of the gases in it. Carbon dioxide, the dominant atmospheric constituent, annually condenses into and resublimes from the Martian polar caps. This process produces a global pressure change of about 37% relative to the global mean pressure of 6.36 mbars. As a consequence the mixing ratios, but not the column densities of the non-condensible gases are seasonally variable. The abundances of two other con-

TABLE 7. Chemical Composition of the Atmosphere of Mars[a]

Gas	Abundance	Source(s)	Sink(s)	Notes & References
CO_2	95.32%	Outgassing & evaporation	Condensation	[124,168]
N_2	2.7%	Outgassing	Escape as N	[168]
Ar	1.6%	Outgassing (^{40}K)	---	[168]
O_2	0.13%	CO_2 Photolysis	Photoreduction	[6,32,205]
CO	0.08%	CO_2 Photolysis	Photooxidation	[35,114,115]
H_2O[b]	~210 ppm	Evaporation & desorption	Condensation & adsorption	[112,116]
NO	~100 ppm	Photochemistry (N_2, CO_2)	Photochemistry	120 km, [156]
Ne	2.5 ppm	Outgassing, primordial	---	[168]
HDO	0.85±0.02 ppm	Evaporation & desorption	Condensation & adsorption	[27,170]
Kr	0.3 ppm	Outgassing, primordial	---	[168]
Xe	0.08 ppm	Outgassing, primordial	---	[168]
O_3[b]	~(0.04-0.2) ppm	Photochemistry (CO_2)	Photochemistry	[7,8]

[a]The mixing ratios, but not the column densities of non-condensible gases are seasonally variable due to the annual condensation and sublimation of CO_2.

[b]Spatially & temporally variable.

stituents, water vapor and O_3 are also observed to be variable. The average water vapor abundance observed by the Viking Mars Atmospheric Water Vapor Detector (MAWD) experiment is about 15 precipitable (ppt) μm (~210 ppm). The maximum observed value was about 90 ppt μm, and the lowest observed value was below the detection limit of 1 ppt μm [112]. Recent Earth-based microwave observations of the 1.35 cm water line gave a global average water vapor abundance of only 3±1 ppt μm during the 1990 northern winter [34]. This is about a factor of two lower that the Viking MAWD data during the 1977-78 northern winter. The O_3 abundance is highly variable. Ozone is present in cold and dry atmospheric regions, such as those found over the winter polar caps. It is absent in warmer, wetter regions, such as those over the polar caps in the summer [7]. The implications of the observed CO, O_2, and O_3 abundances for models of Martian atmospheric photochemistry are reviewed by Barth [7] and Lewis and Prinn [134].

Table 8 summarizes the isotopic composition of the Martian atmosphere. Only the $^{12}C/^{13}C$ ratio is terrestrial within measurement uncertainties. The observed D/H ratio is about 5 times higher than the terrestrial value as defined by SMOW. Mechanisms for producing the enhanced D/H ratio are discussed by Yung et al [221] and Jakosky [111]). The $^{14}N/^{15}N$ ratio is about 62% of the terrestrial value. Nonthermal escape processes which may have enriched ^{15}N on Mars have been discussed in several papers by Fox and Dalgarno (e.g., [82,83]). Earth-based IR spectroscopic measurements of the oxygen isotopic composition of Martian water vapor [27] show that the $^{16}O/^{17}O$ ratio is Earth-like but that the $^{16}O/^{18}O$ ratio is about 9% larger. A prior measurement of the $^{16}O/^{18}O$ ratio in Martian CO_2 gave a value identical, within the uncertainties, to that in SMOW [156]. In contrast to Venus where ^{40}Ar is depleted relative to the Earth, the $^{40}Ar/^{36}Ar$ ratio on Mars is about 10 times larger than the terrestrial value. The Martian $^{129}Xe/^{132}Xe$ ratio has also been measured and is about 2.5 times larger than the terrestrial value. Again, the reader is referred to Pepin [174] and Lewis and Prinn [134] for the implications of the noble gas isotopic data for the origin and evolution of the Martian atmosphere.

2.5 The Jovian Planets: Jupiter, Saturn, Uranus and Neptune

Compositional data for these four planets are summarized in Tables 9-11. Observed isotopic ratios are presented in Table 12. Their atmospheres are predominantly H_2 + He with minor amounts of all other gases. Schematic P,T profiles for the upper atmospheres of the Jovian planets are il-

TABLE 8. Isotopic Composition of the Atmosphere of Mars[a]

Isotopic Ratio	Observed Value	Notes & References
D/H	$(9\pm4) \times 10^{-4}$	IR spectroscopy, [170]
	$(7.8\pm0.3) \times 10^{-4}$	IR spectroscopy, [27]
$^{12}C/^{13}C$	90±5	Viking MS, [156]
$^{14}N/^{15}N$	170±15	Viking MS, [156]
$^{16}O/^{17}O$	2655±25	IR spectroscopy, [27]
$^{16}O/^{18}O$	490±25	Viking MS, [156]
	545±20	IR spectroscopy, [27]
$^{36}Ar/^{38}Ar$	5.5±1.5	Viking MS, [22]
$^{40}Ar/^{36}Ar$	3000±500	Viking MS, [168]
$^{129}Xe/^{132}Xe$	2.5^{+2}_{-1}	Viking MS, [168]

[a]Isotopic compositions inferred from measurements on different SNC meteorites are tabulated by [174]. However, only direct observations of the isotopic composition of the Martian atmosphere are listed here.

lustrated in Figure 2. These profiles are derived from radio wavelength observations by the Voyager spacecraft [135,136,138,139], which extend down to a few bars pressure. Observational data and theoretical models of the planetary interiors indicate that the atmospheric P,T profiles are adiabatic below the tropopause levels, which typically occur at 100 mb pressure.

The data in Tables 9-11 illustrate several important points. The observed He/H_2 ratios vary from planet to planet. The solar He/H_2 ratio (~13.6% atomic or ~27% by mass) is difficult to determine by direct observations of the Sun. Despite this uncertainty, He is clearly depleted in the atmosphere of Saturn, and may also be slightly depleted in the Jovian atmosphere. In contrast, Uranus apparently has a solar He/H_2 ratio and Neptune may have a He enrichment relative to the solar ratio. The compositional data also show that the elemental compositions of the atmospheres of Jupiter and Saturn are close to solar composition. However, both planets are slightly enriched in elements heavier than He. The apparent depletion of water vapor on Jupiter may be an exception to this trend or more plausibly, may be due to meteorological effects. The observations of the CH_4/H_2 ratio on Uranus and Neptune, and the higher mean densities of these two planets indicate that they have substantial heavy element enrichments.

The Earth-based and spacecraft spectroscopic observations show a wealth of species in the atmospheres of Jupiter and Saturn. Some of these, such as hydrocarbons, are produced by the photochemical destruction of CH_4 while others, such as CO, PH_3, GeH_4, and AsH_3, are mixed upward from the hot, deep atmospheres of these two planets. Isotopically substituted species such as HD, CH_3D, $^{13}CH_4$, and $^{15}NH_3$ are also observed. The D/H ratio on Jupiter and Saturn is about 2×10^{-5} and is similar to the primordial D/H ratio estimated from noble gases in meteorites [2]. The $^{12}C/^{13}C$ ratio obtained by Earth-based and spacecraft observations of CH_4, C_2H_2, and C_2H_6 ranges from 20-160. The reasons for this large range are unclear. However, an emerging consensus is that Jupiter has an Earth-like carbon isotope ratio. The $^{14}N/^{15}N$ ratio determined from observations of NH_3 is poorly constrained; the most recent observations apparently indicate a value only about half the terrestrial ratio. Less compositional diversity is observed on Uranus and Neptune, presumably because the observable regions of their atmospheres are substantially colder than the observable regions of the Jovian and Saturnian atmospheres.

2.6 Titan

Titan is the largest satellite of Saturn and possesses the most massive atmosphere of any satellite in the solar system. The chemical composition of its atmosphere is summarized in Table 13. The abundances of the major atmospheric constituents N_2, CH_4, and Ar are indirectly inferred from Voyager IRIS and radio occultation data that constrain the mean molecular weight of the atmosphere. The direct spectroscopic detection of N_2 at high altitudes by the Voyager UVS and of CH_4 by the Voyager IRIS do

TABLE 9. Chemical Composition of the Atmosphere of Jupiter

Gas	Abundance	Comments	References
H_2	89.8±2.0 %	Voyager IRIS & radio occultation result, many studies of the H_2 pressure-induced dipole and quadrupole lines and the ortho-para ratio	[36,41,52,53,72,86, 181,202]
He	10.2±2.0 %	Voyager IRIS & radio occultation	[41,86]
CH_4	$(3.0\pm1.0) \times 10^{-3}$	abundance ~4 × solar C/H_2 ratio [92], CH_4 photolyzed to hydrocarbons in stratosphere	[25,72,84,181,185]
NH_3	$(2.6\pm0.4) \times 10^{-4}$	abundance ~ solar N/H_2 ratio [91], NH_3 undergoes condensation & photolysis in the upper troposphere & stratosphere	[25,57,126,181,185, 218]
HD	28^{+30}_{-8} ppm	reevaluation for HD by [190]	[72,151,190,206,207]
$^{13}CH_4$	33 ppm	for $^{12}C/^{13}C$ ~ 90, Voyager data give ~ 160, but all other values are ~ 90	[38,45]
H_2O	30±20 ppm	refers to 6 bar level, drops to 4±1 ppm at 2-4 bar range, apparently depleted below solar O/H_2 ratio, see text	[25,26,126,131]
C_2H_6	5.8±1.5 ppm	abundance from [162], C_2H_6 is due to CH_4 photolysis in stratosphere, abundance varies with altitude and latitude	[37,119,120,123,162, 180,181,197-199]
$^{15}NH_3$	~2 ppm	$^{14}N/^{15}N$ ~ 125 from [64]	[64,73,198]
PH_3	0.7±0.1 ppm	due to vertical mixing from deep atmosphere, photolyzed in stratosphere	[25,65,67,126,130, 181]
C_2H_2	0.11±0.03 ppm	abundance of [162], C_2H_2 is due to CH_4 photolysis in stratosphere, abundance varies with altitude and latitude	[37,63,119,162,165, 180,181,197,199]
CH_3D	0.20±0.04 ppm	formed by D/H exchange of CH_4 + HD in the deep atmosphere	[11,12,25,65,126]
$^{13}CCH_6$	~ 58 ppb	for $^{12}C/^{13}C$ ~ 94 as reported	[215]
$^{13}CCH_2$	~10 ppb	for $C_2H_2/^{13}CCH_2$ ~ 10 as reported	[66]
C_2H_4	7±3 ppb	in N. polar auroral zone, 0.4 ppb in equatorial region	[119,121]
CH_3C_2H	2.5^{+2}_{-1} ppb	in N. polar auroral zone	[119]
HCN	2^{+2}_{-1} ppb	due to vertical mixing from deep atmosphere or photochemistry	[195]
C_6H_6	2^{+2}_{-1} ppb	in N. polar auroral zone	[119]
CO	1.6±0.3 ppb	due to vertical mixing from deep atmosphere	[10,13,25,129, 161]
GeH_4	$0.7^{+0.4}_{-0.2}$ ppb	due to vertical mixing from deep atmosphere, destroyed in stratosphere	[25, 65,81,126]
C_4H_2	0.3±0.2 ppb	midlatitude region	[88]

TABLE 9. (continued).

Gas	Abundance	Comments	References
AsH_3	0.22±0.11 ppb	due to vertical mixing from deep atmosphere, destroyed in stratosphere	[158,163]
H_3^+	---	in auroral regions	[23,68]
C_3H_8	<0.6 ppm	in N. polar auroral zone	[119]
H_2S	<40 ppb	upper limit from IR spectroscopy	[127]

TABLE 10. Chemical Composition of the Atmosphere of Saturn[a]

Gas	Abundance	Comments	References
H_2	96.3±2.4 %	abundance from Voyager IRIS & radio occultation results, many spectroscopic studies of the pressure-induced dipole and quadrupole lines of H_2, and the ortho-para ratio	[30,36,41,52,53, 202]
He	3.25±2.4 %	Voyager IRIS & radio occultation	[41]
CH_4	$4.5^{+2.4}_{-1.9} \times 10^{-3}$	abundance from Voyager IRIS is ~6 × solar C/H_2 ratio [92], CH_4 is photolyzed to hydrocarbons in stratosphere	[38,44,79,178]
NH_3	$(0.5\text{-}2.0) \times 10^{-4}$	abundance from Voyager IRIS is ~(0.2-1.0) × solar N/H_2 ratio[91], NH_3 undergoes condensation & photolysis in the upper troposphere & stratosphere	[44,57,80,178, 189,218]
HD	110±58 ppm	discovered on Saturn by[207]	[144]
$^{13}CH_4$	~51 ppm	$^{12}C/^{13}C \sim 89$	[38]
C_2H_6	7.0±1.5 ppm	abundance of [162], C_2H_6 is due to CH_4 photolysis in stratosphere, abundance varies with altitude and latitude	[24,44,162,196, 217]
PH_3	1.4±0.8 ppm	due to vertical mixing from deep atmosphere, photolyzed in stratosphere	[44,128,157,178]
CH_3D	0.39±0.25 ppm	formed by D/H exchange of CH_4 + HD in the deep atmosphere	[44,78,157]
C_2H_2	0.30±0.10 ppm	due to CH_4 photolysis in stratosphere	[44,162]
AsH_3	3±1 ppb	due to vertical mixing from deep atmosphere, destroyed in stratosphere	[20,157,163]
CO	1.0±0.3 ppb	due to vertical mixing from deep atmosphere, destroyed in upper atmosphere	[157,159]
GeH_4	0.4±0.4 ppb	due to vertical mixing from deep atmosphere, destroyed in stratosphere	[20,157,160]
C_3H_4	---	tentative detection, no abundance given	[97]
C_3H_8	---	tentative detection, no abundance given	[97]
H_2S[b]	<0.2 ppm	upper limit of 1 cm amagat	[171]

TABLE 10. (continued).

Gas	Abundance	Comments	References
H_2O[b]	<0.02 ppm	upper limit of 15 ppt μm	[128]
HCN[b]	<4 ppb	upper limit of 0.025 cm amagat	[195]
SiH_4[b]	<4 ppb	upper limit of 0.025 cm amagat	[128]

[a]Definitions: 1 ppt μm = 10^{-4} g cm^{-2} = 0.124 cm amagat. 1 amagat = 2.69×10^{19} molecules cm^{-3}.

[b]Converted to a mixing ratio using a H_2 column abundance of 70 km amagat from [201].

TABLE 11. Chemical Composition of the Atmospheres of Uranus and Neptune

Gas	Uranus	Neptune	Comments	References
H_2	~82.5±3.3%	~80±3.2 %	Voyager IRIS & radio occultation, by difference from sum of He + CH_4, many studies of the pressure-induced dipole & quadrupole lines and the ortho-para ratio	[5,16,36,42,43, 79,188,203]
He	15.2±3.3 %	19.0±3.2 %	Voyager IRIS & radio occultation	[42, 43]
CH_4	~2.3 %	~1-2 %	Uranus & Neptune CH_4 ~32 & ~14-28 × solar C/H_2 ratio [92], respectively, abundances from Voyager radio occultation data on lapse rate, abundance from vis/IR spectroscopy is 1-10 %	[4,5,7,15,138, 139,142,145]
HD	~148 ppm	~192 ppm	based on D/H ~ 9×10^{-5} for Uranus and D/H ~ 1.2×10^{-4} for Neptune, no reliable observations of HD lines on these planets according to[191]	[36,144,191,204]
CH_3D	~8.3 ppm	~12 ppm	based on $CH_3D/CH_4 = 3.6^{+3.6}_{-2.8} \times 10^{-4}$ [54] and 2.3 % CH_4 for Uranus and $CH_3D/CH_4 = 6^{+6}_{-4} \times 10^{-4}$ [54], and 2 % CH_4 for Neptune	[17,54]
C_2H_6	~1-20 ppb	$1.5^{+2.5}_{-0.5}$ ppm	due to CH_4 photolysis, abundance varies with height & latitude, Uranus abundance from Voyager is a few times 10^{-8}	[3,21,100,122, 166,167]
C_2H_2	~10 ppb	60^{+140}_{-40} ppb	due to CH_4 photolysis, abundance varies with height & latitude	[3,21,31,100,143, 166,167]
H_2S[a]	<0.8 ppm	<3 ppm	upper limits of 30 and 100 cm amagat on Uranus & Neptune	[79]
NH_3[a]	<100 ppb	<600 ppb	upper limit of 5 cm amagat on Uranus from IR spectroscopy, abundance varies with height and latitude and is larger at lower lev-	[58,79,93,94,103, 139]

TABLE 11. (continued).

Gas	Uranus	Neptune	Comments	References
			els, extensive microwave studies, Voyager radio occultation upper limit at 6 bar level on Neptune	
CO	<40 ppb	0.65±0.35 ppm	Uranus upper limit for stratosphere, present in troposphere & stratosphere of Neptune, abundances of Rosenqvist et al 1992	[150,183]
CH_3CN	---	<5 ppb	in stratosphere	[183]
HCN	<15 ppb	0.3±0.15 ppb	in stratosphere, abundances of Rosenqvist et al 1992	[150,183]
HC_3N	<0.8 ppb	<0.4 ppb	in stratosphere	[183]

[a]Converted to a mixing ratio using a H_2 column abundance of 400 km amagat from [79].

TABLE 12. Isotopic Ratios in the Atmospheres of the Outer Planets

Isotopic Ratio	Jupiter	Saturn	Uranus	Neptune	Notes
D/H	$(2.6\pm1.0) \times 10^{-5}$	$(1.7\pm1.0) \times 10^{-5}$	$9.0^{+9.0}_{-4.5} \times 10^{-5}$	$1.2^{+1.2}_{-0.8} \times 10^{-4}$	a
$^{12}C/^{13}C$	94±12	89^{+25}_{-18}			b
$^{14}N/^{15}N$	125^{+145}_{-75}				c

[a]D/H for Jupiter & Saturn from [76]; D/H for Uranus and Neptune from [17,54].

[b]The $^{12}C/^{13}C$ for Jupiter is from ^{13}C-ethane [215], other reported values for methane are 110±35 , 70^{+35}_{-15}, 89^{+12}_{-11}, and 160^{+40}_{-55}, [38,45] and 20^{+20}_{-10} [66] for C_2H_2. No data are available for Uranus & Neptune as of the time of writing (6/92).

[c]The $^{14}N/^{15}N$ for Jupiter is from [64], earlier work by [73,198] gave $^{14}N/^{15}N$ ~ terrestrial, within about a factor of 2. No data are available for Saturn, Uranus & Neptune as of the time of writing (6/92).

TABLE 13. Chemical Composition of the Atmosphere of Titan

Gas	Abundance	Comments	References
N_2	65-98 %	Abundance indirectly inferred from Voyager IRIS & radio occultation data that constrain mean mol. wt. of atmosphere, directly detected by Voyager UVS in upper atmosphere	[74,109,137]
Ar	≤25 %	Upper limit from deduced mean mol. wt. of atmosphere, UVS data show $Ar/N_2 < 6$ % at 3900 km	[28,109]
CH_4	2-10 %	Indirectly inferred from Voyager IRIS & radio occultation data, about 2% at tropopause	[74,97,137]
H_2	0.2%	Directly measured by Voyager IRIS, detected by Trafton 1972	[109,200]

TABLE 13. (continued).

Gas	Abundance	Comments	References
CO	60-150 ppm	From Earth-based IR spectroscopy	[109,141]
CH_3D	110^{+70}_{-60} ppm	Voyager IRIS measurements, gives D/H = $1.5^{+1.4}_{-0.5} \times 10^{-4}$	[47,55,118,169]
C_2H_6	13-20 ppm	Voyager IRIS measurements, uniformly mixed over disk	[46,48,97,125]
C_3H_8	0.5-4 ppm	Voyager IRIS measurements, uniformly mixed over disk	[46,48,109]
C_2H_2	2-5 ppm	Voyager IRIS measurements, uniformly mixed over disk	[46,48,97,125]
C_2H_4	0.09-3 ppm	Voyager IRIS measurements, polar/equatorial ratio ~30	[46,48,97,125]
HCN	0.2-2 ppm	Voyager IRIS measurements & Earth-based mm wavelength observations, polar/equatorial ratio ≤2 from Coustenis et al 1991	[46,48,125,194]
HC_3N	80-250 ppb	Voyager IRIS measurements, abundances in N. polar region, no detection in equatorial region	[46,48]
CH_3C_2H	4-60 ppb	Voyager IRIS measurements, polar/equatorial ratio ~2-5	[46,48,125,147]
C_4H_2	1-40 ppb	Voyager IRIS measurements, polar/equatorial ratio ~16	[46,48,125]
C_2N_2	5-16 ppb	Voyager IRIS measurements, abundances in N. polar region, no detection in equatorial region	[46,48]
CO_2	1.5-14 ppb	Voyager IRIS measurements, polar/equatorial ratio ~0.5	[46,48,109]

not provide constraints on their abundances in the lower atmosphere. Implications of the observed abundances for origin and evolution of Titan's atmosphere and for atmospheric photochemistry are reviewed by Hunten et al [109] and Yung et al [220].

2.7 Triton

Voyager observations of Triton during the August 1989 Neptune encounter showed that it has a thin atmosphere predominantly composed of N_2 containing about 100 ppm of CH_4 at the surface [29,211]. Voyager UVS data give an upper limit of about 1% for the CO/N_2 ratio in Triton's atmosphere. The observed surface temperature and pressure are 38±4 K and 16±3 μbars. Its low surface temperature makes Triton the coldest natural body in the solar system.

2.8 Pluto

The discovery of CH_4 absorption features in spectra of Pluto provided the first inconclusive evidence for an atmosphere. This was finally confirmed by stellar occultation observations made by several groups in 1988 [71,107]. The occultation data constrain the ratio of the temperature to the mean molecular weight, and thus derived atmospheric compositions are model dependent. In addition to CH_4, other plausible constituents are CO and/or N_2. Atmospheric models based on the occultation data are discussed in the papers cited above.

Acknowledgments. This work was supported by grants from the NASA Planetary Atmospheres and Origins of Solar Systems Programs.

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