N. N. MOSKVITIN, Academician M. M. DUBININ, and A. I. SARAKHOV

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N. N. MOSKVITIN, Academician M. M. DUBININ, and A. I. SARAKHOV

ADSORPTION OF WATER VAPOR ON CRYSTALLINE POWDERS OF SILVER AND LEAD HALIDES

Aerosols of silver iodide and lead iodide have found practical application as active centers of crystallization in the artificial formation of precipitation from supercooled clouds. Earlier a hypothesis was proposed according to which the primary act in the process of formation of artificial precipitation is due to adsorption of water vapor on particles of AgJ and PbJ_2, followed by ordering of the sorbed molecules into the structure of normal ice ([1–4]). In the authors' opinion, disturbance of the phase equilibrium in a supercooled cloud leads to rapid crystallization of water vapor and precipitation. Attempts to establish a connection between the adsorption properties and the ability of AgJ and AgCl particles to serve as nuclei of crystallization and condensation have not been successful ([4,5]). This may be explained in part by the fact that experimental isotherms of adsorption of water vapor on crystals with a hexagonal lattice, analogous to the lattice of ice—such as AgJ, PbJ_2, and others, which are centers of crystallization—were not compared, for example, with isotherms for crystals with a cubic lattice that do not serve as crystallization nuclei (AgCl, CdJ_2, and others). In the present investigation we have compared adsorption isotherms on typical representatives of the above-mentioned groups of crystals over a sufficiently wide temperature interval.

Studies of the isotherms of adsorption of water vapor were carried out on quartz microbalances ([6,7]) with a sensitivity of $2.5 \cdot 10^{-7}$ g for a sample of 1 g. As manometers for measuring pressure in the range from 10^{-4} to 1 mm Hg, a Pirani-type manometer was used, and for pressures above 0.5 mm Hg—a membrane manometer with a sensitivity of 0.05 mm Hg. For thermostating the sample, a thermostat operating at temperatures from +60 to −40° ([8]) was used. The objects of study were spectrally pure powders of lead iodide, and silver iodide and chloride, with specific surface areas of, respectively, 0.25, 0.2, and 0.08 m^2/g*. The standard preparation of the adsorbents for study consisted of heating on the balance in vacuum at a temperature of 110-120° for 8-10 hours. The upper temperature limit was dictated by the fact that at 120° the adsorbents studied do not yet sinter and do not sublime noticeably. Work with AgJ and AgCl—substances that undergo photolysis—was carried out under red light. The adsorbent sample weighed 0.75-0.8 g.

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

On AgJ and AgCl crystals, isotherms of water adsorption were measured at 20, 10, 0, and −20°. All the isotherms obtained (type II according to Brunauer' s classification) are reversible over the entire interval of measured pressures and completely reproducible at all temperatures, regardless of whether the sample had been heated before the measurements or not. Water adsorption isotherms plotted in relative coordinates for each adsorbent at temperatures

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* The samples were obtained by precipitation from solutions in the laboratory of I. I. Angelov, Institute of Pure Chemical Reagents.

20, 10, and 0° practically coincide with one another. This means that the heat effect of water adsorption is close to the heat of condensation.

The adsorption isotherms of water on AgJ and AgCl are described by the Brunauer, Emmett, and Teller (BET) polymolecular adsorption equation in the range of relative pressures from 0.05 to 0.4. From these isotherms, by the BET method, the capacities of the statistical monomolecular layers (a_m) and the values of the specific surfaces were calculated (see above). Thus, for AgJ $a_m = 1.32$ μmol/g, and for AgCl $a_m = 0.54$ μmol/g. The absolute adsorption isotherms of water on silver iodide and silver chloride practically coincide. At temperatures from 20 to −20° no thick adsorption films are formed on the crystals studied. For example, at a relative pressure of 0.8, about three monomolecular layers were sorbed.

Fig. 1

Fig. 2

At a temperature of −20°, certain peculiarities of water sorption on silver iodide (Fig. 1) and silver chloride (Fig. 2) were observed. These isotherms were constructed from experimental points with allowance for corrections for adsorption of water vapor on the glass pan of the balance. In these graphs the lower isotherms are completely reversible if the water-vapor pressure in the system did not exceed the vapor pressure of saturated vapor over ice at −20° ($P_s = 0.77$ mm Hg). In our case, in the adsorption apparatus it is in principle impossible to obtain a pressure above 0.77 mm Hg because of condensation of the excess water vapor on the walls of the balance. Therefore any temporarily created (artificial) pressure above 0.77 mm Hg we called supersaturation. At a pressure close to 0.77 mm Hg the limiting sorption value on AgJ was about

Fig. 3

Figure 3: Fig. 3

Fig. 4

Figure 4: Fig. 4

4 μmol/g, and on AgCl about 2 μmol/g. By creating supersaturation in the system, we observed that during the first 15 min the weight of the adsorbent increased sharply and corresponded to several tens of micromoles of water per gram of adsorbent. As equilibrium was established in the system, the amount of adsorbed water decreased. Equilibrium was established after 2.5–3 hours, and the amount of adsorbed water became equal to that which corresponded to a water-vapor pressure of 0.77 mm Hg (point A in Figs. 1 and 2). After this, the desorption points no longer lay on the adsorption curve but consistently lay above it (upper curves). The hysteresis loop formed in this way was observed every time supersaturation was created in the system. It should be noted that after creation of supersaturation and subsequent prolonged evacuation at the temperature of the experiment (-20°), a certain amount of irreversibly retained water remains on the sorbents (0.6 μmol/g on AgJ and 0.3 μmol/g on AgCl), which was removed by pumping only at room temperature or at a temperature higher than room temperature.

Of principal interest is the question of the phase state of adsorbed water on AgJ and AgCl at temperatures below 0°. In earlier works ([4]) it was unjustifiably assumed that, at a temperature of -20°, water adsorbed on AgJ powder is present in the form of ice. We attempted to elucidate this question, for which purpose we presented our experimental da–

in the form of isosteres. Figs. 3 and 4 show, respectively, the isosteres for different amounts of adsorption on silver iodide and silver chloride, calculated from the isotherms for temperatures of 20, 10, 0, and -20° (for -20° the reversible adsorption branch was used).

In Fig. 3 each isostere consists of two linear portions intersecting in a temperature interval close to 0°. In the upper part of the graph, the dashed line gives the curve $\lg P = f(1/T)$ for water in the bulk phase. The break in this curve at 0° corresponds to the melting of ice. The difference between the tangents of the angles of inclination of the linear segments at the phase-transition point determines the thermal effect of the transition, equal to 1450 cal/mole. By analogy, the break in the adsorption isosteres can apparently be regarded as a formal indication of the existence of a phase transition in adsorbed

Fig. 3

Fig. 4

water. We assume that the phase transition occurs only in some part of the

adsorbed water, since the heat effect of adsorption of water in the second and subsequent monomolecular layers at −20° does not approach the heat of fusion of the normal bulk phase. A similar character of the isosteres can be explained by the fact that the phase transition probably occurs in the first adsorption layer. Then all the remaining adsorbed water is in a quasi-liquid or quasi-crystalline state. It is preferable to assume that at a temperature of −20°, on the surface of AgJ, the adsorbed water represents a quasi-crystalline phase, since the field of the adsorbent should cause a strong orientation of the polar water molecules, which may lead to a two-dimensional analogue of ice. This conclusion is also supported by the fact that the crystal lattice of silver iodide is almost identical with the crystal lattice of ice.

The adsorption isosteres of water vapor on silver chloride shown in Fig. 4 have no break. Consequently, the heat effect of adsorption, both at positive and at negative temperatures, is practically equal to the heat of condensation. It is natural to assume that at −20° the water adsorbed on AgCl crystals is in the form of a supercooled liquid. Similar effects of supercooling of liquids in the adsorbed state have also been observed earlier [9–13]. It was mentioned above that, under certain experimental conditions at a temperature of −20°, a peculiar hysteresis loop appears. The presence of desorption branches of the isotherms in Figs. 1 and 2 shows that, at any pressure value, the properties of adsor-

the water calibrated on the sorption and desorption isotherm curves must differ sharply from one another. If, during the adsorption of water vapor on silver chloride at −20°, supersaturation is created in the system, then in the thick adsorption films that form the probability of spontaneous crystallization increases greatly. This is all the more true for silver iodide, since the water adsorbed on its surface is in a quasi-solid state. It may be suggested that the difference in the character of the isotherms of water vapor on AgJ and AgCl, caused by the presence of a phase transition in the adsorption layer on silver iodide and its absence on silver chloride, may be connected with the difference in the behavior of these aerosols during the artificial seeding of supercooled clouds.

In studying the process of water sorption on crystals of lead iodide, we encountered the circumstance that sorption equilibrium in the system was not established even over the course of 35 days. In all probability, this is due to the fact that a qualitatively different process, greatly extended in time, is superimposed on the process of physical adsorption. One of such processes complicating the van der Waals sorption of water on PbJ_2 may be hydration. Thus, in the case of water sorption on PbJ_2, at all the temperatures investigated we were dealing with a nonequilibrium vapor–adsorbent system. Therefore, we were unable to establish a relationship between the adsorption behavior of PbJ_2 and the ability of its particles to serve as crystallization nuclei.

Institute of Physical Chemistry
Academy of Sciences of the USSR

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REFERENCES

1. B. Vonnegut, J. Appl. Phys., **18**, No. 7, 593 (1947).
2. V. Schaefer, J. Meteor., **11**, 417 (1954).
3. E. Fournier d' Albe, Quart. J. R. Meteor. Soc., **75**, No. 323, 1 (1949).
4. S. Birstein, J. Meteor., **12**, No. 4, 324 (1955).
5. L. Coulter, G. Candela, Zs. f. Electrochem., **56**, No. 5, 449 (1952).
6. B. P. Bering, V. V. Serpinsky, DAN, **94**, No. 3, 497 (1954).
7. A. I. Sarakhov, DAN, **112**, No. 3, 464 (1957).
8. M. G. Batrukova, N. N. Moskvitin, A. I. Sarakhov, Zav. lab., **9**, 1149 (1958).
9. A. Coolidge, J. Am. Chem. Soc., **46**, 596 (1924).
10. J. Jones, R. Gortner, J. Phys. Chem., **36**, 387 (1932).
11. W. Patrick, W. Land, J. Phys. Chem., **38**, 1201 (1934).
12. W. Patrick, W. Kemper, J. Phys. Chem., **42**, 369 (1938).
13. B. N. Vasil' ev, B. P. Bering, M. M. Dubinin, V. V. Serpinsky, DAN, **114**, No. 1, 131 (1957).

Note: Figure translations are in progress. See original paper for figures.