

## THE MECHANISM OF ATMOSPHERIC ICE FORMATION, I: THE CHEMICAL COMPOSITION OF NUCLEATING AGENTS

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### ABSTRACT

A careful study has been made of the nucleating ability of various chemicals. The nuclei were prepared in a nitrogen atmosphere, rather than air, to prevent a reaction at the hot filament with atmospheric oxygen. With use of these carefully controlled conditions, numerous materials previously reported as effective were found to be poor nucleating agents. The discrepancies among the various sets of data were found to be due to reaction at the filament of the solid material and oxygen in previous investigations. The results are examined to determine how they support prevailing theories on ice-crystal formation.

### 1. Introduction

One of the most perplexing, yet extremely important, problems confronting contemporary cloud physics is the question of how ice crystals are formed in the free atmosphere. This problem has occupied the attention of various able investigators in this country and abroad during the past two decades, with the result that a fairly imposing body of literature has been compiled on various aspects of the problem.

Aside from the establishment of a temperature dependence for the number of ice crystals appearing in natural air [1], this activity has yielded little quantitative information concerning the physical or chemical conditions surrounding the atmospheric phase transition which produces ice crystals. Those experimental studies which have been performed to elucidate the mechanism for natural ice-crystal formation present little agreement in interpretation of experimental results [2; 3; 4; 5]; consequently, no generally acceptable theory exists today. The inability of this past effort to solve the problem constitutes no adverse reflection on the capabilities of the various investigators; rather, it is a tribute to the complexity of, and the inherent difficulties involved in, this problem.

A part of the work in cloud physics at the Geophysics Research Directorate, Air Force Cambridge Research Center, has been concerned with a number of aspects of this question since 1950. Aircraft icing, ice fog, precipitation, and exhaust trails are examples of operational problems where a connection to ice-crystal formation processes is obvious.

Our approach to this subject has stressed the formulation of model mechanisms, which could be tested rigorously under controlled laboratory conditions, in the hope of acquiring a better appreciation of the atmospheric process. Since the formation of ice crystals in the laboratory and in the atmosphere is be-

lieved to result mainly from the action of specific nuclei, we have devoted a great deal of attention toward studying the behavior of specific chemicals under closely controlled conditions.

The excellent work Vonnegut [6] performed on silver iodide did much to advance the idea that ice-crystal formation proceeds principally on the surface of an ice-like solid nucleus. We have followed up this approach by making detailed studies of the interaction between water-vapor molecules and various solid substrates, by means of adsorption measurements [7] which tend to confirm the validity of Vonnegut's explanation. We were extremely interested, therefore, in Hosler's discovery [8] of a variety of effective chemicals, many of which might act differently than the proposed silver-iodide mechanism.

Before accepting the apparent failure of the solid surface-adsorption argument to account for the action of obvious liquid or gaseous nuclei, in 1951 we made a preliminary check of many of Hosler's compounds (plus some not reported by Hosler) in a supercooled cloud below  $-5^{\circ}\text{C}$ . The results are given in table 1.

In the main, these results agreed with those reported by Hosler. Notable exceptions were silver-nitrate spray, and  $\text{PbO}$  and  $\text{AgNO}_3$  when heated under less drastic conditions.

It was clear that the method of dispersal of the nuclei had a pronounced effect on the results. Hosler had pointed out the possibility of the substances undergoing chemical change during heating, making it difficult to state precisely what is causing the nucleation. However, this very knowledge is needed before one can attempt a connection between the chemical structure of the nucleus and its ability to nucleate.

In the summer of 1952, it was decided to repeat this preliminary work under conditions which would lend

themselves to better interpretation of the results. The aerosols were generated in a closed system from hot-wire spirals, regulated to prevent thermal decomposition, and the system was under a nitrogen atmosphere to avoid oxidation.

## 2. Experimental procedure and results

All runs were made in an atmosphere of dried, purified nitrogen, rather than air; in this way, most of the side reactions on the filament were eliminated. Filament temperatures were carefully controlled, to avoid thermal decomposition of the solid material. The particles generated in all runs were studied in the electron microscope, and their size distributions were determined.

The apparatus used in this work (fig. 1) consisted

TABLE 1. 1951 investigation on ice nuclei.

Substance	Dispersal method	Results
AgI	Heated in flask and sampled with rubber bulb	Very effective for ice crystals
AgNO <sub>3</sub>	Heated in flask and sampled with rubber bulb	No conclusive results
	Spray of dilute solution	No conclusive results
	Deposited AgNO <sub>3</sub> directly on wire heated and inserted fuming assembly into cloud	Produced many ice crystals
I <sub>2</sub>	Vapor from stock bottle at room temperature drawn into bulb	Negative
	Heated in flask and sampled with bulb	Positive
NaI	Heated in flask and sampled with bulb	Positive
KI	Heated in flask and sampled with bulb	Positive
PbCl <sub>2</sub>	Heated directly on wire in supercooled cloud	Positive
BaI <sub>2</sub>	Heated in flask and sampled with rubber bulb	Positive with evidence of decomposition
CuI	Heated in flask and sampled with bulb	Positive
Br <sub>2</sub>	Sampled from stock bottle at room temperature with bulb	Negative
PbO	Heated in flask and sampled with rubber bulb	Negative
	Heated directly on wire in supercooled cloud	Positive
Hg <sub>2</sub> Cl <sub>2</sub>	Heated in flask and sampled with bulb	Negative
CuBr	Heated directly on wire in supercooled cloud	Positive
NH <sub>4</sub> Br	Heated directly on wire in supercooled cloud	Slightly active
HgCl <sub>2</sub>	Heated directly on wire in supercooled cloud	Positive
As <sub>2</sub> O <sub>3</sub>	Heated directly on wire in supercooled cloud	Positive
CrBr <sub>3</sub>	Heated directly on wire in supercooled cloud	Positive
CuSO <sub>4</sub>	Heated directly on wire in supercooled cloud	Negative
CuCO <sub>3</sub>	Heated directly on wire in supercooled cloud	Negative
NaCl	Heated directly on wire in supercooled cloud	Negative
CdS	Heated directly on wire in supercooled cloud	Negative
NH <sub>4</sub> NO <sub>3</sub>	Heated directly on wire in supercooled cloud	Negative
AgBrO <sub>3</sub>	Heated in flask and sampled with bulb	Positive

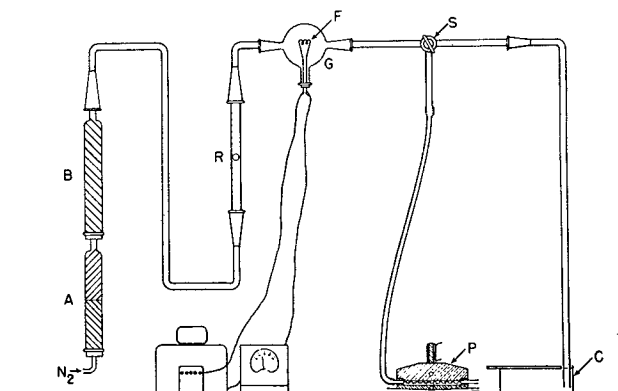


FIG. 1. Nuclei generator.

of a glass column (A) filled with drierite and caroxite, and column (B) filled with a glass-wool filter. Nitrogen which entered at the bottom of (A) was dried, and the CO<sub>2</sub> was removed; the nitrogen was then filtered in (B), to remove foreign particles. The clean, dry gas was metered through rotameter (R) and passed through generator (G), and over filament (F) coated with the material under investigation. A controlled current was passed through the filament, and the particles formed by the sublimation of the vapor from (F), followed by condensation, were swept along in the nitrogen stream to the three-way stopcock (S). A portion of the nuclei was collected in thermal precipitator (P) for electron microscope study, and the remainder passed into glass cell (C) for storage until nucleation tests were made. The entire generator beyond column (A) was constructed of glass and joined with ungreased standard-taper ground joints.

After the particles were prepared, they were withdrawn from (C) and pipetted into a cryostat maintained for most experiments at  $-20^{\circ}\text{C}$ . The cryostat (fig. 2) consisted of three dewar flasks and a centrifugal pump. The copper coil immersed in (J) was covered with a dry-ice and acetone mixture. Acetone from dewar (K) was pumped by the centrifugal pump (D) through the coils in (L), and then discharged into reservoir (K). The cold coils in (L) were used to cool

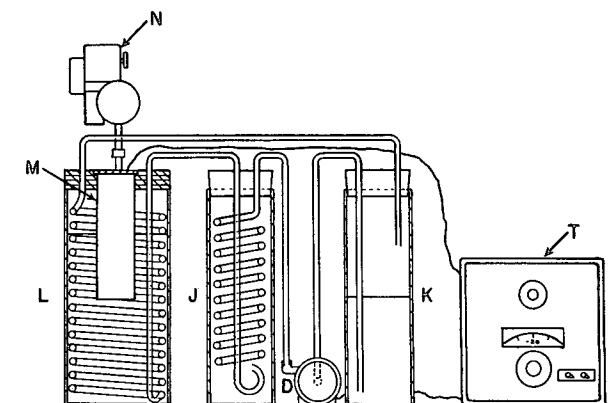


FIG. 2. Supercooled cloud cryostat.

the acetone with which the dewar flask had been filled. A brass cylinder (M) (5 in deep and 3 in in diameter), closed on one end and covered on the other with a plexiglass window, was suspended in the acetone. The bath in (L) was stirred with stirrer (N). When the centrifugal pump was going, therefore, the liquid in (L) and chamber (M) were being cooled. A thermocouple in (M), attached to a "Tag" Temperature Controller-Indicator (T), controlled the centrifugal pump. When (M) was cooled to the desired temperature, the pump was automatically shut off; when the temperature rose, the cooling system was again turned on. Using this system and neglecting the warmer upper quarter of the brass cylinder, we were able to control the temperature within 1C.

A cloud was produced in the cold chamber. After the material being tested was injected, ice formation was monitored visually by illuminating the interior of the cylinder with a beam of parallel light and watching for the characteristic glitter of ice crystals.

The filaments used in all nucleation experiments were prepared in a similar manner. Sixteen-inch lengths of 21-gauge nichrome wire were wound around a (5/16)-in steel rod, and twelve evenly spaced turns were made. The resistance of a filament was 1 ohm. After the filaments had been checked for uniformity, they were coated. If soluble salts were used, this was accomplished by dipping the coil in a saturated solution of the salt being studied, drying in an oven, and continuing the dip-and-dry process until a sufficiently thick deposit had been built up on the wire. If a suitable solvent could not be found for the salt, and the salt was not easily decomposed by extreme heat, the nichrome wire was heated to red heat and plunged into a solid salt. The salt then melted, became fused

to the hot wire, and in most cases gave a coating suitable for nuclei preparation.

The temperature of the filaments as a function of current applied was determined by coating a series of filaments with compounds of known melting points. Nitrogen was passed through the system at a constant rate, approximating the flow rate during a run, and current was applied. When the compound on the filament melted, the current was determined. The results were plotted (fig. 3) to give a usable curve for temperature as a function of filament current.

During every run, a fraction of the particles was collected in thermal precipitator (P) (fig. 1) for electron-microscope study. The thermal precipitator consisted of a bottom section cooled with water, upon which rested a brass plate containing electron-microscope sampling screens. The upper section of the precipitator was heated with a resistance-wire heater. A temperature difference of 65C was maintained between sections. The gas stream passed over the cold sampling plate, and the particles were precipitated on the formvar-coated sampling screens.

For a constant flow rate and a constant temperature gradient in the precipitator, the point of precipitation is a function of particle mass, or, for a particular substance, a function of size. To achieve unbiased sampling, the flow rate was adjusted to permit complete nuclei removal from the gas stream within the confines of the precipitator. These nuclei were caught on a series of sample screens, whose subsequent combined analysis yielded the complete size distribution.

TABLE 2. 1952 investigation of ice nuclei.

Compound	Behavior as an ice nucleus in this investigation	Behavior as an ice nucleus when prepared in air
AgI	yes	yes [1; 6; 8; 20; 21; table 1]
AgNO <sub>3</sub>	no	yes [8; table 1]
Ag <sub>2</sub> S	yes	yes [8]
PbI <sub>2</sub>	yes	yes [6; 8; 20]
NH <sub>4</sub> I	no	yes [8]
NH <sub>4</sub> I (spray)	no	yes (spray [8])
Cu <sub>2</sub> I <sub>2</sub>	no	yes [8; table 1]
I <sub>2</sub>	yes	yes [6; 8; table 1]
NaI	yes	yes [8; table 1]
NaI (spray)	no	yes (spray [8])
KI	yes	yes [8; table 1]
KI (spray)	no	yes (spray [8])
SnCl <sub>2</sub>	no	...
HgCl <sub>2</sub>	no	yes [8; table 1]
CdI <sub>2</sub>	no	yes [1; 8], no (spray [22])
PbO	no	yes [8; table 1]
O <sub>3</sub>	no	yes [8], no [17]
HgI <sub>2</sub>	no	yes [8]
PbCl <sub>2</sub>	no	yes [8; 21; table 1]
CuSO <sub>4</sub>	no	yes [8], no [table 1]
HgO	no	yes [8]
MnCl <sub>2</sub>	yes	yes [21]
SnI <sub>2</sub>	yes	...
LiF	no	no [8]
LiCl	no	...
CaCl <sub>2</sub>	no	no [8]
KBr	no	no [8]
BaCl <sub>2</sub>	no	no [8], yes [21]
NaCl	no	no [8; table 1], yes [21]
SnBr <sub>2</sub>	no	...

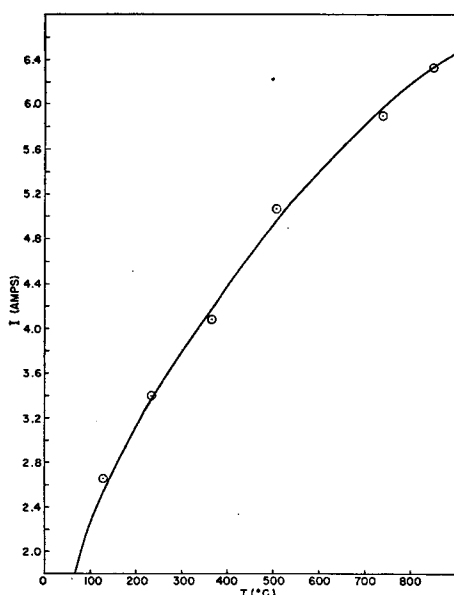


FIG. 3. Filament temperature as function of current.

Spray experiments were run by dissolving the salt in question in distilled water and spraying the solution from a nebulizer directly into the supercooled cloud.

We chose  $-20^{\circ}\text{C}$  as the arbitrary temperature to define good nucleating ability. The cryostat was set to maintain a temperature of  $-20^{\circ}\text{C}$ , and all materials that gave ice particles above that temperature when injected into a supercooled cloud were classified as good nucleating agents. Those which produced no ice were termed poor.

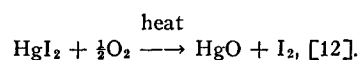
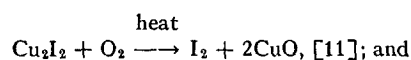
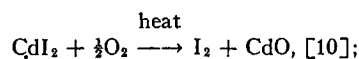
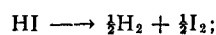
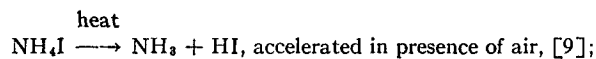
### 3. Discussion of results

The results of the more closely controlled experiments are shown in table 2. It is apparent that a number of substances previously found to be effective as ice nuclei by the present writers and others failed in this respect under the new set of conditions.

These discrepancies raise two immediate questions. First, the suspicion is that one is not dealing with identical chemical substances under the two different circumstances. And secondly, do these latter experiments shed new light on the manner in which ice crystals originate?

A discussion at this time of the effect of free iodine will prove helpful in explaining the discrepancies involving iodides. Vonnegut [6] first pointed out the ability of iodine vapor to nucleate supercooled clouds. He attributed this effect to a reaction between the iodine vapor and minute traces of silver in the air, to produce silver-iodide particles. Hosler [8] suggests sodium-iodide salts as the foreign material, because of the greater abundance of sodium salts in ordinary air. The necessity for invoking an intermediate compound arises because Vonnegut found the ice-nucleating property of iodine vapor disappears in a closed atmosphere. Although at the moment one is not sure how iodine vapor acts, its effectiveness is unmistakable.

The activity of those iodides which we found inactive under a nitrogen atmosphere may be explained nicely by decomposition-oxidation reactions leading to the formation of free iodine when these materials are heated in air. Recourse to the literature shows the following reactions involving the subject iodides:



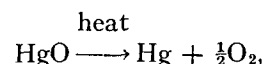
In each of these reactions, heating at elevated temperatures in air is sufficient to give an appreciable reaction. Once iodine vapor is produced, it can react

further with unknowns to form ice nuclei. We were not able to produce ice nuclei when cadmium iodide, cuprous iodide, and mercuric iodide were prepared in a nitrogen atmosphere. In agreement with Hosler, we observed ice crystals when ammonium iodide was used. Because of its ease of decomposition ( $400^{\circ}\text{C}$ ), and because we observed, issuing from the nuclei generator, a faintly violet-colored vapor which showed the positive presence of iodine by turning starch-KI paper black, we concluded that it is the iodine vapor, not the ammonium-iodide which is active as a nucleating agent, and therefore, listed ammonium iodide as inactive.

The cases of silver nitrate, mercuric chloride, lead oxide, and lead chloride offer no ready explanation as do the iodides. We found these substances active when heated in air, but inactive when heated in nitrogen. Each of these materials decomposes and oxidizes when heated strongly in air. The principal reaction products are oxides of varying composition [10; 13; 14; 15], and apparently these are active as ice nuclei.

The remaining compounds, copper sulfate and ozone, prepared in air and in nitrogen were found to be inactive. Hosler reports activity under his conditions. This disagreement should be settled by other independent studies, although Regener [16] reported ozone as ineffective as an ice nucleus as early as 1940.

Negative results were obtained on mercuric oxide under nitrogen atmosphere. In the 1951 study we did not test this substance, and thus have no check on its behavior in air, although this material decomposes readily on heating to mercury and oxygen [12],



neither of which is effective as an ice nucleus.

Manganese chloride, reported active by Facy [21] when vaporized in air, was found active also when generated under the nitrogen atmosphere. The manganese chloride, however, was found to darken on the hot filament in spite of the nitrogen atmosphere. Additional purification, by passage of the carrier gas over hot copper, did not completely prevent darkening from taking place. In view of this darkening, it is uncertain whether manganese chloride, manganese dioxide, or manganese monoxide was the nucleating agent. Manganese chloride reacts with oxygen to form manganese dioxide; heating the manganese dioxide further produces manganese monoxide [17]. More study is necessary before the nucleating material can be identified.

Stannous iodide, though unstable when heated in oxygen, is stable at red heat in an oxygen-free atmosphere. While it hydrolyzes rapidly in moist air at room temperature, it is stable at low temperatures and is sparingly soluble in cold water [18]. In view of these

results, it appears that the stannous iodide remained unchanged in the generation experiments and is an effective nucleating agent.

Aqueous solutions of potassium iodide, sodium iodide, and ammonium iodide were found to be ineffective when atomized into a cloud of supercooled water droplets at  $-20^{\circ}\text{C}$ .

Silver iodide, lead iodide, sodium iodide, potassium iodide, iodine, and silver sulfide were found to nucleate when prepared under an air or under a nitrogen atmosphere. All of these compounds, except iodine, are stable at high temperatures.

Where possible, after every run we examined a portion of our nuclei in an electron microscope. In all cases we were able to collect well-defined particles with mean diameters ranging from  $0.04$  to  $0.4 \mu$ . A typical size distribution is shown in fig. 4. Initial runs were made at lower temperatures with the smaller particles, and the temperature was gradually increased until the material was sublimed from the filament just below the melting point. These results preclude the possibility that poor nucleating ability was due to a failure to produce a sufficient supply of adequately sized particles.

#### 4. Conclusions

The results in table 2 are strong evidence that our initial surmise was true; the manner of preparation leads to different chemical products, if decomposition or oxidation of the starting chemical is possible. Yet, having established this as the reason for those disagreements between table 2 and table 1 or between table 2 and Hosler's active list, we find ourselves at no advantage in understanding the roles of these chemicals in the nucleation process. In fact, we have succeeded in removing these chemicals from the list of known ice nuclei and only can offer unknown substitutes.

On the other hand, the fact that silver iodide, lead

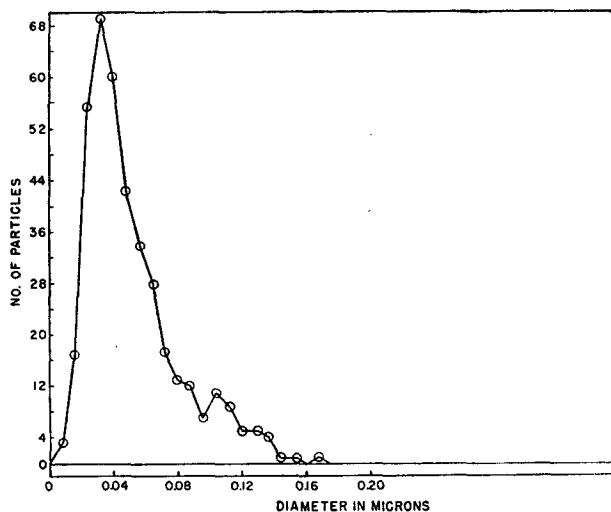


FIG. 4. Particle size-distribution of lead iodide.

iodide, sodium iodide, potassium iodide, stannous iodide, and silver sulfide either were unaffected by the temperature or by the oxidation, provides logical support for making a direct connection between these substances and their nucleating effectiveness without the danger of involving unknown reaction products.

This certainly constitutes a step forward toward the ultimate solution of the mechanism, since now one has available a reproducible and reasonably well-defined experiment. Some recent X-ray diffraction studies at this laboratory further establish the unchanged character of lead iodide and silver iodide after strong heating [19].

The failure of spray solutions of the soluble salts in both sets of our experiments lends more weight to our previous concept of a solid surface-adsorption mechanism for ice-crystal initiation. In this connection, Schaefer [20] describes a very interesting experiment to differentiate between freezing nuclei and sublimation nuclei. From his observations on lead iodide, he concluded that, once solvation commences, this substance loses its ice-nucleating property. We found a similar phenomenon in the case of sea salt. One might infer from these results that a freezing nucleus must be insoluble in water. Silver iodide and silver sulfide fit this description adequately. Lead iodide and stannous iodide are only slightly soluble, while sodium iodide and potassium iodide are highly soluble. This agrees with our observation that sprays of ammonium iodide, silver nitrate, and sodium iodide were ineffective ice nuclei, and with the general observation of Facy [21] that saline sprays are inactive above  $-41^{\circ}\text{C}$ .

The negative results on the sprays are at variance with the results published by Hosler [22] and Mason [23], and while we are in no position to explain the differences in results at present, it is hoped that they will be resolved in the near future by other investigators.

There remains the fact that sodium-iodide and potassium-iodide smokes, although soluble, did produce ice crystals.

Facy [21] reported a considerable number of hygroscopic chlorides as active ice nuclei at temperatures below  $-22^{\circ}\text{C}$ , when prepared as smokes. Facy felt that the reason why the smokes were active, while the aqueous solutions were not, was the preservation of a solid nucleus below the eutectic temperatures of the respective salts. This solid nucleus, according to Facy, was then able to cause the freezing of supercooled droplets by penetrating their surfaces.

Schaefer's [20] explanation of the anomalous behavior of lead iodide, wherein he proposes that no appreciable solution occurs when vapor molecules are condensed to form an ice crystal directly from the gaseous phase on the active nuclei crystals, seems

more acceptable to us to account for the observed behavior of soluble, hygroscopic smokes.

Facy's observation that the hygroscopic chlorides acted principally below  $-26$  and  $-33\text{C}$  suggests to us that the temperature where solution is not favored over direct vapor condensation is somehow connected to the concept of the eutectic point. Fournier D'Albe's [24] experience with cadmium iodide, in which he found it to serve as a sublimation nucleus below  $-10\text{C}$  and as a condensation (droplet) nucleus above  $-9.1\text{C}$ , is another interesting example which belongs to this category of temperature-dependent behavior.

In all these cases, it is clear that one was dealing with a solid crystalline surface as the initiating point for ice formation. We feel this piece of evidence is the basic clue to the mystery of the atmospheric process, and that the final solution will develop from a better understanding of the adsorption-solvation-crystallization processes.

Finally, the action of the unknown substances points to the necessity of additional research in this area. It is obvious that carefully controlled experiments are required before we can hope to accelerate our understanding in this phase of experimental meteorology.

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