

THE ROLE OF ADSORPTION IN HETEROGENEOUS NUCLEATION, II: THE ADSORPTION OF WATER VAPOR ON PHOTOLYZED SILVER IODIDE

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(Manuscript received 8 June 1955)

ABSTRACT

Studies have been made of the adsorption of water vapor on photolyzed silver iodide. Adsorption isotherms, run at +20 and -20C, have been compared with the isotherms of water vapor on unphotolyzed silver iodide at the same temperatures. It has been found that, while water on silver iodide gives a type III isotherm characterized by extremely high multilayer adsorption, as the silver iodide is photolyzed and its nucleating ability destroyed, water adsorption is greatly diminished.

1. Introduction

Recent adsorption studies on nucleating agents have shown a striking relationship between the ability of a substance to adsorb and orient water layers on its surface and its ability to nucleate supercooled water clouds. Other experiments have shown that silver iodide, after the reduction of its surface by exposure to ultraviolet light or sunlight, no longer retains the ability to nucleate a supercooled cloud. In view of these facts, it was felt that, since nucleation appears to proceed by the adsorption of water vapor on a particle surface followed by oriented growth to form an ice crystal, it might be desirable to study the adsorption of water vapor on photolyzed silver iodide.

These studies, which were carried out at +20 and -20C, measured the adsorption of water vapor on photolyzed silver iodide and compared the results with the curves obtained for the adsorption of water vapor on unphotolyzed silver iodide at the same temperatures.

2. Experimental

The apparatus used in these experiments has been thoroughly described in a previous article [1]. The adsorption studies were carried out with use of a gravimetric adsorption system (fig. 1), in which the solid studied was placed in a platinum bucket (B) attached to a quartz spiral (Q). Any increase in weight of the material in the bucket due to adsorption was reflected in an increase in the length of the spiral. The elongation of the spiral was measured with the aid of a microcathetometer trained at point (P) on the spiral. The microcathetometer could be read directly to 1μ or estimated to $\frac{1}{2}\mu$. The displacement of the spiral was approximately 1μ per $11\mu\text{g}$. Adsorption on an empty bucket and the quartz spiral was found to be negligible.

In making a run, the platinum bucket was filled with approximately 600 mg of silver iodide, and the

system was evacuated until a vacuum of 10^{-5} mm Hg could be held for 3 min. Small portions of the adsorbate were allowed to diffuse into the system and come to equilibrium with the thermostatted silver iodide. The pressure of the system and elongation of the spiral were then measured. This procedure was continued until the saturation vapor-pressure of the water at the temperature of the isotherm was attained.

Desorption measurements were made in a manner that essentially reversed adsorption measurements. Small portions of water vapor were removed from the system by momentarily opening it to a region of lower pressure and then allowing it again to come to equilibrium. The pressure and spiral length were then measured. This procedure was repeated until all of the water vapor had been removed.

Two silver-iodide samples were used in these experiments, one a commercially available, chemically pure silver iodide, and the other a sample prepared in the laboratory from ammonium iodide and silver nitrate

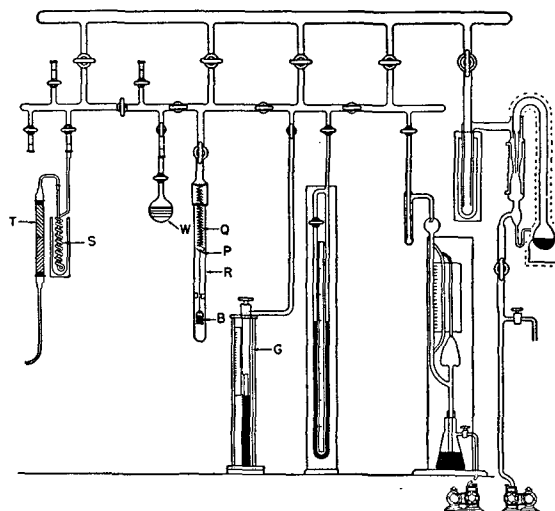


FIG. 1. Adsorption apparatus.

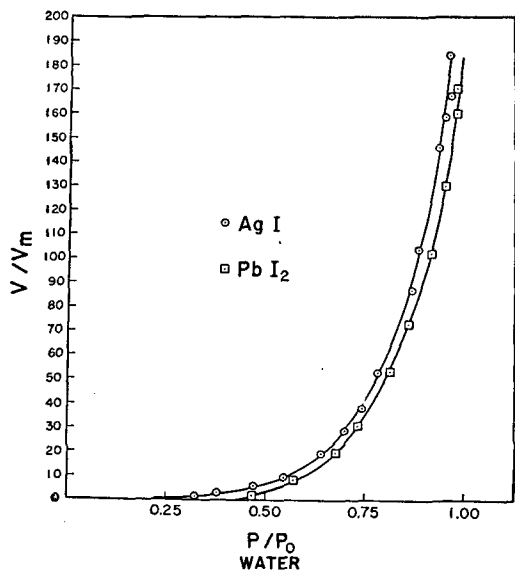


FIG. 2. Adsorption of water vapor on silver iodide and lead iodide at +20°C.

[2]. Both samples were ground before use until they had been reduced to a mean diameter of between 1 and 2 μ . Surface areas were determined from the size distributions and also from BET water and nitrogen isotherms [3].

Photolysis of the silver-iodide samples was carried out by exposing the samples, placed on glass slides, to an Hanovia ultraviolet light source. The energy flux of the light source was approximately 10^{16} quanta/cm²/min after allowance had been made for the cut-off of the glass. The intensity of sunlight on a clear day is approximately 10^{15} to 10^{16} quanta/cm²/min in the spectral range from 2900 to 4100 Å [4]; this is of the same magnitude as our light source. The sample was

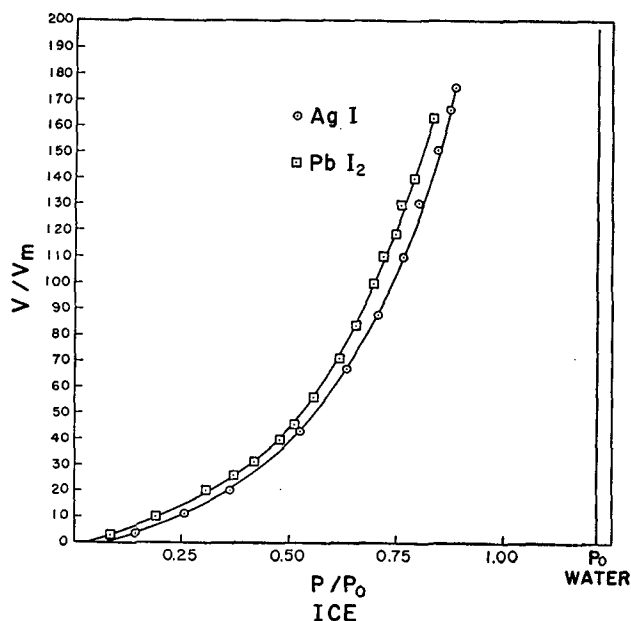


FIG. 3. Adsorption of water vapor on silver iodide and lead iodide at -20°C.

exposed to the light source for 48 hr and was continually agitated with a spatula to insure even irradiation of all particles. After irradiation, portions of the silver iodide were weighed and transferred to the adsorption apparatus for study.

3. Discussion

Previous work has shown that, while silver-iodide nuclei are effective in producing ice crystals from supercooled water clouds, if these nuclei are exposed to ultraviolet light, or strong sunlight, and their surfaces partially reduced to silver [5; 6], their effectiveness in causing ice formation is considerably diminished [7; 8]. Inn [9] found that the nucleating ability of his silver iodide was completely destroyed in 10 to 20 min when it was exposed to an ultraviolet light source with an energy flux of approximately 10^{16} quanta/cm²/min. Birstein [10] confirmed these results and found that the destruction of a silver-iodide particle's nucleating effectiveness is greatly dependent on the state of the particle's surface. If water vapor is adsorbed on silver-iodide nuclei before exposure to ultraviolet light, the ability of the particles to resist destruction of their nucleating ability is considerably increased. The ability to resist destruction of nucleating properties is directly dependent on the amount of water vapor adsorbed on the particle surface.

Later studies by Birstein on the adsorption of water vapor on nucleating agents [1] have shown that a unique type of adsorption isotherm is obtained for water on silver iodide and lead iodide. The curves obtained, where V/V_m , the total volume of gas adsorbed divided by the volume of gas in a monolayer, is plotted against P/P_0 , the partial pressure or relative humidity, can generally be described as a family of "type III" curves [11]. Adsorption is low at low partial pressures and increases as the pressure of the system is increased. The steepest portion of the curve begins at a partial pressure greater than 0.50 and continues until saturation is reached at the temperature of the isotherm. While most non-nucleating solids adsorb water vapor to thicknesses of the order of nine layers at saturation, silver iodide and lead iodide will adsorb almost 200 layers of water vapor on their surfaces at 20°C (fig. 2). As the temperature of the isotherm is decreased, adsorption increases. At temperatures below 0°C, where the saturation approached may be either ice or water saturation depending on whether the adsorbed layers are oriented in an ice-like or water-like structure, the isotherms approach ice saturation in all cases (fig. 3).

The conclusion that ice-crystal formation can take place by an adsorption mechanism was further substantiated by an experiment in which silver iodide and lead iodide were introduced into a cryostat held at

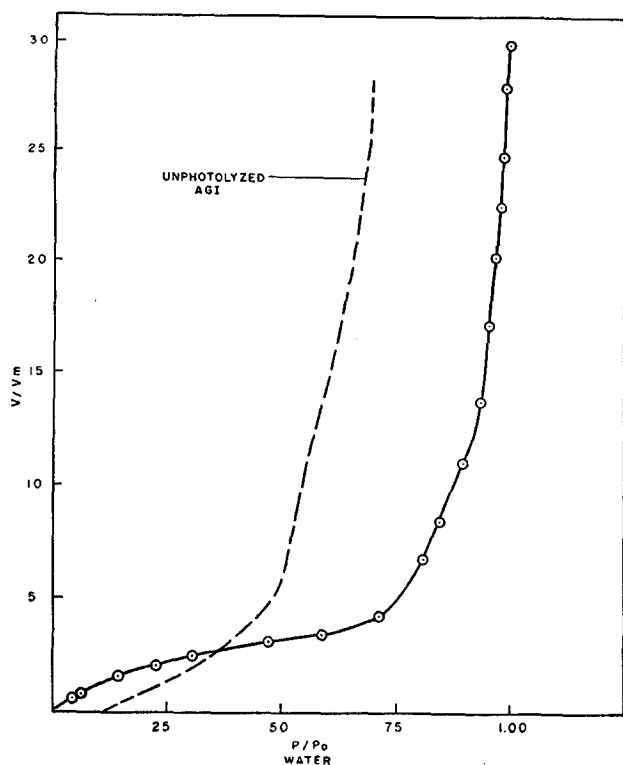


FIG. 4. Adsorption of water vapor on photolyzed and unphotolyzed silver iodide at +20°C.

-20°C and ice saturation. In both of these experiments, after a time lag of about 1 min, ice crystals appeared. The only source of water in these experiments was the vapor in equilibrium with the ice frozen out on the walls.

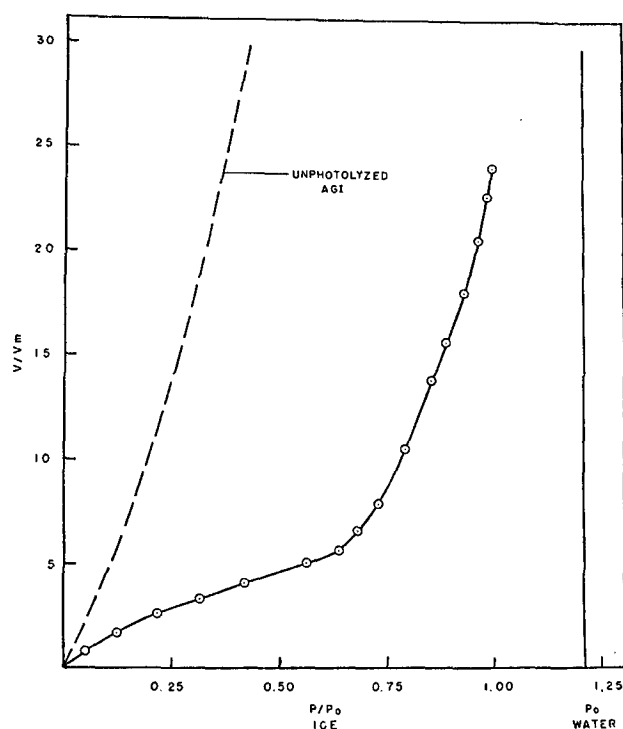


FIG. 5. Adsorption of water vapor on photolyzed and unphotolyzed silver iodide at -20°C.

Because of the evidence that nucleation on silver iodide and lead iodide proceeds by a surface or adsorption mechanism, and because of the work showing that, as a silver-iodide particle surface is reduced, its nucleating effectiveness decreases, and also since destruction of nucleating ability by photolysis was shown to be so strongly dependent upon the initial condition of the surface, it was decided to measure the adsorption isotherms of water vapor on photolyzed silver iodide. Since water vapor on unphotolyzed silver iodide gives an isotherm characterized by extremely high adsorption at high partial pressures, and since this type of curve is also characteristic of lead iodide, another excellent nucleating agent, these experiments were run to determine the change in its adsorption isotherm as a silver iodide sample had its nucleating ability destroyed.

The results of the +20°C isotherm are illustrated in fig. 4. Comparison with the unphotolyzed silver-iodide curve illustrates the marked difference. While the silver-iodide curve exhibits little adsorption at low partial pressures and a steep rise above a partial pressure of approximately 0.60, the photolyzed silver iodide shows marked adsorption at the lowest partial pressures. In this type II curve, monolayer formation is complete at a partial pressure of approximately 0.08. At $P/P_0 = 0.17$, two layers are complete; however, at the inflection point of $P/P_0 = 0.75$, only four complete layers have been adsorbed. For the unphotolyzed material, the first adsorbed layer is not complete until the partial pressure has reached 0.30; two layers are complete at a pressure of approximately 0.35; but at $P/P_0 = 0.75$, 68 layers have been oriented on the silver-iodide surface.

The results are equally striking on the isotherm obtained for water on photolyzed silver iodide at -20°C (fig. 5). At this temperature, the curve is similar in shape to that obtained at +20°C; it is a type II curve with highest adsorption at the lower partial pressures. When the +20°C curves on photolyzed silver iodide are compared quantitatively, adsorption is greater at -20°C than at +20°C at coverages below five layers when volume of gas adsorbed is plotted as a function of partial pressure. As the partial pressure increases, however, adsorption falls off more rapidly than at +20°C, and the total number of layers adsorbed at saturation is 24 compared with 30 at the higher temperature. For the unphotolyzed silver iodide, the adsorption at -20°C is greater than at +20°C at all partial pressures.

From a comparison of the adsorption isotherms on photolyzed and unphotolyzed silver iodide, certain conclusions can be drawn. As the silver-iodide surface is reduced, the number of high energy sites available for water adsorption increases, and water adsorption increases at the lower pressures. These sites differ, however, from those on unphotolyzed silver iodide in

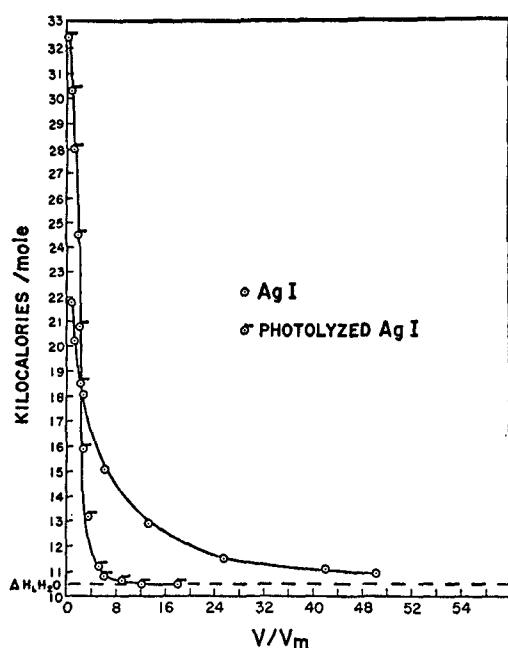


FIG. 6. Heat of adsorption of water vapor on photolyzed and unphotolyzed silver iodide.

the manner of orientation of the water molecules. The water molecules on the photolyzed silver iodide are oriented in a manner which inhibits the adsorption of ice-oriented layers on top of the first few. At -20°C , on unphotolyzed silver iodide, the adsorbed layers grow until an ice crystal is formed. At -20°C on the photolyzed silver iodide, however, because the surface of the crystal and orientation of the adsorbed layers are changed, growth can no longer occur in an ice-like structure; and at ice saturation, with only 26 layers adsorbed on its surface, the photolyzed material does not form an ice crystal.

The difference in adsorption between the photolyzed and unphotolyzed materials is also quite apparent from a study of the heat-of-adsorption curves of these two materials.

By use of the $[d(\ln P)/d(1/T) = -\Delta H/R]$ Clausius-Clapeyron relationship [12] to determine the heat of adsorption, a curve is obtained (fig. 6) for the photolyzed silver iodide. It shows an extremely high heat of adsorption at coverages below five layers; as the coverage increases beyond this point, the heat of adsorption drops until it becomes equal to the heat of liquefaction of water. This contrasts strongly with the curve for unphotolyzed silver iodide, in which the heat of adsorption at the lower coverages is smaller, but remains greater than the heat of liquefaction of water even at coverages exceeding 50 layers.

4. Conclusions

These experiments confirm earlier conclusions about the sensitivity of nucleating ability of a solid to surface structure, and also about the dependence of nucleating

ability upon the ability of the solid to adsorb and orient water molecules on its surface. As the surface is treated in a manner which will reduce the adsorption of water vapor, nucleating effectiveness also falls off; or conversely, as nucleating ability falls off, adsorption of water vapor is also diminished.

These data offer a number of interesting possibilities for future work in the heterogeneous nucleation of supercooled clouds. Since it is possible to decrease the nucleating effectiveness of silver iodide in the laboratory by treating its surface in a manner which will reduce water adsorption (and since lead iodide, the only other substance known with a nucleating efficiency approaching that of silver iodide, gives a water isotherm similar to the silver iodide), it should be possible to inhibit nucleation of lead iodide, too, by treating it in a manner to reduce water adsorption.

While an adsorption-type mechanism has been postulated for ice-crystal formation from supercooled clouds by use of insoluble nuclei in the laboratory, there is at present no good evidence of the mechanism responsible for atmospheric ice-crystal formation at temperatures of the order of -20°C . If, however, techniques can be found for the inhibition of nucleation in the laboratory, where the mechanism is known, and these same techniques can be extended to inhibit atmospheric ice formation, much valuable evidence will be gained concerning the mechanism of atmospheric ice formation.

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