Comparative Ecological Study of the Chemistry of the Planetary Atmospheres

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THE comparative study of planetary atmospheres has become a major topic in recent astronomical literature.^{8,9,11a,12,19a,20,21,22,28,30} Tt might be of considerable interest to view the planetary atmospheres also from a biological point of view. This has been done by the writer in former publications with regard to temperature.23,24† An attempt will be made in the following discussion to examine the chemistry of the planetary atmospheres from a biological point of view. This will enable us to differentiate between certain characteristic *ccological* types of atmospheres.

In comparing the planetary atmospheres as to their biological—or more precisely, ecological—qualities, it is logical to start with the earth's atmosphere as the one of reference.^{6,33} In addition, it is important to include in such a study the various stages in the historical development of this atmosphere.

The present-day atmosphere of the earth has a mass of $5.2 \ge 10^{21}$ gm. or 5.2 quadrillion metric tons. Of this air mass $1.2 \ge 10^{21}$ gm. is oxygen (O_2) ; $2.0 \ge 10^{18}$ gm. is carbon dioxide (CO_2) . The amount of water and water vapor in the total atmosphere is around $1.5 \ge 10^{19}$ gm. Here we ignore the inert gases, since only the

aforementioned components are those which give the atmosphere its biological characteristics. It is the free oxygen (O_2) which is the most suitable vardstick in an ecological classification of the planetary atmospheres. With oxygen, an atmosphere posseses actual or manifest oxidizing power.* The strong oxidizing power found in our atmosphere has been and still is the basis for the existence and development of higher plants, animals, and man. This oxidizing capability based on the presence of oxygen decreases with increasing altitude—a fact which has been the main topic of discussion for physical and physiological research ever since the air became a medium of transportation.1a,33 In addition to the actual oxidizing power, the atmosphere possesses a potential or latent oxidizing power, the explanation of which will be given later.

The chemical composition of our atmosphere was not always the same. Rather, it has undergone drastic

[†]See also the well-known books of P. Lowell, E. W. Maunder, H. S. Jones, G. de Vaucouleurs, and A. C. Clarke, concerning the possibility of life on other planets.

^{*}Monatomic oxygen (O) and triatomic oxygen (O₃, ozone), are ignored here, since biatomic oxygen (O₂) only is important in the process of biological oxidation.

The expressions "oxidizing and oxidized" and "reducing and reduced" condition of an atmosphere are used by H. Urey in his geochemical discussion of the historical development of the atmospheres. Confined to the biological temperature range, they may also be convenient terms for biological and aeromedical discussions like this. Oxidation and reduction are used here in their original conception. Oxidation: Union with oxygen or removal of hydrogen. Reduction: Union with hydrogen or removal of oxygen.

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	Main Components of the Terrestial Protoatmosphere and Atmosphere in Order of Abundance									
Protoatmosphere Atmosphere	H2 N2	He O2	Ne H2O	H2O A	NH3 CO2	CH₄	A			

TABLE I.

changes in the course of its development from the protoatmosphere to its present stage. These changes have been discussed in a most inspiring manner in the recently published books of Kuiper¹² and Urev.²⁸

The protoatmosphere of the earth is understood as that gaseous envelope which surrounded our planet during its developmental stage as a protoplanet, or protoearth. This stage embraced the range of time during which the accumulation of the solar dust and planetesimals into a planetary body was completed-or nearly completed-and finally the surface was formed into a semisolid to solid crust. It was at the time that the temperature approached its present-day level. This particular range of time can be estimated at about 2 to 2.5 billion years ago-near the turn from astronomical or pregeological time to geological time.

The protoatmosphere so defined showed a chemical composition very different from that of the present-day atmosphere.^{12,28} The principal components in the order of their abundance (according to Kuiper) can be seen in Table I.

Since this atmosphere contained mainly hydrogen and hydrogen compounds such as water, methane, and ammonia—but no oxygen or carbon dioxide—this type of atmosphere is a reducing and reduced atmosphere. It has no actual oxidizing power but contains potential or latent oxidizing power. This potential or latent oxidizing power is hidden in the water molecule.

According to Tammann²⁶ and Wild³⁴ the water molecules have been thermally decomposed into hydrogen and oxygen at the border zone of the protoatmosphere. According to Harteck and Jensen,⁷ Poole,¹⁸ and Suess,²⁵ they have been split by photodissociation.** The hydrogen escaped into space, and the oxygen remained. With the appearance of this initial oxygen the gaseous envelope of the earth attained actual oxidizing power. It became an oxidizing atmosphere. This started a new step in development. Ammonia (NH₃) was oxidized to free nitrogen (N_2) and water (H_2O) , and methane (CH_4) to carbon dioxide (CO_2) and water. In addition, large amounts of carbon dioxide were injected into the air by volcanic exhalations.

During this process of evolution, the atmosphere represented a mixed medium with both reduced and oxidized compounds. It was a suboxidized atmosphere with a high potential and, to some extent with an actual, oxidizing However, the development power. continued in the direction of a highly oxidized atmosphere. This process was accelerated by the appearance of chlorophyll.⁵ If this molecule is present, the combination of water plus carbon dioxide offers a new possibility for producing oxygen, if sunlight is adequate. The process in question is photosynthesis. The oxygen produced in this process oxidized most of the reduced compounds, and was accumulated in rather large amounts—such as

^{**}Chemical processes of this and other kind are still going on in some areas of the present-day upper atmosphere for which Kaplan¹¹ recently coined the term "chemosphere."

those observed today in our atmosphere. Thus the present-day atmosphere is a gaseous mixture still with a high potential oxidizing power as well as a strong actual one. With chlorophyll present, the high potential oxidizing power is based on the inexhaustible amounts of water in the oceans $(1.4 \times 10^{24} \text{ gm.})$ and on the large supply of carbon dioxide.

Concluding this part of the discussion, it might be of interest to note that in the transformation of the protoatmosphere to the present-day atmosphere, with regard to the molecular weight, the chemical components have shifted from lighter to heavier ones. For more detail see Kuiper.¹²

Summarizing, we find in the historical development of the terrestrial atmosphere three types of atmospheres:

I. A reducing and reduced atmosphere with a potential but no actual oxidizing power—a nonoxidizing atmosphere. In this anoxic atmosphere, which was found in the early phase of the protoatmosphere, organisms are hardly conceivable. If, however, organic compounds like amino acids, et cetera, were produced by solar radiation^{3,15,17,28} with some CO₂ available, anoxibionts could have existed in this primitive atmosphere.

II. A *transitional stage* in the form of a partly reduced and partly oxidized atmosphere, with potential and increasing actual oxidizing power. In this stage of the protoatmosphere, chemoautotrophs (iron, sulfur, and ammonia bacteria) and photoautotrophs (chlorophyll-bearing organisms of lower order) could have existed.

III. A highly oxidized atmosphere with strong actual oxidizing and high OCTOBER, 1953 potential oxidizing power. This type of atmosphere, which we observe today, provided the basis for the development of higher plants, animals, and man.

This survey of the chemical characteristics of the earth's atmosphere during its development from the protoatmosphere to the present-day atmosphere (or neoatmosphere) facilitates the understanding of those of the other planets.^{10,12,14,22,28,34}

A decisive factor in the chemistry of a planetary atmosphere is the distance from the sun and the resulting intensity of radiation. As mentioned earlier, radiation causes photochemical reactions, especially at the border zone of the atmosphere. Another factor in the evolution of an atmosphere is the escape of the molecules into space. This phenomenon is dependent upon the temperature and mass of the planet.

In the following we shall consider the planets—not with increasing distance, as is usually done—but rather with decreasing distance from the sun, since this sequence conforms better with the foregoing discussion concerning the historical development of the terrestrial atmosphere.

Table II shows the main chemical components of the *planetary atmospheres* in the order of their abundance. Since the distance from the sun and the resulting solar constants and temperatures have a great influence on the chemical composition, their respective values are added.

Approaching the solar system from the outside, we first encounter Pluto, the outermost planet. Considering the solar constant, Pluto receives, per square unit, only 1,600th the amount of heat which the earth receives. The maximum temperature on Pluto is around 60° K. (about -210° C.). The chemical composition is not known.

to -140° C., less ammonia would be frozen and more would exist in the form of vapor.

The atmospheres of the larger plan-

Planet	I Solar Constant (Earth—1)	II* Maximum Temperature (°K)	III** Most Important Probable Atmospheric Components in Order of Abundance				
Pluto Neptune Uranus Saturn Jupiter Mars Earth Venus Mercury	$\begin{array}{c} \hline 1/1600\\ 1/900\\ 1/400\\ 1/100\\ 1/100\\ 1/25\\ 3/7\\ 1\\ 2\\ 6 \end{array}$	$\begin{array}{r} 60\\ 56\\ 69\\ 107\\ 145\\ 307\\ 349\\ 324\\ 625\\ \end{array}$	H2 H2 H2 H2 H2 N2? N2? N2?	He He He He A? O ₂ CO ₂	(CH4) CH4 CH4 CH4 CH4 CO2 H2O	(NH3) (NH3) NH3 NH3 H2O A	(H ₂ O) (H ₂ O) (H ₂ O) (H ₂ O) CO ₂

TABLE II. COMPONENTS OF THE PLANETARY ATMOSPHERES

*According to Kuiper (12) **According to Hess (9), Kuiper (12), and Urey (28). () Probably present in a frozen state only.

It is assumed that it consists of hydrogen, helium, and methane.

Neptune, Uranus, Saturn, and Jupiter can be considered here as a group. The atmosphere of these larger planets consist mainly of hydrogen, helium, methane, ammonia, and probably wa-The similarity of this compositer. tion to that of the protoatmosphere of the earth is striking. Apparently, escape of these light components has been prevented because of the strong gravitational forces of these planets. They seem to be preserved in a frozen state because of their greater distance from the sun.

Table II shows no ammonia vapor in the more distant planets Uranus and Neptune. This has been explained with the different freezing points of ammonia (-77° C.) and of methane (-184° C.).^{10,12,26} At the extremely low temperatures on Neptune and Uranus, only traces of ammonia exist as vapor. Their atmospheres are relatively strong in gaseous methane. On Saturn, with a temperature of about -165° C., and on Jupiter with -130 ets (and Pluto) containing hydrogen and hydrogen compounds are reduced atmospheres. They have no actual oxidizing power since there is no oxygen. They may have latent oxidizing power, if water (frozen) is found in some layers. Because of the great distance from the sun, however, it is questionable if this potential power will ever be released. For this reason, none of these planets offer a suitable ecological environment for any known kind of organism. The atmospheres are comparable to the terrestrial protoatmosphere in its early phase. In addition to this chemical point of view, the temperature of this entire group of planets is so low that active life is prohibited.

The main constituents in the Martian atmosphere are probably nitrogen and argon.9,12,23,28,29 The amount of CO₂ is higher than on earth.¹² Water is present in very small amounts, mainly in the form of ice and vapor.12 This atmosphere is qualitatively similar to that of the earth, except that it contains no oxygen or only traces of

		Chemical Characteristics	Oxidizing Power	Biological Oxvgen Condition*	Planet	
I. Hydrogen atmosphere	Hydrogen Hydrogen compounds	Reduced atmosphere	Potential oxidizing power; no actual oxidizing power.	Anoxie	Outer planets; protoatmosphero of earth, early phase	
II. Hydrogen oxygen atmosphere	Hydrogen Hydrogen compounds Oxides Oxygen	Transitional atmosphere (partly reduced and partly oxi- dized)	Potential and increas- ing actual oxidizing power	Hypoxic	Protoatmosphere of earth, later phase	
III. Oxygen atmosphere	Oxygen Oxides Hydrogen	Highly oxidized	High actual and high potential oxidizing power	Normoxic	Present day atmosphere of Earth	
IV. Carbon Dioxide water-vapor atmosphere	compounds Oxides Hydrogen compounds	Highly oxidized	Low potential oxidiz- ing power; low or no actual oxidizing power	Hypoxic or Anoxic	Mais	
V. Carbon dioxide atmosphere	Oxides	Highly oxidized	No potential oxidiz- ing power; no actual oxidizing power	Anoxic	Venus	

TABLE III. ECOLOGICAL TYPES OF ATMOSPHERES OF THE PLANETARY SYSTEM

*Anoxia: no oxygen at all.

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it. Quantitatively, it is comparable to the upper terrestrial atmosphere above the eleven-mile level. During its evolution it lost most of its atmosphere because of its low gravitational force. Not only hydrogen but also oxygen might have escaped from proto-Mars. The Martian atmosphere is an oxidized atmosphere with low potential oxidizing power. This may be sufficient to permit the existence of vegetation of lower order.^{12,14} The actual oxidizing power may be very weak or nonexistent, depending on the presence or absence of free oxygen.

Venus probably contains nitrogen and carbon dioxide-the latter in large amounts-but no water or oxygen.^{9,12,28} The Venusian atmosphere is a completely oxidized atmosphere. If it does not contain water and oxygen,12 it has, therefore, no potential or actual oxidizing power.† This being true, it could not support any kind of life. However, this point is still

a matter of astronomical dispute.

We find a type of atmosphere resembling that of Venus in volcanic fumaroles, which are little craters, where carbon dioxide has escaped from the interior of the earth and has displaced the air on the ground, because of its heavier weight. Such places are the Grotto del Cane at Puzzuoli near Naples; the Moffettes (vents in the last stages of volcanic activity) on the eastern shore of Lake Laach in the Rhineland and the Death Valley on the Dieng Plateau in Java. These places are closed to animal life on account of their carbon dioxide atmospheres. Bodies of birds and mice are sometimes found in these areas. They died when they ventured into this toxic air.1,15a

Table III gives a summary on the types of planetary atmospheres as they must be considered from a biological point of view. The first type (protoatmosphere and outer planets) is essentially a hydrogen atmosphere. The second type (transitional atmosphere) may be a hydrogen-oxygen atmosphere.

[†]This is true, if we ignore CO_2 as a possible source of oxygen, as Arrhenius² suggested.

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The third type (present-day atmosphere of the earth) must be characterized as an oxygen atmosphere. The fourth type (Mars) is a carbon dithan the inner planets insofar as their atmospheric metabolic life cycle is concerned.

In conclusion, as previously men-

			TAB	LE IV	•					
Planet	The Main Components of Planetary Atmospheres In the Order of Their Molecular Weight									
	H ₂ 2	He 4	CH4 16	NH3 17	H2O 18	N 2 28	02 32	A 40	CO2 44	
Pluto Neptune Uranus Saturn	* * * *	* *	* * *	(*) (*) *	(*) (*) (*)					
Jupiter Belt of Asteroids Mars Earth Venus Mercury		7			(*) * *	* * *	*	*	*	

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(*) Probably present in a frozen state only.

oxide-water vapor atmosphere, and the fifth type is a carbon dioxide atmosphere. The classification may be somewhat artificial. However, by and large, it complies essentially with astronomical considerations, as well as with biological ones. It clarifies the ecological qualities of the planetary atmospheres insofar as their chemistry is concerned. In particular, it demonstrates clearly the position of the terrestrial atmosphere.

In aeromedical parlance, with the the atmosphere exception of of earth, all planetary atmospheres are anoxic or hypoxic atmospheres. Those of the larger planets are still primarily anoxic; those of Mars and Venus may be already secondarily hypoxic or anoxic. Therefore, despite the probability that, according to the theory of von Weizsaeker,32 Ter Haar,27 Kuiper,12 and Urey,28 all planets originated about the same time and therefore have the same age, chronologically, the outer planets are younger tioned with regard to the development of the terrestrial atmosphere, the consideration of the molecular weight of the chemical components of the present-day planetary atmosphere is of interest. Table IV shows these components in the order of their molecular weight. It indicates that they shift from lighter molecular weight to heavier compounds with decreasing distance from the sun. This has, as previously mentioned, some relation to escape into space, which is dependent upon the temperature and gravitational force of the planet.

The space shown in Table IV between Mars and Jupiter represents the belt of asteroids. If these asteroids have originated from a former planet -the so-called "Meteorite" planetfrom this table we could conclude the probable chemical composition of the atmosphere and the possibility of life on this perished Atlantis in the solar system. If this planet existed today, it might perhaps show the transitional type of atmosphere (type II). But it is also possible that disturbances by the gravitational field of Jupiter, or

^{*}One astronomical unit is equal to the distance between the sun and earth (93,-000,000 miles).

physical properties of the accumulating material (coagulating effect of frozen water,28) prevented the planetisimals from forming a planet.

At this point a brief remark about the comets seems appropriate. According to a new comet model suggested by Whipple³¹ the cometary nucleus is visualized as a conglomerate of lumps of meteoritic material held together by various ices such as water, ammonia, methane and other materials, all initially at extremely low temperatures (250° K.). The place of origin of the comets is probably beyond the planetary system.

Basically, the volatile components of Whipple's "ices" are nearly the same as the chemical components of the protoatmosphere of earth and the present-day atmospheres of the outer planets. If a comet approaches closer than three astronomical units* to the sun. the frozen ammonia, methane, and water evaporate and under the effect of solar radiation similar photochemical reactions take place as they did in the primitive atmospheres of the inner planets. By photodissociation and photoionization from the aforementioned (not observed) hydrogen compounds as parent molecules, substances like OH, NH, CN, CO, et cetera, which have been observed spectroscopically in tail or head, are produced.

In this way the comets undergo periodically, in a matter of months or vears, almost the same process which took place in the atmospheres of the primitive inner planets over a period of hundreds of millions of years. At the same time these ice mountains in space, during one revolution lose about 1/2000th of their mass. After several hundreds of such photochemical events during perihelion the comets disintegrate and disappear foreverlike the Biela Comet in 1846.

Showers of *meteorites* are assumed to be the remnants of disintegrated comets.13,16 Among the gases found in heated meteorite powder¹⁰ are vapors of hydrogen, carbon monoxide, carbon dioxide, nitrogen, and methane-again a combination of compounds which are similar to those found in types I and II of the above-described ecological classification of the planetary atmospheres of the solar system.

The purpose of this paper is to broaden the basis of our thinking in the aeromedical field. Its preparation was possible, however, only because the author could rely upon the extraordinary progress made in astrophysics and geochemistry, as referred to in the attached list of books and papers.

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^{*}One astronomical unit is equal to the distance between the sun and earth (93,-000,000 miles).

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