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EXPERIMENTS ON THE CONDENSATION AND SUBLIMATION OF WATER VAPOUR AT LOW TEMPERATURES

(VERSUCHE ÜBER DIE KONDENSATION UND SUBLIMATION DES WASSERDAMPFES BEI TIEFEN TEMPERATUREN)

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EXPERIMENTS ON THE CONDENSATION AND SUBLIMATION OF WATER VAPOUR AT LOW TEMPERATURES

One of the most important problems in the physics of clouds is the question, under what conditions can supercooled water droplets form in the free atmosphere at sub-zero temperatures, and under what conditions may ice crystals occur.

From analogy with conditions at higher temperatures it is a justifiable conclusion that at low temperatures, too, when supersaturations occur in the atmosphere, condensation nuclei must always be present if either condensation or sublimation is to take place. But since under apparently identical conditions sometimes supercooled water droplets and at other times ice crystals are observed in the atmosphere, the meteorologists have sought to explain the difference by the existence of two different types of nucleus. There are said to be condensation nuclei leading to the formation of water droplets, and differently constituted nuclei on which the water vapour from the air sublimes directly to ice. Alfred Wegener[1)], in particular, expressed the hypothesis that small quartz particles might act as sublimation nuclei, since quartz has the same crystal form as ice, and this would favour the crystallization of water vapour on it. Findeisen[2)] has also recently proposed the same theory.

The physical chemists on the other hand have long had the so-called Ostwald law of states,*according to which when water vapour is supersaturated at low temperatures the unstable, supercooled water of higher energy content must first condense out from it and can then, by freezing, become ice of lower energy content. The problem of separating the new phase has recently been formulated more precisely and given exact theoretical treatment by M. Volmer[3)]. According to Volmer the decisive factor for condensation and sublimation is the amount of work which must be performed against the surface forces during the formation of a droplet or crystal core (Troepfchen- oder Kristallkeim). The smaller the amount of work required to produce a given core, the greater the probability that such cores will occur. For the ice core, this work, generally speaking, is greater, and, except for the case of very low temperatures, condensation droplets always occur first. The work of core formation is reduced by solid, fluid and chemical condensation nuclei, as well as by electrical charges on the ions. Thus condensation is facilitated, al-

* Known in English as: "Ostwald's Law of Successive Reactions".

though in certain cases, indeed, only in a barely discernible manner. Volmer's theory has recently been discussed by Krastanow[4] in its application to the problem of water vapour condensation in the atmosphere. Until now laboratory tests to determine the conditions of condensation and sublimation of water vapour at low temperature have been lacking. A preliminary report of the author's own experiments in this field is given here.

The water vapour supersaturations were produced by sudden expansion of air saturated with water vapour. Figure 1 shows the plan of the test arrangement used. The expansion vessel A can be filled either from a with air containing condensation nuclei drawn from the atmosphere or the room, or from b with air containing no nuclei drawn through the Schott bacteria filter B and the storage vessel C. A contains a quantity of water or ice. By means of a cold-bath it can be brought to various temperatures. By suddenly opening the valve D[(1)], leading to the previously evacuated space v', the volume of air v contained in A can be suddenly expanded, cooled and supersaturated according to the degree of expansion $\frac{v + v'}{v}$. By varying v' the degree of expansion can be varied. From the small vessel E, which is connected at the side, given condensation nuclei can be introduced into the expansion space A by means of suitable evacuation.

By illuminating from the side with an arc lamp the ultra-microscopic condensation phenomenon can easily be observed. A fifteen-power binocular microscope is very convenient for this purpose. Tiny ice crystals are easily distinguishable from water droplets even with the naked eye by their glitter and sparkle.

First those experiments will be considered in which the air was cleared of condensation nuclei by the bacteria filter and which also, from the outset, contained no ice particles. It should be explained that tiny ice crystals form at temperatures below zero on the walls of the expansion chamber and in the air intake tube. It is necessary, especially at very low temperatures when the ice deposit is very considerable and takes the form of needles, to introduce the air slowly in order to ensure that nothing breaks away from these small crystals to float in the air as ice dust. In the presence of such ice dust any expansions will result in a sublimation of the water vapour on these ice dust particles. Streaks of these ice particles then

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(1) The very light valve is opened by gas pressure in 1 to 2 x 10^{-3} second. The expansion is therefore entirely adiabatic.

appear. They are rather coarse and clearly visible, the more so, of course, the greater the expansion.

Hence if care is taken to have no ice dust in the air, then, in accordance with results at higher temperatures, no condensation whatsoever will occur with small expansions in air free from nuclei even at temperatures below zero. The air will thus be left supersaturated with water vapour. The single coarse droplets which are sometimes observed are apparently caused by chemical condensation nuclei which are not held back by the bacteria filter. Not until the degree of expansion reaches a greater value, about 1.3, does the number of droplets gradually begin to increase, while a condensation takes place, as is known, on the ions which are always present in the air. However, this condensation is still in the form of droplets down to -50°C, where the present observations have stopped. Hence even with higher supersaturation of water vapour in the air (the degree of expansion 1.3 corresponds to more than a fivefold supersaturation) the droplets always form first at low temperatures. With expansions somewhat greater than about 1.4 the droplet cloud suddenly becomes much denser, and at 1.5 a few very coarse ice particles are usually found within this cloud. The author is uncertain whether these ice particles represent primarily a sublimation in a given crystal form from the water vapour, or whether they are a secondary phenomenon, i.e., very fine ice particles or ice nuclei, torn from the walls, which are then able to grow very rapidly owing to the high degree of supersaturation.

If the expansion is increased to 1.5 or 1.6 the clusters of coarse ice particles become more frequent. Then ice clusters and supercooled water droplets are usually found side by side, and it is interesting to observe how the ice crystals quite rapidly in one to two minutes absorb the supercooled water droplets as the water vapour from the latter sublimes into ice.

With expansions from 1.6 to 1.8 (depending on the initial temperature) another phenomenon suddenly occurs. Water droplets cease to form and instead a characteristic, very fine, whitish ice cloud appears, recognizable as such by its sparkle. This sparkling increases visibly, indicating that the mist is becoming coarser as the small particles sublime over into the larger ones.

The phenomenon just described occurs more or less equally at all initial temperatures between 0° and approximately -40°C(ii). At temperatures below these, observation, especially of the transition stages of the various forms of ice cloud from one into another, becomes more difficult and therefore less certain(iii). It should also be noted that the lower the initial temperature before expansion, the lower will be the water vapour content of the air, which results in an ever thinner droplet or ice cloud. However, even at -50°C, with fairly small expansions, droplet clouds have been distinctly observed by the author. In addition, the sparkling of the ice particles differs with the test conditions, since their form is different for various degrees of supersaturation.

Entirely analogous phenomena occur if, instead of air which has passed through the bacteria filter and is therefore free from nuclei, air containing condensation nuclei from the atmosphere or from the room is expanded. The chief difference is merely that even at very slight degrees of expansion, droplet cloud forms, and this continues to be the case even down to temperatures of approximately -50°C. The degree of expansion at which the transition from droplet to ice condensation takes place appears to be somewhat reduced; but more accurate measurements are only now being made. The author would also prefer to postpone the precise calculation of the temperature at which ice cloud appears alongside the droplet cloud until the difference between the occurrence of the coarser ice clusters and the finer ice clouds at somewhat higher expansions is more clearly understood.

The observations of the freezing of supercooled water droplets are also uncertain. Under present test conditions the supercooled water droplets are usually maintained only from two to three minutes, after which they distil onto the larger water or ice surface which is always present in the vessel.

(ii) Even above 0°C an ice cloud is obtained in this apparatus with its quick acting valve when the expansions are sufficiently great. However it melts very quickly and changes into water droplet cloud. The higher the temperatures at which operation takes place, the faster this process will be.

(iii) The incidental experimental difficulties (cracking of vessels, coating of observation windows) also increase greatly at low temperatures.

In any case one fact seems to be clear: that in the air investigated by the author, which must have contained nuclei of every possible kind, there were no special sublimation nuclei which would lead to the direct formation of ice particles even in low supersaturations, as assumed previously by Alfred Wegener's theory. In view of the importance of establishing this, an attempt was made to confirm it by even more direct experiments. Very fine, purified quartz powder was mixed together with nucleus-free air in a small vessel (E in Fig. 1), and this air, containing the quartz dust, was then introduced into the previously evacuated expansion vessel. With the preferred side illumination this quartz dust could be identified absolutely as quartz, for the larger particles exhibited a quite unmistakable sparkling under the microscope. When expansion now took place slowly the particles rapidly grew larger and brighter, and their sparkle vanished, indicating that water vapour was condensing on the quartz particles. This process could even be reversed, for when air was again admitted, increasing the pressure and temperature, the water evaporated from the quartz particles again and the pure quartz particles appeared once more. This behaviour of quartz particles could be observed very clearly at -15° and -33°C. At high expansions the formation of ice seems to occur rather sooner with quartz dust than without. More accurate measurements concerning this are still to be made. For conditions in the atmosphere, however, the high expansions and extreme supersaturations are of no importance, since they rarely occur, and moreover at expansions of 1.25 to 1.3 (or alternatively at the corresponding supersaturations) the ions which are always present in abundance in the atmosphere act, of course, as condensation nuclei, in which case water droplets occur even at low temperatures.

Experiments corresponding exactly to the quartz dust tests were also carried out at approximately -15°C using ordinary table salt. Here, too, droplet condensation always occurred at low and moderate expansions. At the moderate expansions, a few coarse ice particles sometimes appeared along with the droplets. The degree of expansion of 1.8, however, again brought about the very characteristic formation of fine ice clouds as previously described.

As an example of chemical condensation nuclei, ozone was next investigated. The ozone was produced in a small ozone tube and was then added to core-free air. Again only droplets occurred at relatively small and moderate degrees of expansion. The droplets were very abundant in this case owing to the known, very powerful condensation-promoting properties of ozone. However the limits for ice crystal formation were not noticeably changed.

Finally a strong α-ray emitter was placed in the expansion space in order to determine whether a very high, locally concentrated ionization had any effect on the formation of ice. Even with this arrangement, however, ice particles occurred only at high degrees of expansion.

In conclusion the question of how ice clouds can form in the free atmosphere will be just briefly touched upon in the light of the results obtained in the laboratory. The experiments confirm Volmer's theory that a primary sublimation of water vapour into ice can take place only at low temperatures - perhaps -60° or even lower - although the numerical value cannot be regarded as very reliable until more accurate tests have been made. Secondly, ice can, of course, form as a result of the freezing of the supercooled water droplets, in which case the most likely explanation seems to be that this process is one of impingement of solid particles on the surface of the droplet. Finally it also appears possible that in the free atmosphere at fairly high altitudes the air always contains permanent ice cores. In contrast to the laboratory test conditions, the air at high altitudes remains at low temperatures, of course, for relatively long periods. It does not seem inconceivable that under these circumstances stable ice cores of microscopic size are formed which grow into visible ice particles as the water vapour concentration increases. Even in the laboratory tests it was difficult to avoid fine ice dust which, when present, always leads to ice formation.

These brief observations, of course, make no claim to completeness, nor do the reported laboratory experiments. The condensation and sublimation of water vapour, not only in the free atmosphere, but in the laboratory experiments as well, are shown to be very complex phenomena, and many more experiments will assuredly be needed before they can be better understood. The author believes, however, that the laboratory tests are necessary if it is desired to gain a reliable basis for the explanation of the processes in the free atmosphere.

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2) W. Findeisen, e.g., Meteorol. Zs. 55 (1938), p. 121.

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4) L. Krastanow, Meteorol. Zs. 57 (1940), p. 357.

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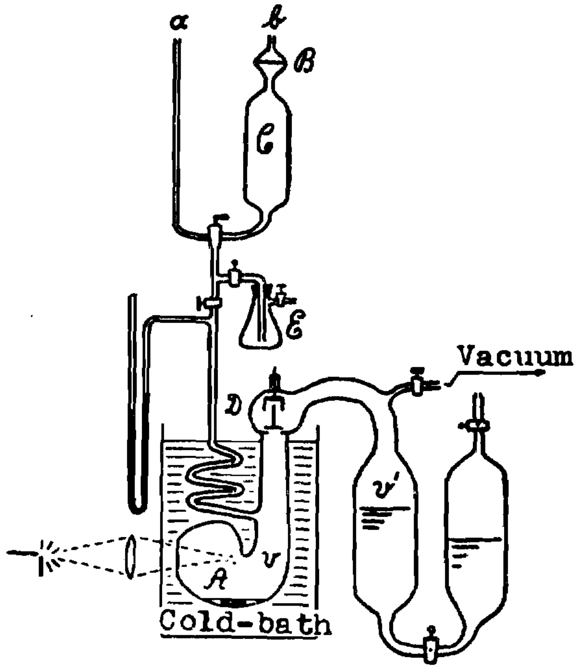

FIGURE 1