

## PROPERTIES OF ATMOSPHERIC WATER

**G.N. Panin**

*Institute of Water Problems, Russian Academy of Sciences, Moscow, Russia*

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### Summary

The present article gives a brief overview of the physical, chemical, and biological properties of the atmosphere, including the three phases of water, and the global variations of atmospheric water. Information on the principal geophysical processes in the atmosphere, and a list of atmosphere physical parameters as well as atmospheric composition characteristics are offered, together with their typical and extreme values. The present model schemes of synoptic processes, atmospheric aerosol, clouds and weather phenomena are given. This information contains descriptions of cloud structure; general physical and statistical laws including those about the atmosphere and atmospheric aerosols, and cloud thermodynamics—their amount, repetition, phasal condition, water content, crystalline phase in cloud, precipitation particles, etc. Optical and radiational properties of clouds as well as ice formation conditions, ice precipitation and artificial modification of precipitation are also given here.

The article provides a brief overview of molecular properties and chemical fate of individual water molecules. Particular attention is paid to the aggregation of water molecules to form small hydrogen-bonded associates or clusters. The latter are extensively studied nowadays in laboratory controlled conditions by virtue of sophisticated spectroscopic tools. The role of a number of these minor water aggregates in atmospheric processes is still a matter of discussions. There is no doubt, however, that the water molecules in dual interaction with molecular perturbers plays a key role in the transmission of short-wave radiation through the atmosphere. Also minor neutral and ion clusters are of importance for the atmospheric photochemistry, nucleation processes, and cloud physics and chemistry. Aqueous and solid water particles of larger size play an inestimable role in various atmospheric processes since these are major constituents of aerosol, haze, fog and precipitation. Heterogeneous chemistry carried out on the surface of condensed water particles is recognized to be of great value for stratospheric photochemistry. The rates of reactions increase significantly when the reactants are stuck to the surface of tiny water droplets and ice crystals. To understand molecular mechanisms which govern aqueous and surface chemistry in particles and drops it is necessary to possess reliable knowledge of elementary pair-wise and many-body interactions of the individual water molecules. To achieve this goal the consideration and modeling of small water clusters is inestimable. This will allow unambiguous incorporation of the concept of interacting water molecules in a variety of atmospheric models.

Additionally, the article elucidates the feedback role in the climate system and shows that water vapor temperature rise is followed by an increase in global surface temperatures which leads to enhanced evaporation of water vapor from the oceans, thus cooling the atmosphere. Because water vapor is the most important of the greenhouse gases, an increase in its atmospheric concentration amplifies climate warming. It should be pointed out that the environments of the Earth and especially the atmosphere have

always been subject to change but that at present the changes are occurring at a rate far faster than any in history.

Finally, the Caspian Sea is given as an example of a local climate change. These results are interesting because they show that local climate changes have already taken place. They prove that modern global climate models (GCM) may be successfully used not only for prediction of global climate changes but also for local climate change.

The article is intended for specialists in different fields of science and technology, those engaged in design and assessment of conditions for operation of various technical systems in the atmosphere as well as for hydrometeorologists, both graduate and post graduate.

## 1. Introduction

The atmosphere is a gaseous envelope surrounding the Earth, held by gravity, with its maximum density just above the solid surface. It becomes gradually thinner with distance from the ground, until it finally becomes indistinguishable from the interplanetary gas.

There is no distinct upper limit of the atmosphere. Starting from the surface of the Earth, various regions can be defined with widely different properties, showing a great variety of physical and chemical phenomena. It is known, that atmospheric mass varies according to the distance from the earth. It is also known that 90% of the mass is contained within the first 20 km (top at 100mb level), and that 99.9% of the mass is contained within the first 50km (top at 1mb level). The atmosphere has a practically constant mass, which is about  $5.157 \cdot 10^{15}$  T (compared with the mass of the Earth at  $5.98 \cdot 10^{21}$  T). The atmosphere is vertically divided into layers which are verified according to different classifications to separate regions based on their temperature distribution, chemical composition, electron density, etc. The classification based on temperature distribution is particularly important.

Starting from the ground and up to a certain height, the temperature normally increases at a rate of 5 to 7 degrees per km. This is a variable with time and place, and occasionally there are even shallow layers within which the temperature increases with height—the so-called inversions. The region under consideration is called the troposphere and it is the seat of the weather phenomena that affects the ground. It is also, for obvious reasons, the best known region and it contains about 4/5 of the total air mass. Its upper limit is defined by a sudden change in the temperature trend, often appearing as a discontinuity in the curve: the temperature stops decreasing more or less suddenly and remains constant or starts increasing slightly. This limit is called the tropopause and its height, also depends on time and place (being larger at the Equator than at the Poles), and can vary between 7 and 17 km. The temperature at the tropopause in middle latitudes is  $-50$  to  $-55$  °C.

The next region shows a gradual increase of temperature, reaching a maximum of around 0 °C at 50 km. The region is called the stratosphere and its upper limit (at the maximum temperature), the stratopause. Then the temperature drops again through the region called the mesosphere, to a minimum of the order of  $-100$  °C, defining the

mesopause, at about 85 km. From there on the temperature increases steadily and the region is called the thermosphere. The temperature there reaches high values and then remains constant; at 500 km it may reach values between 400 and 2000 °C, depending on the time of the day, degree of solar activity and latitude. The diurnal variation is 500 to 800 °C, with minimum near sunrise and maximum at about 2 p.m.

The physical reasons for this peculiar distribution of temperature in the atmosphere are related to the absorption of radiation. Reactions of ionization and dissociation occur in the upper levels, producing the high temperatures of the thermosphere. The maximum at the stratopause is associated with the presence of ozone. The ground is again normally at a maximum temperature, due to the absorption at the surface of a large fraction of the solar energy that reaches that level.

The atmosphere contains about  $1.3 \cdot 10^4 \text{ km}^3$  (2.53 cm conditionally sedimentary layer) or 0.0001% of the total natural water resources on the Earth (Atmosphere Handbook, 1991). Despite the relatively small moisture content in the atmosphere, it is the only source of fresh water regeneration in nature (through evaporation) and the main source of water reserve replenishment (through precipitation). The total evaporation from the ocean surface and continents amounts to  $577\,000 \text{ km}^3$  per year; it consumes on average  $88 \text{ Wt/m}^2$  of heat that amounts to more than a third of the solar energy supply of the Earth. Atmospheric water, changing from one state into another, participates in water circulation in nature. All the  $577\,000 \text{ km}^3$  precipitates on the Earth, creating the Earth's water circulation. Meridional water vapor transfer is a significant peculiarity of water circulation.

There are three forms of water existing on the Earth—liquid, solid and gaseous or vapor. The atmosphere is the only blanket coating of the planet containing water in three aggregate states (gaseous, solid, and liquid). Different phase water conversions always occur in the atmosphere, the most important being processes of evaporation and condensation accompanied by absorption and the liberation of huge amounts of heat.

Water vapor in a unit volume does not exceed a certain value, corresponding to a saturation state. Moisture is always below 100% and water vapor is a small, but very important component of the atmosphere (MGS). Here all the thermodynamic processes occur similarly to those in dry air. If vapor pressure reaches the value corresponding to saturation, then vapor condensation occurs and drops form. These are always available in the atmosphere and serves as condensation nuclei. The phase conversions of water vapor-water and water vapor-ice occur when pressure of the available water vapor becomes more than that of vapor, saturated under this temperature over water and over ice correspondingly.

Air under a high temperature (for instance, in low latitudes or near the surface of ocean or land) can contain a large amount of water vapor. Thus, wet air transport from warmer areas of low latitudes to higher ones, or from lower layers upward, provides for cooling, vapor condensation and the liberation of vast reserves of condensation latent heat.

Condensation nuclei (CN) availability should provide for condensation. Soluble CN are either particles of marine salt in splashes, occurring on the wave crests under a heavy

wind, or particles, formed out of atmospheric gases. Dust particles of different origin and other atmosphere pollutants, for instance, some bacteria, and etc. belong to insoluble nuclei. CN are subdivided into the following types: 1) small CN or Aitken nuclei with a radius of 0.005-0.2 Mkm; 2) cloud CN with a radius of 0.2-1 mkm, active in the main cloud processes; 3) giant CN with a radius of more than 1 mkm, most often these are marine salt particles. Most CN are complex. CN are removed out of the atmosphere due to the already described water vapor condensation process, and besides, due to Brownian coagulation, reducing the number of the smallest CN, and, as a result, of capturing and washing them out by particles precipitation, i.e. rain drops and, particularly, big snow flakes, thus purifying the air. It causes a large amount of sulfate, nitrate, calcium and potassium ions in the water of precipitation. Sedimentation (precipitation) of CN is very slow and thus its effect on concentration is insignificant. It is substantial only for big dust particles.

There are also ice nuclei (IN), or the so-called nuclei of freezing or sublimation, in the atmosphere. They can initiate freezing of previously formed overcooled drops under relatively low temperatures, and also forming of ice crystals out of vapor (sublimation). Ice nuclei (ice particles) can be formed under the break-up of large crystals (snowflakes).

The Mechanisms of IN can be as follows: 1) vapor can sublimate directly on them resulting in snowflake formation; 2) being inside available drops, IN cause their freezing under the temperatures of IN activation; 3) IN can initiate drop freezing by capturing them. A transition from liquid phase into a solid provides for a quick growth of ice. Snowflakes can also grow until they fall out, if there are overcooled drops in the vicinity.

Water is among the most abundant molecular species in nature. Water molecules are ubiquitous in the universe: the spectroscopic signatures of water are found in the spectra of the sunspots, in the interstellar media, in environments of comets, and, of course, in the planetary atmospheres. Although water in the atmosphere represents only minor admixture to more abundant constituents, the role played by water molecules in atmospheric processes is inestimable. Primarily this concerns radiative properties of the Earth's atmosphere, since the water vapor is recognized among the principal absorbers of radiation in the atmosphere. Atmospheric chemistry and photochemistry are also strongly affected by the presence of water. The water molecule gives rise to a good deal of members of the atmospheric water family, which extends from the separate hydrogen and oxygen atoms to condensed phase, i.e. liquid water and ice. Products of both fragmentation and aggregation of atmospheric water are of particular importance for the organic life on Earth. The detachment of the hydrogen atom from the water molecule is possible under the action of short-wave UV radiation (with  $\lambda$  shorter than 242 nm). Direct photolysis of water happens readily only in the upper atmosphere, since at lower altitudes UV-radiation is strongly depleted by the oxygen (Herzberg absorption). Consequently, the chemical decomposition and transformations of H<sub>2</sub>O prevail below 50 km. The aggregation of water occurs mainly in the troposphere where partial density of the water vapor is significant. This aggregation is due to very weak intermolecular forces arising at close distance between water-water and water-foreign gas molecules. The so-called hydrogen bonding is among the key features characterizing the interaction

of water molecules. Interestingly, the hydrogen bonding is a cornerstone of organic life in general, since a multiplicity of hydrogen bonds is responsible for unique rearrangements in complicated nucleotic acids and bases. The present survey concentrates mainly on the water species built up from several individual water molecules (monomers). Water aggregates may have no definite structure in a common sense. In other words these molecular species being loosely bound result in significant distortion of their structure as a function of thermal excitation. Broad distribution over geometric and energetic characteristics is appropriate to these species at ambient temperature. That is why the detailed study of the complete potential energy surface is of crucial importance for the modeling of the water molecule in interaction with other molecular or particulate atmospheric species. Prior to the consideration of the water aggregates, the basic properties of isolated water monomers seem worthy of characterizing.

## **2. Physical Properties including the Three States of Water**

There are three forms of water existing on the Earth—liquid, solid and gaseous and vapor. Atmosphere is the only blanket coating of the planet containing water in three aggregate states (gaseous, solid, and liquid). Phase conversions in atmospheric water are continuously occurring, the most important being processes of evaporation and condensation, accompanied by absorption and liberation of huge amounts of heat.

### **2.1. Water Substance**

The cycle of water substance is linked to very important processes in the atmosphere:

1. The condensation and evaporation of water have important consequences for the thermodynamics of atmospheric processes and for the vertical stability of the atmosphere.
2. The water substance is, of course, essential in the formation of clouds and development of precipitation.
3. The water cycle is important in the cleansing of the atmosphere by two mechanisms:
  - Rainout - this is the name given to the processes of removal of substances occurring within the clouds. The main process is the participation of hygroscopic aerosol particles in the formation of cloud droplets ('cloud condensation nuclei'). Many of these cloud droplets become part of raindrops or other precipitation elements and are thus carried down to the ground. Other processes of minor importance, like capturing of small particles by the droplets, due to Brownian motion, may also contribute to the rainout.
  - Washout – this is the name given to the elimination of gases by dissolution and of aerosol particles through capture by falling over drops. Washout includes the processes occurring below the clouds.

4. Water is directly involved in atmospheric chemistry either as water vapor participating in chemical reactions or through reactions of other substances occurring in aqueous solution.
5. Both water vapor and clouds play an important role in radiation transfer through the atmosphere

The water substance can also be used as an indicator of circulation in the stratosphere. The isotopic composition of water (Content of HDO<sup>16</sup> or in H<sub>2</sub>O<sup>18</sup>) can be used as a tracer in the study of certain processes.

Consideration of water substance in the atmosphere is therefore of the utmost importance but first to be considered are the vertical distribution of water vapor in the troposphere and stratosphere.

The concentration of water vapor is very variable, and in spite of the large total mass contained in the atmosphere, its residence time is very short. It can be estimated as 10 days. But there is, for every temperature, an upper limit for the concentration of water vapor in air; this is given by the partial pressure that saturates it. By definition, this saturation vapor pressure is the partial pressure at which water vapor can coexist in equilibrium with liquid water. It is practically independent of the presence and pressure of dry air. It can be derived, thermodynamically, that the dependence of saturation vapor pressure with temperature is given by the expression.

$$\frac{d \ln p_s}{dT} = \frac{\lambda M_V}{RT^2} \quad (1)$$

called the Clausius – Clapeyron equation. Here  $p_s$  = saturation vapor pressure, T= absolute temperature,  $\lambda$  = latent heat of vaporization,  $M_V$  = molecular weight of water vapor, R = gas constant.  $\lambda$  varies with T, but not much; if in first approximation after integration it becomes:

$$p_s = const \cdot e^{-\lambda M_V / RT} \quad (2)$$

which indicates a very rapid increase of  $p_s$  with temperature. An immediate consequence of these properties is that only the lower, warmer, layers of the troposphere can contain high concentrations of water vapor. In cold regions and in the higher layers (which are always cold) the water vapor is sharply limited by the saturation value. The partial pressure of water vapor can reach up to about 32 mb in air at 25 °C, but only to 1.2 mb at –20 °C. When humid air becomes colder (for instance, due to adiabatic ascent) water vapor condenses, giving rise to the formation of clouds. Notice that below 0 °C water vapor can condense into water (supercooled water) or into ice.

Now the vertical distribution of water vapor in the troposphere and stratosphere in middle latitudes will be considered. The measurements in the stratosphere can be performed by different methods, including determination of dew point in flights,

spectroscopy and dew point radiosondes. Although some measurements have been the subject of some controversy, it seems now well established that very low humidity exists in the lower stratosphere above middle latitudes. Such humidity variable becomes the mass mixing ratio, defined in the mass (in g) of water vapor per unit mass (kg) of dry air; the advantage of this stoichiometric variable being that it is not dependent on the pressure changes or on any process not involving condensation. Thus, if there was an active exchange of air through the tropopause, the mixing ratio should keep the same value above the tropopause, because in this region the temperature does not decrease any longer with height and therefore no further condensation can occur.

## 2.2. Atmospheric Aerosol

An aerosol is a stable suspension of solid or liquid particles or both in air (Atmospheric Handbook, 1991). The atmospheric aerosol is therefore the combination of all the condensed-phase material present in the atmosphere as well as the air within which the suspended material resides. Similarly, a hydrosol is a stable suspension of solid particles in water. It most often refers to particles in fresh waters or in the ocean but it is also appropriate for atmospheric water droplets containing large numbers of small particles—a common occurrence.

## 2.3. The Tropospheric Aerosol.

A common way to display the sizes of a group of particles is to plot the number distribution. Because of the wide size range, this display is generally accomplished by using a logarithmic scale for the abscissa and plotting normalized values, that is, the number of particles per unit size interval, on the ordinate. A typical spectrum for atmospheric particles in an urban area shows a high number concentration near an equivalent radius of about 5 nm (0.005  $\mu\text{m}$ ); this region is termed the nuclei mode. The second enhancement, near  $r = 0.2 \mu\text{m}$ , is termed the accumulation mode, because it is formed primarily from an accumulation of nuclei mode particles and deposited gases.

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### Biographical Sketch

**Gennady Panin** graduated from the Geographical Faculty, Moscow State University in 1967. He received his Candidate of Sciences degree (equivalent to Ph.D.) in evaporation of sea in 1973 at the Institute of Oceanology, Russian Academy of Sciences and a Doctor of Sciences degree in air-sea interaction in 1986 at the Institute of Water Problems, Russian Academy of Sciences. Since 1989 he held a position of head of Laboratory of Evaporation and Humidity Transport at the Institute of Water Problems, Russian Academy of Sciences in Moscow. His research interests are in the fields of surface fluxes; climatic change; parametrization of surface fluxes, and the theory of interaction between the water/land surface and atmosphere. His main publications are in leading international journals on the physics of atmosphere and ocean, and water resources. His main publications total 127, including four books (in Russian):

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During the past ten years he has held a number of short and long term research visiting positions in various European universities and scientific institutions.