EARLY EXPERIMENTS WITH SILVER IODIDE

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Ladies and Gentlemen: During the past several minutes I became so interested in Vince's talk and thinking back on some of the historic things that I have almost forgotten what I was going to say. I note the invitation to talk about the early work on silver iodide affords such a pleasant opportunity to think back and reminisce on some of the things that Vince has shown you that I have decided to tell you a similar and closely related story concerning how I happened to get involved with silver iodide and cloud seeding. What I'll try to do first is go back and tell you the chain of events which led to my involvement with silver iodide and then comment on this chain of events.....how it came about! The earliest memory I have of becoming interested in supercooling was during World War II when I was working at Massachusettes Institute of Technology in the Chemical Warfare Service. I was busy working on filters for smoke and aerosols, making radio active Triphenyl Phosphate smoke. This is an extremely interesting chemical to play with because it too supercools very nicely.

Through a friend, I became interested in the problem of aircraft icing and soon developed an association with our friend, Jim Dodson. His mentor, Henry Houghton, and I were working on the airplane icing problem. At this time I was still worried about supercooling in very large experiments where I dispersed water as an oil emulsion, eventually taking this below freezing and following the rate of nucleation by the change in volume. After the war I came to the General Electric Company and decided, "well, Vince Schaefer was working on supercool water and I knew that supercooling was a general phenomenon in physics and chemistry, so I decided to work on tin". About this time Vince conducted the cold box experiment you just saw in which he discovered nucleation with dry ice. Dr. Langmuir suggested that I might come over and work with their group because Vince's discovery produced a need for some detailed quantitative studies of ice crystal formation. Anyway, I came over and began working in Schaefer's and Langmuir's laboratory using the cold box apparatus, conducting some further studies on ice crystal production from carbon dioxide. However, I began wondering about the problem of foreign nuclei and it occurred to me that it might be possible to find a substance which had a crystal structure very close to water ice. If such a substance could be found perhaps it would be a good nucleus. I looked in the chem rubber handbook for data on crystal structures, (incidentally, that may not be possible anymore because I don't think the current chem rubber handbook contains any crystal structure information).

Anyway, I found several candidates that were closely related to ice. Of course, ammonium floride was no good because it is soluble and would act as its own anti-freeze. Then there was leadiodide and silver iodide. I tried lead iodide as an ice nucleus and it worked moderately well. I then tried silver iodide and it did not work at all! A few days later I got

talking with Vince about the problem and he said, "Well, maybe iodoform will work". So, we tried it out and it worked pretty well. Then, I believe Vince found out that iodine worked pretty well too, so the crystal structure here had no relation at all to ice. This was rather puzzling because the substances we used were somewhat erratic. That is, they worked pretty well to begin with and then the effect kind of tapered off.

I finally decided to look at other substances. For no particular reason, I wondered how metallic smokes might work. It was easy to make the smoke from metal by simply producing an electric spark between two electrodes. Among other things, I made a spark with silver coins as the elctrodes and was very surprised to get a nice display of ice crystals. But this too wore off after a few tries. Then it occurred to me that maybe this was because of a reaction with the iodine, so I put a little iodine in and, "oh boy", it worked fine!

I soon discovered that the silver iodide I had used was badly contaminated with sodium nitrate, an anti-freeze, and that was the reason that it did not work. So it soon became clear that silver iodide was actually a good ice nucleus.

It soon turned out, much to my surprise, that a particle of silver iodide did not have to be very large to work very well. With a particle as small as about 100 angstroms, you still had a pretty good nucleus. This was good news from the standpoint of economics because it meant you could produce a tremendous number of ice crystals from a single gram of silver iodide. Thus, we proved that it was possible to produce enough crystals to seed in the real atmosphere.

Of course, this immediately raised the question of how do you make a lot of these crystals in the real atmosphere. This led us to playing around with a variety of silver iodide generators. I guess the first was just an adaptation of the original experiment. We made an arc between two silver electrodes and blew air which contained iodine vapor past the electrodes. We also used the blow torch method where you put some silver iodide on a piece of fire brick and heat it with a simple blow torch. This works fairly well but most of the silver iodide decomposes to silver and the method is not very efficient. We also tried electrical resistance heaters coated with silver iodide. We even had string impregnated with silver iodide paste which we fed into a flame. We also had flares and pyrotechnic devices which contained silver iodide.

I believe one of the happiest things that I ran across in a textbook on inorganic chemistry was the fact that silver iodide, although it is one of the most insoluble salts, is readily soluble if you complex it with a soluble iodide. So, we made solutions of silver iodide in acetone by adding sodium iodide. This enabled us to do things like impregnating charcoal, or other such experiments as impregnating paper with silver iodide and then burning the paper to produce silver iodide smoke. We also made a generator consisting of an ordinary type spray nozzle. We would atomize the solution of silver iodide in acetone but instead of using air we used hydrogen or a hydrocarbon gas. We would light this and the flame would evaporate the spray of silver iodide and the resultant particles would ultimately condense to form an aerosol. We also made a super sized generator with the help of some people

from the General Electric Company who were working on ram jets. This device would burn an awful lot of silver iodide. Over this early period we tried a variety of these pieces of apparatus. Some of them are still in use.

So that is briefly the story of how the original work at G.E. happened upon silver iodide. Looking back, it has been interesting to watch the various steps which have occurred. The very necessary steps that have happened without which I would never have become involved in silver iodide. When I was a senior at M.I.T., the question came up, "What would I do on a thesis?" As a chemist, the various thesis projects available in chemistry looked more work than fun to me. I talked to a friend of mine who was a graduate student in physics and he suggested taking a thesis with Dr. Warren in the Physics Department. He was an x-ray crystallographer. I followed this advice and I am very happy I did because I had a very good time working with him and I learned a lot about x-ray crystalographic analysis. So that was a very important part. Without having this experience I'm sure that I would not have bothered with crystal structure.

Another important thing that occurred was a suggestion from my friend, Jim Dodson, to come and work on icing with him in the Meteorological Department at M.I.T. Eventually I became knowledgeable about the atmosphere. Like Vince, I hadn't even noticed the atmosphere until somebody showed it to me. Unhappily, Dodson was eventually killed on one of our aircraft missions.

Certainly most important of all was that I happened to be at General Electric at the right place and at the right time to be able to work with Vince Schaefer and Dr. Langmuir. In fact, I think I was the second guy to work with Vince's cold box. Most importantly, right after he had developed this beautifully simple apparatus, I had the chance to play with it. I think if I had not done this, somebody else would have done so very soon afterwards.

There is yet another point I believe is very interesting to bring up at this time. The work that I have just described about nucleation by silver iodide was not the earliest work on this substance. I would like to read you a letter I received back in 1968. This was still about 20 years after the silver iodide work. The letter is written in long hand and came from a man at the Max Planck Institute in Heidelburg. It reads.....

"Dear Dr. Vonnegut,

I am somewhat reluctant to approach you on a delicate matter which, thought important for me, might offend you. I hope to make it clear that no offense is intended. The matter concerns the ability of silver iodide to prevent undercooling of water which you used in a primary way first for rain induction. I was discovering the water nucleating power of silver iodide in 1936 and using it in a freeze thermostat with a water mixture. The thermostat patents were applied for but I could not follow up the matter since I had to leave the work in Germany. I discovered now that the refrigerator which I had built which incorporated the silver iodide freezing mixture was investigated by allied intelligence teams. Their reports were partly made public in 1946-1948. Reading your figures, I noted that, of course I might not have seen all, that you never mentioned in any way how you found out that AgI prevents undercooling of water

especially well, so it occurred to me that you might have heard of my device and might have considered this quality of silver iodide as common knowledge with an unknown source. You can imagine the matter, considering the success of your proposal, is greatly interesting to me.

Yours sincerely,

M.R. Block"

I wrote to Dr. Block to see if he had any publications on the matter. It turned out he did not. Because of the war, this information was not available. However, he did send me a scientific paper from a German scientific publication showing me that he had done x-ray crystallographic analysis on silver iodide. And also, back in the 30's he had published a very nice paper on nucleation. There is no question that this is probably the first work on silver iodide.

In concluding, I guess there are a couple of points that Vince has already touched on but I'd like to repeat. One is that the work on cloud seeding.....work that led to cloud seeding.....was internally sponsored work at the General Electric Company. This reflects great credit to G.E. for making it possible to create the climate for basic research. Another important thing is that the work Vince did, and the work that I did, was, I believe, primarily a matter of following one's curiosity. It came as a complete surprise to me some days after the initial discovery of silver iodide that, "Gee, this could be used in the atmosphere".

Thank you.