# THE PHYSICAL PROPERTIES OF ATMOSPHERIC WATER, INCLUDING ITS THREE PHASES

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### Summary

This article is a brief overview of the physical and chemical properties of the Earth's atmosphere, including the three stages of water. Information on the principal geophysical processes in the atmosphere, and a list of physical atmospheric parameters, as well as atmospheric composition characteristics, is offered, together with their typical and extreme values. The current model schemes of synoptic processes, atmospheric aerosol, clouds and weather phenomena are given. This information contains descriptions of the clouds' structure, general physical and statistical laws, including those concerning the atmosphere and atmospheric aerosols, cloud thermodynamics (their amount, repetition, phasal condition, water content, crystalline phase in cloud, precipitation particles etc.). The optical and radiative properties of clouds as well as ice formation conditions, ice precipitation and artificial modification of precipitation are also described.

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

# 1. Introduction

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). Water phase conversions always occur in TYPES AND PROPERTIES OF WATER – Vol. I – The Physical Properties of Atmospheric Water, including its Three Phases – G.N. Panin

the atmosphere, the most important being the processes of evaporation and condensation accompanied by the absorption and liberation of huge amounts of heat.

Until the water content of a unit volume does not exceed a certain value corresponding to the saturation state, the water occurs only in a vapor state. In this case it is said that moisture is below 100% and this water vapor is a small, though very important component of the atmosphere. In these cases, all the thermodynamic processes occur similarly to those in dry air. If vapor pressure reaches the value corresponding to saturation, then vapor condenses around condensation nuclei—small particles always available in the atmosphere. Phase conversions of water vapor-water and water vapor-ice occur when the pressure of the available water vapor becomes more than that allowed by the vapor phase, being saturated under a temperature over water and over ice correspondingly.

Air at 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 of the air mass and subsequent vapor condensation and the liberation of vast reserves of latent condensation heat.

The availability of condensation nuclei (CN) provides for condensation. Soluble CN are either particles of marine salt in spray from the crests of waves under a heavy wind, or particles formed out of atmospheric gases. Dust particles of various origins and other atmospheric pollutants, for instance, and some bacteria serve as 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, and 3) giant CN with a radius of more than 1 mkm, most often marine salt particles. Most CN are complex. CN are removed out of the atmosphere through the already described water vapor condensation process, and due to Brownian coagulation, reducing the number of the smallest CN by capturing and washing them out as precipitation, i.e. rain drops and large snow flakes, thus purifying the air. For this reason there are large concentrations of sulfates and nitrates, 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 particular ice nuclei (IN), or the so-called nuclei of freezing or sublimation, in the atmosphere. These can initiate the freezing of previously formed overcooled drops under relatively low temperatures, and also cause the formation of ice crystals out of vapor (sublimation). Ice nuclei (ice particles) can be formed under breaking of big crystals (snow flakes).

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

Particles of some chemical elements, such as silver iodide AgI and lead iodide  $PbI_2$ , can serve as artificial IN. Some organic compounds can generate IN, for instance, phloroglucinol  $C_6H_3(OH)_3$  and metaldegid  $(HCOH)_n$ . A similar role is played by particles of solid carbon dioxide  $CO_2$  in the vicinity of which water drops are frozen immediately, forming IN. These materials are used for affecting clouds with the aim of causing artificial precipitation or a change in precipitation intensity.

Big drops of drizzle and then rain can be formed by the collision and consolidation (coagulation) of cloud drops due to Brownian movement (at a small size), air turbulence or gravitational coagulation, i.e. the capturing of smaller drops by larger and, hence, faster falling drops. This process is particularly important in cumuli and cumulonimbi where upward air flux holds both small and large drops, preventing them from precipitating.

Ice crystals grow larger surrounded by overcooled drops in the clouds under negative temperature. The growth of snow crystals is a major process of forming snow falls in areas with negative temperature and rain in those places where snow flakes precipitate and melt in lower, warmer atmospheric layers. Most ice crystals are comprised of hexagonal columns—prisms and plates. Snow flakes, when falling through a cloud of overcooled drops and capturing them (when coming in contact with ice, overcooled drops, white amorphous layers are formed in the hail; when large drops are entrapped, spilling over the hail surface, layers of transparent ice are formed. An upward airflow continues hail growth by keeping them in the cloud for a long time.

# 2. Dry Air

Atmospheric air is composed of: a mixture of gases which is called dry air; water substance in any of its three physical states; and solid or liquid particles in suspension, called atmospheric aerosol.

Although there are many components in dry air, there is a sharp distinction between the more abundant main components and the minor components only present in trace amounts. The four main components are nitrogen, oxygen, argon and carbon dioxide. N<sub>2</sub> and O<sub>2</sub> make up >99% of dry air; N<sub>2</sub>, O<sub>2</sub> and Ar make up 99. 97% of dry air, and N<sub>2</sub>, O<sub>2</sub>, Ar and CO<sub>2</sub> make up >99. 997% of dry air.

 $CO_2$  is somewhat variable at the ground, as its concentration is affected by any type of combustion (fires, industrial activities), photosynthesis and exchange with the oceans, but it is very constant above the surface layers. In fact, the dry air composition is remarkably constant throughout the entire homosphere, indicating that mixing processes are very efficient.

# Minor Constituents:

The minor components amount to less than 0.003% or 30 ppm (parts per million). They are, however, very important in the chemical picture of the atmosphere, especially when

considering problems of such practical importance as those related to pollution, or to the state of the ozonosphere.

Several classifications can be done of all the constituents of dry air, which illustrate the different roles played by them in the atmosphere -

### *By abundance*:

As mentioned above, the four main constituents account for more than 99.997% of dry air, all four with concentration >300ppm. The minor components could be divided into non-variable and variable groups. Thus, the non-variable minor constituents are present in concentrations of 0.1 to 20 ppm. The variable components are all below 0.1 ppm (except in polluted air and stratospheric ozone). The distinction between the groups, regarding their abundance, is quite sharp.

### *By variability*:

All the main components are non-variable, and so are the non-variables classified as minor components.

Variability is important in that it indicates something about the behavior of the gas in the atmosphere. It is linked to abundance, with reactivity and with the molecules' time of residence in the atmosphere. Thus,  $CO_2$  is non-variable in spite of localized sources of production, because the atmospheric reservoir of  $CO_2$  is too large to allow appreciable fluctuations in concentration. Minor components of high reactivity, such as  $SO_2$  or NO and  $NO_2$ , are variable because they react quickly, and their abundance is low.

Water vapor was not been mentioned in the composition so far, but of course it is a major component of atmospheric air and the only one subject to considerable variations. These variations are linked to the processes of condensation and precipitation and, as is the case with many highly reactive gases, may occur either in solution or with the help of water vapor. The evolution of the reactive, variable minor components of air is usually closely connected with the cycle of water.

# By chemical composition:

This aspect is linked to the reactivity and other characteristics of the component gases. For instance, the complete inertness of noble gases makes them permanent and stable, even at low concentrations. Most of the relevant chemistry in the atmosphere is concerned with compounds of sulfur and nitrogen. Carbon compounds, including some organic compounds, are also important. Other compounds, like halogen derivatives, play a smaller role.

#### *By residence time:*

For the atmospheric chemist, an important characteristic of each gas is the mean life or average residence time,  $\tau$ .

It is usually defined as  $\tau = M/F$ , where M is the total average mass of the gas in the atmosphere, while F is the total average influx (over time, averages for the total atmosphere must be equal).  $1/\tau$  is called the rate of turnover.

If every molecule of gas stays in average  $\tau$  in the atmosphere, it takes a time  $\tau$  to effect a complete turnover; and if F is the influx,  $\tau$  (F) must be equal to the total mass M, thus justifying the previous definition.

The importance of  $\tau$  is that it indicates how actively a given gas is going through a cycle. If M is small and the gas is very reactive,  $\tau$  will be small and the gas concentration will be variable, because it does not have time to distribute homogeneously through the atmosphere from the localized sources.

From the point of view of resident time, the air components can be roughly classified in 3 categories:

Permanent gases with very large  $\tau$ , e.g.  $\tau \sim 2$  million years for He;

Semi-permanent gases, with  $\tau$  from some months to years. This is the case of the four gases mentioned above as 'semi-permanent', which have several similarities in spite of their different chemical composition;

Variable gases with  $\tau$  from days to weeks. These are the chemically active gases. Their cycles are related to the water cycle.  $\tau$  for water vapor is on the order of 10 days.

# By origin:

The following classification of origins, with examples of gases, covers the main cases:

- Combustion
  - 1. natural e.g. CO<sub>2</sub>.
  - 2. anthropogenic e.g. CO<sub>2</sub>, SO<sub>2</sub>, NO.
- Biological processes (bacterial activity, photosynthesis) e.g. CH<sub>4</sub>, N<sub>2</sub>O, H<sub>2</sub>, NH<sub>3</sub>, H<sub>2</sub>S, NO.
- Chemical reactions in the atmosphere e.g. HCl.

Other origins, like volcanic activity, are of minor importance.

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#### **Biographical Sketch**

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

1) Panin G.N.-"Heat- and mass exchange between the water and the atmosphere in the nature."- 1985. Nauka, Moscow, 206 p. (in Russian).

2) Panin G.N.-"Evaporation and heat exchange of the Caspian Sea."- 1987. Nauka, Moscow, 89 p. (in Russian).

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