Journal of Fluorine Chemistry, 32 (1986) 7–24

THE SEVEN AGES OF FLUORINE CHEMISTRY

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Address presented July 19, 1973 at Santa Cruz, California, on receipt of the award 'For Creative Work in Fluorine Chemistry' sponsored by PCR

Members of the Fluorine Division, American Chemical Society, Ladies and Gentlemen

You have greatly honored me by my selection as the recipient of the Fluorine Award. The honor is magnified by the fact that Fluorine Chemistry will become much more important both relatively and absolutely in the future than it has been in the past, more significant culturally, scientifically, and industrially. In response to your request that I address this meeting, there is little that a person my age can do, who has been out of the laboratory for some years, except reminisce on the past or dream of the future. These, with your leave, I shall do.

As with man, Fluorine Chemistry can be seen to have seven periods or ages, and about these I can both reminisce and dream.

The beginning of the <u>first</u> age of Fluorine Chemistry is lost in antiquity. Early technologies both ceramic and metallurgical depended upon the temperatures which could be obtained in the fires then in use. Ceramic glazes and the gangue material associated with metallurgical ores needed to be melted. Just when, where, and by whom it was found that the melting process could be facilitated and the melting point lowered by the rock that flows (fluorite or fluorspar) is not known. Two things are, however, significant. It was very important in accelerating technology, and it gave us the name of our element. Fluorides are still important as fluxes in the metallurgy of iron, as electrolytes in those of aluminum and magnesium, and as addition agents in ceramics.

0020-1139/86/$3.50

The second age began about 200 years ago with the reaction of fluorspar and sulfuric acid by Marggraf in 1768. Repeating this reaction Scheele distilled an acid from it in 1771. Gay-Lussac and Thenard in about 1800 distilled the reaction mixture in lead or silver vessels and obtained hydrofluoric acid. Davy tried to obtain the element from this acid but was unsuccessful. This age came to close when Moissan in 1885 [1] did obtain the element by the electrolysis of hydrogen fluoride made conducting with potassium fluoride using platinium apparatus and electrodes at an electrical efficiency of 20%. Platinum fluoride was the chief product. The hydrogen fluoride used must be anhydrous. A long and laborious process of dessication of the salt KHF_2 was employed with the product then distilled from it. It is reported that Moissan was to demonstrate this great discovery before a committee of the French Academy. His preparations were careful and elaborate, but his demonstration was a failure, as he purified his hydrogen fluoride too well, and it was nonconducting. This was how he discovered the need for an ion producing salt.

The third age was dominated by the classical researchers of Moissan in France, Swarts in Belgium, and Ruff in Germany. It lasted until about 1920. At this time interest was at a low ebb; Moissan had passed on, Swarts was quite old, and Ruff's work had been retarded by World War I.

I remember very well the state of Fluorine Chemistry at the beginning of its fourth age. In 1922 I left the centers of learning of the middle west and journeyed way beyond the Rocky Mountains to that provincial place called Berkeley. I had heard of its vigorous and refreshing scientific and scholarly atmosphere, had met men from there and liked their attitudes, and understood that the emphasis was on scholarship and discovery and not on memorized factual material and the taking of unnecessary courses. After Dr. G. N. Lewis had turned down my application for an assistantship, I wrote him that I wished to go to no other place and pleaded for a chance. I believe I was the least imposing of that year's crop of graduate students. I was small, puny, and very scared. In selecting a research problem I needed something that did not require a large amount of library work and in a field where there were few competitors. Lewis and Randall's Thermodynamics had not yet been published, and data were being collected. Professor Joel H. Hildebrand had a related problem, the direct measurement of the potential of the fluorine electrode. It seemed to satisfy my requirements. The literature on fluorine was almost completely contained in a little book of 128 pages by Otto Ruff [2] published in 1920; and fluorine was not what most people desired to work with, so I would have few if any competitors. Incidently, this measurement has not yet been made. This was fortunate choice. Professor Hildebrand at that time was writing his book on solubility, was in charge of Freshman chemistry, and was also Dean of Men. I had plenty of stimulation for my efforts but neither sympathy nor reprimand for my mistakes.

Before measurements were possible it was necessary to have a reliable and steady stream of elementary fluorine. Moissan's method using platinum electrodes was beyond us. In Washington during World War I, a fluorine generator was developed made of copper with a graphite electrode and a mixed HF-KF electrolyte. After several months of laborious preparation it could be run for up to a maximum of two hours, when the insulating seals failed. In desperation I made an insulating seal of Portland Cement [3]. It was illogical but it worked, and I could run the cell twenty-four hours a day.

Anhydrous hydrogen fluoride was needed for vapor pressure measurements. We had only an aqueous solution in a lead carboy at the time. Converting this to the bifluoride, melting and electrolysing out the water, and then heating the dry salt gave the anhydrous material. We determined some of its properties. I am particularly proud of the freezing point measurement [4], which differed from the literature value by about ten degrees, but which has not been significantly changed in fifty years. The formula H_2F_2 was in use at that time based on a single measurement of the vapor density. By measuring the vapor pressure both statically and dynamically I found this formula to be without meaning. It was shown that the vapor was a mixture, and that an equilibrium between HF and H_6F_6 satisfied the vapor pressure data [5].

The demonstration that fluorine could be produced in the laboratory without too great an effort stimulated interest in its reactions and reaction products. Other laboratories began using similar or differently designed generators. I made one for Harvard University and set one up for the Edgewood Arsenal. In the years that followed Bancroft at Cornell and Cady at M.I.T. used newly designed generators. Many fluorides, particularly the higher valence and more volatile ones, were made and studied.

The properties of these compounds and the structure and binding forces of the H_6F_6 molecule challenged the then current chemical theories and stimulated further interest in Fluorine Chemistry. I became interested in the forces between atoms, molecules, ions, and free radicals. At a University far from Berkeley I endeavoured to study these forces by means of atomic and molecular beams and the collisions of the particles in them. In those days institutions had few funds for equipment and apparatus, and none was available from governmental sources. The experimenter made them in his spare time. Progress was slow in the beginning. Fluorine Chemistry, however, could always be depended upon for publications and so was continued for career reasons.

During this period I visited the laboratories of Lebeau in Paris. This was where Moissan had done his great research. I had hoped to see his original platinum apparatus, but this was gone and only a few replicas remained. I also visited Ruff in Breslau. He had half of a fair sized building for his laboratories and many helpers. He apologized for his meagre facilities due to war produced poverty. I was embarrassed when he assumed that in rich America, I would have more and better facilities. I did not.

Many more investigators throughout the world became interested in Fluorine Chemistry in this period. I remember that Henne at Ohio State was continuing the work started by Swarts and Bigelow at Duke by treating organic compounds with fluorine in the confines of metallic mesh and performing the very laborious separation of products.

World War II put a stop to fundamental research and new discoveries but it greatly accelerated the applications of old discoveries. War demand in three areas were to be satisfied by fluorine compounds. First, it was not known whether poison gas would be used or not, but for reasons of preparedness work needed to be done. Second, high octane gasoline was needed for wartime aviation. Third, there was the fear of atomic bombs so that efforts to prepare them were essential. Fluorine Chemistry contributed in a major way to all of these, but it is seldom given due recognition.

In my work with free radical beams long prior to the war I was trying to measure directly the magnetic moment of the free methyl radical and encountered difficulties which have not been resolved to this day. I felt that somehow the hydrogen atoms were the cause of the difficulty and hoped that, if they were replaced with fluorine atoms, a polyatomic free radical would result which would be more easily measured. At that time there were no chemical substances known which would provide a source of the CF_3 radical nor any synthetic methods for making them. It was decided to find such methods and make such compounds. As hydrogen fluoride was familiar to me and as it had not been employed as a chemical reagent by many chemists, I considered it as my starting material. Organic chemists were consulted as to the effect it would have on organic compounds, and their opinion was that it would be destructive. If this were true, fluorine compounds might result. Preliminary experiments soon showed that it was not true in general. We were disappointed, but from these experiments we learned that hydrogen fluoride was an excellent catalyst for many organic chemical reactions such as alkylation, acylation, rearrangements, polymerization and the like. It was superior in large scale operation to other acid catalysts. Used in the alkylation of isoparaffins it became the preferred catalyst for the production of aviation gasoline during the war [6].

An important contribution to theories of chemical reactions should result from the discovery of hydrogen fluoride catalysts. Extensive studies over a period of nine years were made of the rate under different conditions of one alkylation reaction, that of the homogeneous alkylation of toluene with t-butyl chloride as catalysed by hydrogen fluoride. High precision was possible in the measurements as the pressure of the product hydrogen chloride could be accurately determined during the reaction. It was shown that this reaction could not proceed by either an ionic or a free radical mechanism. As these two types of mechanism are relied upon for condensed phase organic reactions, this conclusion is disturbing. This research has not yet been fully considered by organic chemists in their theories of mechanism [7].

At the beginning of the war and the <u>fifth</u> age of Fluorine Chemistry there was concern about poison gas. This was increased when a sample of sulfur hexafluoride from a Canadian source showed very high toxicity. I was asked to prepare a sample of the substance. This I did but purified it in a closed system to constant physical properties. It was found to be completely nontoxic. The toxic agent was then found to be a one percent impurity of S_2F_{10} in the Canadian sample. We were then asked to find a satisfactory method for the preparation of S_2F_{10} which we were unable to do. I did not wish to work on poison gas but was instructed to do so, for I had worked in this field during World War I.

I suggested COFCl as a potential toxic agent, but the knowledgeable people said it could not be one as neither $COCl_2$ nor COF_2 were sufficiently toxic. I proceeded to make some anyway and submitted it for test. Immediately top secrecy was imposed, and the work taken away. H. S. Booth later told me that it had been transfered to his laboratory. The work was then taken from him to Washington where until the end of the war no one was able to repeat the synthesis.

I was consulting for an industrial firm interested in using hydrogen fluoride catalysis. Monofluoroacetic acid derivatives were being made in their laboratories. When its high toxicity to experimental animals was discovered, there was much concern, and the laboratories were closed for a time. The third new potential toxic agent was thus discovered. The fourth was an organic fluorophosphate. There were only five such agents discovered during this period, and four were fluorine-containing.

The war focused enhanced interest in Fluorine Chemistry when UF_6 became militarily significant. The fluorocarbons were soon in demand. Long before the war we had been persisting in the search for compounds from which the CF_3 radical could be obtained. A graduate student was started on a program to prepare CF_3Cl and attempt Grignard or similar reactions with it. This was a futile effort as we now know. The chlorine in fluorocarbon chlorides is much too inert for such reactions. However, we did find a way to prepare CF_3Cl in almost 100% yield and quite easily. We passed CF_2Cl_2 with F_2 through a copper tube at about 160°. This copper tube was not an ordinary one as we shall see. It was old, bent, battered, and discolored. It was salvaged from use in many previous experimental set-ups.

At about this time a small quantity of CF_4 was desired for physical measurements. It was known that it could be obtained by the reaction between the elements but that this was a hazardous procedure as a product tended to explode. The chief product of the explosions, however, was the desired compound. As a fluorine generator was available (one of the early ones with a Portland cement seal) and a new graduate student presented himself seeking a research problem, the preparation of carbon tetrafluoride was started. This was a special student particularly suited for this enterprise. In college he had been an athelete in football and baseball. He was strong and had a fast reaction time. The hazards of the experiment were explained and he was instructed in our ultimate safety procedure. This was, that in case of an explosion, to receive the results thereof on the rear instead of the front of his laboratory coat while hastily leaving the scene. The products made by the explosion, when controlled, were to be captured in cold traps and then evaporated into gas storage vessels.

Powdered carbon but no copper tubing for a reaction vessel was found in the chemical stores. As the other student was not using his beat-up tube at the time, it was borrowed. The rest of the apparatus was assembled, and I waited to hear about the explosions. Several weeks later a sad faced student appeared in my office complaining that he must be doing something wrong, as there were no explosions; and when the products were allowed to warm to room temperature, there was considerable liquid left in the cold traps. I hurried to the laboratory to see this clear transparent liquid remaining in the collection vessels at room temperature. Here was the product of the reaction between carbon and fluorine, and it must contain compounds primarily of these elements with at least two carbon atoms per molecule. I told the student not to be discouraged but to make more of the material and forget for the present the gaseous product in the storage vessels.

The student from whom the copper tube had been borrowed now wanted it back. He had exhausted his supply of CF_3Cl and wished to make more. By then a new copper tube had been obtained, and it was given to him. He soon returned demanding his old tube back as the new one did not give him a good yield. Trading the new tube for the old one satisfied him but soon resulted in complaints from the student, as the carbon-fluorine reaction in it resulted in explosions.

The question now was why this old tube was so superior for both these reactions. Tracing its past history it was soon realized that it had come in contact with mercury in previous use, and it was amalgamated on the inside. Mercury or mercury fluoride was found to be the catalyst for both reactions.

It was possible to make more of this fluorocarbon liquid, so that it could be fractionally distilled, and the fractions analysed, examined, and their properties determined. It soon became apparent that the original liquid was a mixture of saturated fluorocarbons of homologous series, ring as well as chain. In other words, this was the first sample of a mixture of the compounds of a new branch of chemistry, and some of the fractions distilled from it were the first isolated compounds of this new chemistry.

It was difficult to publish these results as there was little background literature to refer to, and there were no published means of analysis for these new compounds. The manuscript was refused several times. At that time it was the opinion of some of the chemists consulted in regard to the work that such compounds could not be made or if made would be unstable. As the then accepted means of analysis was unsatisfactory for these compounds, new ones were devised and used. The nearest literature reference is the work of Ruff in which the product of the reaction of fluorine with wood charcoal in a hard glass tube was collected. From it only CF_4, SiF_4, and CO_2 were identified. An unseparated heavy liquid was also obtained which had an odor and was reactive. It may have contained some higher fluorocarbons which modern techniques could have resolved, but its properties resembled those of the residues frequently found after fluorine comes in contact with glass.

In the manuscript submitted for publication the substances were called fluorocarbons because they were composed of fluorine and carbon. The editor and referees objected strenuously to this. They insisted that these substances, which contain no hydrogen and were not made from hydrocarbons were hydrocarbon derivatives, and they would not publish the paper until they were so named. They were so intent upon the names of the compounds in the text that they overlooked the title of the paper which was Fluorocarbons [8]. This is how the name entered the literature.

Before the start of the war there was fear that Germany would succeed in making atomic bombs. Work in this direction was considered urgent so as to know the possibilities or to beat the enemy to this new weapon. The separation of the uranium isotopes became very important. For methods involving diffusion, UF_6 is the only available compound. Its use on a large scale demanded development of methods of making it, of the large scale preparation of elementary fluorine, and of materials both to contain it and to construct the diffusion and other equipment. Harold Urey had heard of the fluorocarbons of which I had the only samples in existence, and he asked me for some. The sample I gave him was found not to react with the very aggressive UF_6. Immediately a great effort was begun to prepare fluorocarbons. My original method had been published by then. It was rejected as unsuitable for the immediate and urgent purposes, as it is not specific for individual compounds, and the problems of separation of them from the product mixture were too great.

I explained to those in authority at the time that I had another method of fluorocarbon production, which I described in detail. As this method had not been published and had not reached the pilot plant state and as it did not seem reasonable, it was not considered for use. As the fluorocarbons were, at that time, considered to be organic compounds, the search for methods of synthesis was delegated to synthetic chemists. A great deal of effort was expended and some very interesting results obtained. It was not until the end of the war that I was able to disclose the electro-chemical process, which by then was in large scale industrial use despite its unreasonableness. Because of the sensitive nature of anything associated with the atomic bomb work, the fluorocarbons were highly classified during the war. They were even disguised under the security name, Joe's Stuff.

The electro-chemical process for the production of the fluorocarbons and their derivatives was discovered in our continuing search for compounds which would provide a source of the CF_3 radical. The catalysed reaction between the elements gave us a method by which saturated fluorocarbons could be produced and enabled us to determine their properties. As they were found to be very stable and chemically unreactive, they were not promising sources of the radical. This was very good fun, but we were not satisfied. We too desired a method which would be more easily directed toward specific compounds.

The idea that hydrogen fluoride was a promising starting material for the desired compounds was still held. Finally it was decided to try the persuasions of electricity to cause it to react with organic compounds. It was known that oxygen and nitrogen containing organic compounds were very soluble in liquid hydrogen fluoride and formed electrically conducting solutions. The method of testing this occurred to me one evening. The next morning I asked a graduate student to perform a little experiment. In a six inch copper test tube held in an ice bath were placed hydrogen fluoride and butanol. A nickel wire held by a loosely fitting stopper served as the positive electrode. After passage of a direct current for several hours, the contents of the tube were poured over ice and the acid neutralized. A few drops of a clear liquid more dense than water and insoluble in it were obtained. Without doubt these drops contained fluorocarbon substances. The starting materials were water soluble, the product was not. Repeated experiments with other alcohols and then other substances confirmed the hope that a new process had been discovered. It was the electro-chemical process [9]. It was a simple matter to design a cell with alternating electrodes and no separators for larger scale production. The laboratory units were enlarged to plant size and functioned even better. This first commercial unit, as far as I know, is either still in use or is in stand-by condition.

It was soon found that this process could produce not only fluorocarbons but many kinds of fluorocarbon derivatives and fluorocarbons containing other elements such as oxygen, nitrogen, sulfur, and even hydrogen. Many kinds of starting materials could be used. The process cannot be the simple replacement of fluorine atoms for hydrogen atoms in the starting material because the products frequently have structures different from the raw materials.

At first it was thought that fluorocarbon derivatives would have properties more or less parallel those of hydrocarbon derivatives of the same structure. It was soon realized that this was not so and that reasoning by analogy with organic chemistry was unsatisfactory in this new chemistry. Some of the derivatives that were made had unexpected properties. We were hoping to make C_8F_{18} in an early experiment. We thought we had it in good yield as we had a large quantity of a constant boiling product, but its molecular weight was too high and the boiling point too low. The more we purified it the higher the molecular weight and the lower the boiling point. We actually had $[C_4F_9]_2O$ with a molecular weight 16 units higher than C_8F_{18} and a boiling point 3° lower. In addition the product had been scrubbed with sulfuric acid which might have removed $[C_4F_9]_2O$ if it had the properties of an ether.

Difficulties were encountered in trying to publish the results of these experiments. During the war publication was not possible. Afterwards the Journal refused to publish the manuscripts which were submitted. I wished to publish in a way that would give all the loyal graduate students credit for their parts in the work. This did not seem to be acceptable to the editor. In addition I could not adequately explain the mechanism which I might need to do to satisfy the referees.

The sixth age of Fluorine Chemistry began after the end of the war, when the war time restriction could be lifted and the knowledge and experience obtained during the fifth age could be disclosed and used. Teflon and the Freons became available and employed. The electrochemical process was employed on an industrial scale, and fluorine-containing pharmaceuticals appeared. Fluorine was produced on a large scale for the preparation of UF_6. A fluorine containing anaesthetic both nontoxic and noninflammable was tested. Fluorocarbon derivatives were used for fire extinguishing fluids, and fluorocarbons were found to be excellent dielectrics both liquid and gaseous for electrical condensers and transformers. It was finally recognized that fluoride ion was a natural and ever present constituent of natural waters and not an added poison, and that it was a constituent of some foods and drinking waters. The saturated pure fluorocarbons were shown to be so nontoxic that they could be used in the form of emulsions as artificial blood in living animals. The high solubility of oxygen in these liquids enabled experimental animals to be immersed in them with lungs filled and to breathe. They could later be returned to air breathing without apparent harm by draining the liquid from the lungs. The solubility of oxygen and nitrogen in liquid fluorocarbons is not abnormal. They fit Hildebrand's ideal solubility rule.

Experimental and theoretical interest in Fluorine Chemistry increased greatly during this age. Many complex inorganic salts were investigated. Emeleus at Cambridge performed brilliant studies of the halogen fluorides. The more volatile high valence type fluorides were further studied, and the fluorides of the inert gases such as xenon and krypton were made and investigated.

The seventh age of Fluorine Chemistry or perhaps its seventh heaven, is the age of the future. The knowledge and skills acquired in the preceding six ages have laid the foundation for Fluorine Chemistry to finally come into its own. It is to become the dominent division of Chemistry where great strides will be made.

The number of fluorine compounds identified and described will probably exceed those of any other element. The tremendous number of complex and coordination compounds will provide a wealth of substances for many purposes. Many previously unknown higher valence type compounds, some with high oxidation potentials will become known. Some will be used for rocket propellants and battery components. The number of fluorocarbons and their derivatives will exceed all fluorine free organic compounds. The higher molecular weight fluorosilicons and their derivatives, practically unknown in the sixth age, will become a well developed and active field of chemistry.

The great wealth of Fluorine Chemistry in the future will result from the both the development and improvement of presently known processes and the invention of new ones. The electrochemical process will be improved to operate at lower potentials giving much higher yields of desired products. The range of products will also be extended. The products of this basic process will be the raw materials for a new synthetic chemistry of fluorocarbons. For example, a saturated high molecular weight liquid useful as a lubricant will be made from low molecular weight fluorocarbons by use of atomic radiation. The new reactions will not be restricted to those of fluorocarbons with fluorocarbons, they will include reactions of fluorocarbons with organic molecules or other kinds of molecules to produce substances part fluorocarbon and part something else.

One very important class of such substances is the aromatic compounds that have one or more ring hydrogen atoms replaced by the fluorine atoms or fluorocarbon radicals. New syntheses will be found for making such substances particularly those with long chain fluorocarbon groups.

It has long been the scientific goal of chemistry to be able to predict the molecular composition and structure of a pure substance from its physical and chemical properties and conversely the properties from the molecular configuration and components. The availability of fluorocarbons and their derivatives of many known structures will in the future aid greatly in approaching this goal. That the saturated fluorocarbons approached the inert gases in their molecular force fields has been known since the fluorocarbons were first described. Recently it has been shown that the difference between the intermolecular forces of fluorocarbons and hydrocarbons results from the fact that they are primarily between the peripheral fluorine atoms in the fluorocarbons and between the hydrogen atoms of one molecule and the carbon atoms of another in hydrocarbons. The symmetrical fluorocarbons will be shown to be very much like the monoatomic gases, except for rotational energy. From this as a starting point it will be shown how to evaluate the contributions to entropy of various structures. The contributions of electrical dipoles to the properties of a substance will be shown by studies of monohydrofluorocarbons. Fluorochemicals will be of great value to further progress of theories of the liquid state and solubility. They will contribute greatly to knowledge of interatomic and intermolecular forces.

It is evident that our resources are finite and in danger of exhaustion. Anything, therefore, which conserves resources or causes less to be used is highly beneficial. In the next age fluorocarbons will contribute in a major way to these ends. New ways of making useful fluorocarbon articles will be found. These will withstand temperatures up to red heat, resist atomic radiation and both chemical and biological attack. Thus they will be relatively permanent.

The presence of fluorocarbon radicals in organic compounds will enable biologically active compounds to be made with enhanced medical properties and reduced toxicity. Many new medicines containing fluorine will be used in the future.

Eventually, Teflon and Freon will become obsolete like celluloid. The former will be replaced with fluorocarbon plastics which will be purer, resistant to destruction by atomic radiation [10] and will not depolymerize, and thus stand much higher temperatures. The latter will be replaced by chlorine free fluorocarbons which will be safer and will not be converted into toxic substances by ordinary fires.

As scholars we are interested in the preservation and storage of human knowledge. I can dream that in this seventh age, fluorocarbon chemistry will provide an efficient way of doing this. In transparent fluorocarbon plastic tapes will be imbedded micro-images in mineral pigments. These will provide the primary storage facility for libraries. They will be inert and can be expected to last for thousands of years. They will provide an answer to the knowledge explosion, as they will be stored in great quantities in a small space.

It has become very evident that energy sources are finite and limited and that most of them, such as the use of fossil fuels or atomic energy, cause serious pollution. In my dreams of this age seven I see the fluorocarbons solving both the problems of an ample supply of energy and also obtaining it without pollution.

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[*] Teflon is very sensitive to atomic radiation and is rapidly degraded by it. This prevented for a long time the testing of fluorocarbons in an atomic reactor because of the assumed danger to the reactor. I was finally able to persuade the officials at Oak Ridge to permit tests, and samples of hydrogen free fluorocarbons in aluminum containers were placed in an atomic reactor. After four weeks a spread of boiling points was noted but no charing or corrosion of the container.

If the recent article in Science, June of this year [11], correctly states the case there can be an ample supply of energy the world over without using either fossil fuels or atomic energy but only using solar power as provided in ocean thermal gradients. In many places in the tropical seas the surface water averages 25°C in temperature but at a depth of a thousand meters or more the temperature is about 5°C. Ocean currents such as the Gulf Stream keep the water in motion so as to provide a very large reservoir at these temperatures at any one place. The article in Science explains that it is not currently feasible to employ this temperature difference in heat engines despite the large volumes of water available, because the efficiency of current heat engines is too low and the size of the engines, boilers, and condensers is too large. The use of fluorocarbons as the working fluid will solve these problems and can make a major contribution to providing useful energy. First, a mixture of fluorocarbons, [CF_4, C_2F_6, C_3F_{10}, C_5F_{12}] can be used such that any desired vapor pressure can be obtained. This allows the engine to be designed according to the physical environment of the location rather than to the properties of the working fluid and thus gain efficiency. Second, both boiler and condenser can be made much smaller than is possible for hydrogen containing fluids because both boiler and condenser efficiencies are much higher for fluorocarbons. This is because of the low viscosity, low surface tension, and low adhesion to the walls. The stationary surface film is thinner and the rate of heat transfer greater than with any hydrogen containing fluid. Third, because fluorocarbons behave more nearly like ideal gases, the efficiency of the engine should be greater. Fourth, because fluorocarbons vapors have a greater density at the same temperature and have lower viscosities of both liquid and vapor, turbines, connections, parts, and tubing can be smaller. Fifth, an additional gain may be had by using fluorocarbon lubricants. In my dreams I see, therefore, great energy producing plants in the oceans using solar energy by means of fluorocarbon heat engines, and doing this without pollution of any kind. Perhaps we do not need to risk the hazards of nuclear power plants.

I wish to thank the Division for this honor and for the opportunity to unburden my soul of a few stories and a few dreams. I am impressed by the high quality of current research as represented by the papers of this meeting. Keep up the good work as Fluorine Chemistry has a large and promising future.

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