CLOUD PHASE COMPOSITION AND PHASE EVOLUTION AS DEDUCED FROM EXPERIMENTAL EVIDENCE AND PHYSICO-CHEMICAL CONCEPTS

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1. INTRODUCTION

The current knowledge of the phase composition and phase evolution of atmospheric clouds with temperatures below 0°C (cold clouds) is much deficient suffering a variety of uncertainties and manifest paradoxes. This statement may be briefly illustrated by the following examples.

Despite the fact that ice-forming nuclei (IFN) are permanently present in both dry and cloudy atmospheric air, being relatively instantly developed while sampling, purely water clouds typically retain with no detectable glaciation as long as during many hours. Next, a typical mixed cloud is believed from various studies to be transformed with the Bergeron–Findeisen process into an ice cloud in a matter of minutes. However, even routine observations reveal that natural stratiform clouds conserve their phase-mixed state many orders longer than thus predicted. Moreover, in defiance of water evaporation, ice-containing clouds as a rule contain much bigger droplets than purely water ones usually do, which is exhibited by the crystal riming phenomenon, in impactor samples, and on.

The concentrations of cloud ice particles are commonly found to exceed by several orders those of the known IFN and little or not vary with cloud temperature, which is hardly explicable in the context of the temperature-dependent activity of both IFN and hypothetical mechanisms of ice multiplication. Besides, at temperatures below −40°C ice particle concentrations keep the same order in magnitude as at higher temperatures, even though the physical prohibition as taken of liquid water existence itself at so low temperatures makes one suggest that an ice generation mechanism is here other than the result of water freezing.

Yet unsolved remain such problems related to so-called "quasiliquid" transient layer on ice particle surface (Jellinek, 1967) as its physico-chemical nature, its association with ice saturation humidity, and its role in ice − vapor exchange.

Up to now, only speculative hypotheses have been at best offered to explain this kind of gaps and contradictions with no success achieved in their experimental and/or theoretical examination. Unfortunately, the available measurements on cloud microphysics leave aside those properties of cold clouds which might best contribute to adequate explanations of their "abnormal" features.

An effort to solve this problem has been made by CAO in the late 80s, using original aircraft instrumentation (Nevzorov, 1996a, 1997). The assembly of cloud microphysical probes was designed to measure directly or to estimate by calculation from the combined measurements a series of properties of phase mixed clouds: (i) both liquid and solid phase components of water content with the sensitivity of ~0.003 $g \cdot m^{-3}$, (ii) cloud optical extinction, (iii) number concentration of separately spherical and non-spherical particles greater than 12−30 μm depending on their nature, (iv) various approximations of the size spectra of these particles up to 6 mm, (v) the lower estimation of the effective diameter of water droplets, and some others. The size spectra of non-spherical (ice) particles are determined in terms of area-equivalent diameters of their orientation-averaged optical sections.

The representative enough measurements made in layer-type clouds (over 20,000 km of total path of penetration of over 300 clouds at temperatures between 0°C and −55°C) have stated that the above "anomalies" are indeed totally inherent in natural cold clouds. The use of different high-sensitive techniques enabled us to obtain more complete, than ever before, general notion of the phase composition and two-phase microstructure of these clouds. Also among the data obtained there are such that give certain clues to an adequate understanding of the phase kinetic of cold atmospheric clouds.

The measurement results with some physical conclusions made have been previously described in more or less detail (Nevzorov, 1992, 1993, 1996b; Nevzorov and Shugaev, 1992a, 1992b). Briefly summarized here are the most notable and important results obtained, the physico-chemical aspects of their interpretation, and new inference regarding the nature, formation, and evolution of cloud dispersion phases.

2. KEY EVIDENCE

The measurements above have revealed that a vast majority of cold clouds contain simultaneously both liquid and solid disperse phases and thus are

phase mixed even at temperatures down to −55°C, the lowest of met with.

In about 75% of clouds, referred by common evidence to purely water ones, detected was the presence of ice particles smaller than 20–25 μm, contributing 10 to 30 percent to total condensed water content (TWC). The concentrations of these particles were estimated to be well exceeding 3 cm^{-3} to 20 cm^{-3} for different clouds, thus being comparable with those of cloud droplets. Such "latent-ice-containing" clouds (LICC) were classed as having the mixed structure of the 1-st type (M1). Taking into account that the lower limit of ice detection was 10–15% of LWC, the assurance arises that at least a part of the rest conventionally water clouds can actually contain smaller relative amounts of the fine-dispersed ice.

On the contrary, clouds commonly considered as purely ice ones were found to contain free liquid phase in the form of droplets with diameters from several tens to 1–2 hundred micrometers. Only at temperatures below −45°C and, correspondingly, at TWCs lying close to the instrumental sensitivity limit, the LWC component failed to be detected in about 10% of events, which by no means excludes its presence in these clouds as well.

All clouds corresponding to the common notion of ice-containing (ice and mixed) ones include as expected as large ice particles as >200 μm in size. If particles smaller than 20 – 30 μm made a detectable contribution to the cloud extinction (optical density), such clouds were referred to the mixed structure of M2 type. Otherwise mixed clouds were placed in the M3 type that constitutes the vast majority of clouds at temperatures below −20°C. Let us term clouds of M2 and M3 types together as "developed mixed clouds" (DMC) from the following reasoning.

The relative occurrences of the selected types of cloud phase-disperse structure against local cloud temperature are illustrated in Figure 1. Not shown here is the intermediate structure between M1 and M2, M12, where the largest crystals are between 20 μm and 200 μm, because this occupied less than 0.7% of the total cloud space at given temperature. All the listed structure types often alternate with each other within the same cloud.

The positive space correlation between ice and liquid contents was traced in DMC almost without exceptions.

All the above contain ample evidence that in clouds of M2 and M3 types, or DMC, the condensation equilibrium takes place between ice and liquid particles. At the same time, the relative humidity in these clouds corresponds closely to ice saturation as measured by Mezrin at al. (1991) in parallel with

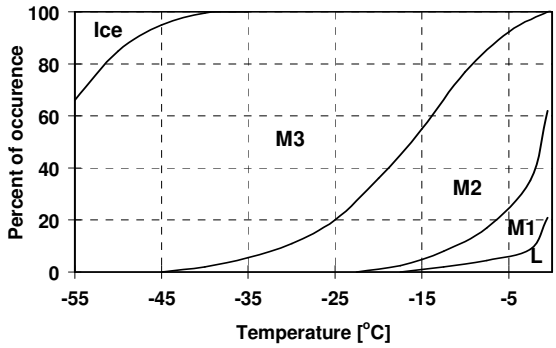

Fig. 1. Temperature diagram of relative occurrence (between the curves) of the types of cloud phase-disperse structure. Here "Ice" and "L" signify the situations where no liquid and ice, respectively, were detected.

our measurements. Also accounting for the stable existence of liquid droplets at T < −40°C, this in turn offers that the liquid droplet substance in DMC differs from the ordinary supercooled water in fundamental physical properties though remaining chemically as pure H_2O as possible under the effect of actual atmospheric pollution. That this liquid substance constitutes an alternative phase state of H_2O, will be demonstrated just below.

3. PROPERTIES AND NATURE OF LIQUID PHASE IN DEVELOPED MIXED CLOUDS

A special, as described in detail by Nevzorov (1992, 1993), analysis of comparative microphysical measurements, made in M3 type clouds using the physically different techniques, have revealed that the substance of liquid droplets has the density 2.17±0.12 $g \cdot cm^{-3}$, the refractive index 1.8 – 1.9, and the evaporation heat 550 $J \cdot g^{-1}$ ±40% at −30°C (around 4.7 times less than that of the familiar ordinary water). To support these results, such yet poorly explained phenomenon as the colored glory around the airplane shadow against sunlight on cold cloud tops alone (!), with its red outer ring viewed under the invariant radial angle of 3.6°, is readily calculated to be the first order bow on spheres with the refractive index of ~1.83. As for the density, a similar value 2.32±0.17 $g \cdot cm^{-3}$ has been earlier found by Delsemme and Wenger (1970) for the low-temperature (around 100 K) water condensate known as "amorphous ice", representing a specific phase state of H_2O.

Numerous laboratory studies reviewed in depth by Skripov and Koverda (1984) have shown that this water condensate: (i) unlike the crystalline ice and ordinary liquid water, is fully disordered in internal structure as examined by structure-sensitive

techniques, thus is devoid of at least regular intermolecular hydrogen bonds, (ii) with temperature rising, experiences smooth fall in viscosity taking the softened state at temperature 135±1 K (vitrification point) and then flowable (liquid) state as temperature becomes above ~150 K (or −120°C), (iii) can originate from vapor directly into any of the listed states, (iv) is metastable relative to crystallization into ice I, like supercooled ordinary water, in the softened and liquid states only. Note that the superhigh density of the amorphous phase of water is expected as the end effect of the decrease in concentration of hydrogen bonds, starting from the transition from crystalline ice I to liquid water acquiring higher density with a part of initial bonds broken.

The conclusion to be drawn from the above reasoning is that droplets in DMC consist of the same amorphous phase of water in liquid state, previously referred to as amorphous, or A-water (Nevzorov, 1992, 1993). The field experiments interpreted in the context of the structural physical chemistry have served to extend our knowledge of the properties of this thus far poorly investigated state of water.

One of the most important features of A-water for the cloud physics, the condensation equilibrium with ice at ice saturation, suggests that the so-called "quasiliquid" film covering ice particles has the surface structure identical to that of free A-water and therefore consists of A-water (similar idea has been earlier proposed by Fletcher (1970)). This in turn implies that it is rather A-water than supercooled water as per Pruppacher and Klett (1978) that contributes a step transient phase in ice deposition from vapor in accordance with the universal Ostwald's rule. Hence the initiation of a cloud ice particle is always preceded by the nucleation of an embryonic droplet of A-water with its subsequent crystallization if a crystallization center is embedded in its condensation nucleus or captured externally. Otherwise the A-water droplet even while growing is capable of preserving its metastable state, as supercooled ordinary water does.

Table 1: Averaged microphysical parameters of mixed clouds of M2 and M3 types at given temperatures

Temperature interval (°C)		−5...−15	−15...−25	−25...−35	−35...−45	−45...−55
A-water content (AWC) ($g \cdot m^{-3}$)	M2	0.42	0.29	0.060	-	-
	M3	0.19	0.18	0.088	0.050	0.028
Ice water content (TWC) ($g \cdot m^{-3}$)	M2	0.031	0.024	0.006	-	-
	M3	0.17	0.12	0.022	0.012	0.007
Ratio AWC/TWC × 100%	M2	93	92	91	-	-
	M3	53	61	80	81	80
Droplet >12 μm concentration (l^{-1})	M2	203	162	193	-	-
	M3	435	248	231	299	582
Crystal >12 μm concentration (l^{-1})	M2	45	63	127	-	-
	M3	192	196	202	259	380

4. ON THE TWO-PHASE MICROSTRUCTURE OF DEVELOPED MIXED CLOUDS

The summarized results of microphysical measurements in stratiform DMC, corrected for the affecting physical properties of A-water, were presented by Nevzorov (1997) in the form of data averaged over sampled clouds of separate types and temperatures, as displayed in Table 1. All the parameters concerned exhibit a very wide scatter from cloud to cloud and as a rule inside the same cloud, whence the statistical uncertainty of the averages is rather great.

Nevertheless, as seen from the Table 1, the distinction between the selected cloud structure types M2 and M3 is pronounced enough in almost all averaged data, and most of all most in ice particle concentration and IWC. The average concentrations of A-water droplets exceeding 12 μm in diameter exhibit markedly less difference between both cloud types than those of ice particles. The concentrations of both kinds of particles with similar threshold sizes are of the same order in magnitude and little, if at all, depend on temperature. The share of A-water in the total condensed water content (TWC) is surprisingly high and essentially independent of temperature. In addition to the presented data, the though roughly estimated average droplet size spectra differ distinctly between the both cloud types in that that in M3 type they possess modes lying between 30 μm and 45 μm equally at all temperatures, whereas those in M2 type always lie to the left of 12 μm.

5. PROCESSES OF PHASE EVOLUTION OF COLD CLOUDS

Being of the highest internal energy among all water condensed phases, A-water can originate only directly from vapor. Therefore, the permanent coexistence of free A-water with cloud ice implies that the processes of condensation and partial crystallization of A-water necessarily play the significant role in the formation of cloud phase composition. Moreover, the high and temperature-independent concentrations of ice crystals, close to those of A-water droplets (see Table 1) and well far from those of the known ice-forming (water freezing) nuclei, give evidence that these processes are dominant in the formation of DMC, and that the primary nucleation of A-water occurs on alternative, specific nuclei.

The question arises about the nature of these A-water condensation nuclei (AWCN) as well as about their origination, because the abundance of atmospheric layers, free of cloud though at ice supersaturation, signifies that no such active nuclei are as a rule present in dry air. One of the mechanisms of their natural initiation is indirectly pointed to by Rosinski et al. (1991) who have found that a supercooled water droplet being just evaporated can be immediately replaced by a newly formed ice crystal. In fact, as follows from the foregoing, the dehydrated residuals of ordinary water droplets acquire the properties of catalytic centers of condensation, and only some part of them of crystallization of A-water. Such secondary AWCN are enable to be collectively generated within a supercooled water cloud, when relative humidity lowers to a degree sufficient for the smallest droplets to evaporate. This occurs near cloud edges, or due to dry air entrainment, or as the final of the cycle of wetting of non-hygroscopic nuclei, etc. In any case, a supercooled water cloud is bound to acquire the "latent-ice-containing" structure M1, containing A-water droplets as well, most probable from the very beginning of its lifetime. The above-mentioned superhigh concentrations of fine ice particles in M1 type clouds evidence that the ice forming mechanism of droplet evaporation is many orders more productive than that of droplet freezing. This thereby removes the need for the ice multiplication version.

In spite of the high vapor supersaturation, just nucleated particles of A-water and ice are initially growing extremely slowly because of the molecular-diffusion growth mode. As they increase and their gravitational sedimentation accordingly accelerates, the resulting microscale disturbance of air makes the Bergeron trans-condensation to become progressively faster. When the particles achieve critical sizes of order of 20 μm, this process proceeds to its avalanche-like stage that culminates in complete evaporation of droplets of ordinary water. A minute duration of this stage is expressed in the negligible occurrence of the transient structure M12.

A developed mixed cloud (DMC) thus formed consists of ice and liquid A-water alone and may be considered, depending on the physical application involved, as either a condensation-stable biphase cloud or a "quasi-ice" cloud wherein a part of potential ice remains in the form of a metastable transient substance.

The two-phase microstructure of DMC is formed under the combined effect of a variety of factors such as: (i) a disbalance in vapor saturation with respect to ice, caused by air motions, trends of air temperature, etc., (ii) a direct relationship between vapor supersaturation and concentration of active AWCN, (iii) an inverse dependence of saturated vapor pressure on particle size, (iv) low condensation enthalpy of A-water, responsible for its small thermal resistance to both condensation and evaporation processes, and so on.

The last factor suggests that the liquid fraction serves as the most fast-acting regulator of relative humidity in clouds, being the most sensitive in microstructure to its variations. All these together provide a certain explanation for the distinction between M2 and M3 cloud structure types. The M2 structure is formed under as high ice supersaturation of vapor as being sufficient for the activation a supplementary portion of condensation nuclei to produce the distinctive fraction of fine-sized particles. Subsequent condensation of vapor occurs preferably on the biggest particles and resulting fall in its supersaturation causes evaporation of the smallest particles of progressively increasing sizes. The cloud thus transforms into the conceptually stable structure of M3 type wherein all droplets are large enough to provide, under given thermodynamical conditions, the best approach to equilibrium between all three phases.

6. CONCLUSION

Great diversity of evidence related to cold clouds are paradoxical to an extent that they need to be interpreted from physical concepts to be radically improved. The conclusions made in this paper include, as a basic finding, the established existence and specific properties of the little- known amorphous phase of water, A-water, constituting a certain part of liquid droplets in mixed clouds. A series of missing physical properties of A-water have been gained in our field studies of cloud properties.

The concepts suggested are most strongly supported by the fact that unlike those leading in today's cloud physics, they furnish the simplest and

quite obvious explanation for every conceivable poorly understood phenomenon associated with cold clouds. Apart from the mentioned above, these are for example such phenomena as the formation of graupel and freezing drizzle in ice-containing clouds, the burst-like and bald-formed glaciation of the tops of cumulus congestus clouds (occurring due to collective evaporation of supercooled water droplets near the cloud boundary), the occurrence of precipitating ice in a initially water cloud while merely penetrated by an aircraft (producing heavy air disturbance that strongly encourages the growth of "latent" fine ice), and others to be encountered.

It is of great importance that the high relative content of free A-water imparts to ice-containing clouds different, than considered up to now, properties in formation and phase composition of winter precipitation, in accumulation, transformation and global transfer of atmospheric aerosol, in propagation and scattering of light and other electromagnetic as well as corpuscular radiation, in aircraft icing, and possible in other problems involved.

There are all reasons to believe that free A-water is an essential constituent of noctilucent and nacreous clouds as well as of clouds encountered in cold atmospheric layers on other planets, all being known to contain spherical particles as found with optical methods.

REFERENCES

Delsemme, A. H., and A. Wenger, 1970: Superdense water ice. Science, 167, 44-45

Fletcher N.H., 1970: The chemical physics of ice. Cambridge Univ. Press

Jellinek H.H.G., 1967: Liquid-like (transition) layer on ice. J. Colloid and Interface Sci., 25, 192-197.

Mezrin, M. Yu., and G. V. Mironova, 1991: Some results of research of air humidity in stratiform clouds. Proc. of CAO, issue 178, 125–132 (in Russian)

Nevzorov, A. N., 1992: Permanence, properties and nature of liquid phase in ice-containing clouds. 11th Int. Conf. on Clouds and Prec., Montreal, Canada, 270-273

Nevzorov, A. N., 1993: Studies into the physics of liquid phase in ice-containing clouds. Russian Meteorology and Hydrology, No 1, 47-59

Nevzorov, A. N., 1996a: CAO aircraft instrumentation for cloud physics. 12th Int. Conf. on Clouds and Precipitation, Zurich, Switzerland, 371-374

Nevzorov, A. N., 1996b: Observations of initial stage of ice development in supercooled clouds. Ibid., 124-127

Nevzorov, A. N., 1997: An experience and promising results of advanced measurements into microphysics of cold clouds. WMO Workshop on Measurements of Cloud Properties for Forecasts of Weather and Climate. Mexico City, 173-182.

Nevzorov, A. N., and V. F. Shugaev, 1992à: Observations of the initial stage of evolution of ice phase in supercooled clouds. Soviet Meteorology and Hydrology, No 1, 69-76.

Nevzorov, A. N., and V. F. Shugaev, 1992b: Experimental studies of phase-dispersion structure of stratiform clouds at negative temperatures. Soviet Meteorology and Hydrology, No 8, 41-51.

Pruppacher H.R., Klett J.D., 1978: Microphysics of clouds and precipitation. D. Reidel.

Rosinski, J., and G. Morgan, 1991: Cloud condensation nuclei as a source of ice-formation nuclei in clouds. – J. Aerosol Sci., 22, No. 2, 123–133.

Skripov, V. P., and Koverda, V. P., 1984: Spontaneous crystallization of supercooled liquids. Nauka, Moscow, 232 pp. (in Russian).