Personal report

A lifetime of fluorine chemistry

At this point in my life, upon receiving the ACS Award for Creative Work in Fluorine Chemistry, it seems like an appropriate occasion for me to provide a retrospective examination of my lifetime of work in the area of fluorine chemistry. I will mention only some of the experiences, some scientific and some nonscientific, that I have encountered. First of all, it might be of interest to mention how I became a fluorine chemist altogether. I did my PhD degree in *nuclear chemistry* and not fluorine chemistry at the Carnegie Institute of Technology now known as the Carnegie-Mellon University under direction of my thesis advisor – Prof. Truman P. Kohman. The subject of my thesis was called "*Search for long-lived natural beta radioactivities.*" and consisted of measuring the half-lives of some natural isotopes with extremely long half-lives. In 1953 I left Carnegie to take up a position at the Argonne National Laboratory (ANL). For the first six years that I was at ANL I worked on a highly classified project. While this work was interesting, it had the disadvantage that I was not able to publish anything. It had nothing to do with fluorine chemistry. At that time, which was about 55 years ago, fluorine chemistry was still considered a hazardous field and only the adventurous ventured into this field. Still the practice of fluorine chemistry had received a tremendous boost during the course of the Manhattan Project, because it had been necessary develop techniques for handling fluorine and many fluorine compounds in order to facilitate the separation of uranium isotopes in the form of UF_6 by the thermal diffusion process. At Argonne the facilities for handling fluorine were very advanced and materials were handled in nickel or monel vacuum lines. In most other laboratories fluorine and its compounds were still handled in glass systems. If these systems were not absolutely dry, fluorine compounds would be hydrolyzed with the liberation of SiF_4 in a chain reaction.

To get back to how I got started in fluorine chemistry. One of the nuclides in the list of long-lived natural radioactivities I had been interested in was the nuclide Re^{187}. This was expected to be radioactive with an extremely long half-life. The reason for this was because in minerals containing Re and Os there was always a high concentration of Os^{187} which must have been a decay product of Re^{187}. One of the problems with measuring the radioactivity of Re^{187} was that the very low energy of the beta particles emitted by the Re would cause them to be self-absorbed in a solid sample and thus the radioactivity of Re^{187} could only be measured in the gas phase. So now our problem was to find a suitable gaseous compound of rhenium. There were very few possibilities. The most

promising seemed to be $Re(CH_3)_3$ [1], which was listed in the literature as a volatile compound with a boiling point of 60 °C. We spent maybe a month trying to prepare this compound according to the directions in the literature, but to no avail. Finally we contacted Henry Gilman, the editor of Organometallic Chemistry, who said that it does not exist. So we had to look for another one. The one rather volatile compound of Re which suggested itself was ReF_6, which was reported to have a vapor pressure of about 300 torr at room temperature. According to the literature [2], ReF_6 was prepared by passing fluorine gas over rhenium metal at 125 °C. Assuming that this might work even better at a higher temperature, we passed fluorine gas over rhenium metal at 400 °C. The resulting compound was trapped downstream in a dry ice trap. The material we trapped out had, however, a much lower vapor pressure than that reported in the literature for ReF_6. So we kept fluorinating it at high fluorine pressures until the vapor pressure remained constant; namely, 25 torr at 0 °C. To make the story short, we had prepared the unknown compound ReF_7 [3]. One could indeed call this, although not earth shaking, at least a serendipitous discovery. It is interesting to note that about the same time we published these results, another paper was published in which it said, and I quote, "the nonexistence of ReF_7 has been amply confirmed". There is a lesson to be learned from this, of course, that one should be careful before publishing anything – a sin of which I have been guilty myself unfortunately (*vide infra*). In retrospect, if the compound $Re(CH_3)_3$ had existed I probably would not have become a fluorine chemist.

Since it was possible at that time to leave the classified project, I decided to devote myself to fluorine chemistry. I continued, for instance, to work on the transition metal hexafluorides. In this work we synthesized for the first time pure ReF_6 [4], free of ReF_7, and the compounds TcF_6 [5] and RuF_6 [6]. The synthesis of TcF_6 solved one of the mysteries of the so-called fluoride volatility process. This is a technique for processing spent fuel elements to separate plutonium and unreacted uranium from the fission products by treating the fuel elements with fluorine or molten fluorides. Technetium is one of the major fission products to the extent of about 6.3%. In the process the technetium disappeared and no one knew where, until it was discovered that it was lost as the volatile TcF_6. It so happened that there was a gram of technetium metal at hand and this was used for the synthesis. At that time technetium was sold by the Oak Ridge National Laboratories for \$2500/g. There was so much technetium stored and to try to get rid of some of it, shortly thereafter Oak Ridge lowered the price to \$100/g. So we bought another 25 g, which we converted to TcF_6. This was used to measure the heat capacity and other properties of TcF_6. The work with technetium on such large
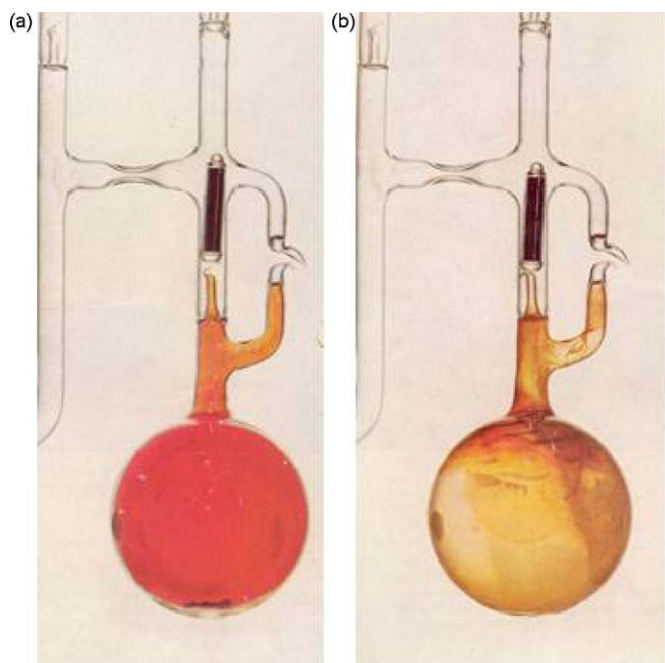
Fig. 1. Bartlett's reaction: $Xe + PtF_6 \rightarrow Xe^+PtF_6^-$. (a) Bulb filled with PtF_6 vapor. *Insert*: Space above break seal filled with xenon gas. (b) Bulb immediately after breaking break seal.

quantities was a bit daunting, because of the radioactivity of technetium. Although it has a long half-life of about 2×10^5 years, 25 g of technetium represents an enormous amount of radioactivity. The work was facilitated, however, by the fact that technetium emits only a very weak beta which did not penetrate the nickel or glass walls of the vessels with which we worked.

Another serendipitous discovery we made was the synthesis of XeF_4. This happened in 1962. The fluorine group at ANL, which at one time was headed by the late Bernard Weinstock, had first synthesized PtF_6 [7]. It is probably well known by now that Neil Bartlett [8], who first prepared $O_2^+PtF_6^-$, realized that the ionization potential of xenon was nearly equal to that of the oxygen molecule. In what has been called one of the most significant chemical discoveries of the 20th century, he oxidized xenon with PtF_6 to obtain what he called $Xe^+PtF_6^-$ (Fig. 1).

Thus the field of noble gas (NG) chemistry was founded. As it turned out, this reaction is somewhat more complicated than depicted here [9]. Instead of $Xe^+PtF_6^-$ the main product seems to be $XeF^+PtF_6^-$. We first heard about this work from Leonard Katzin, one of the chemists at the ANL Chemistry Division, who attended a convention in England. He suggested that we look into this. So we repeated this work as well as extending it to the oxidation of xenon with RuF_6, a much more aggressive fluorinating agent which spontaneously decomposes at room temperature into RuF_5 and fluorine. One of the things we noticed in this reaction was the formation of colorless crystals. We thought that perhaps the xenon is oxidized directly and so we tried oxidizing xenon with fluorine gas. This happened during the week of the International Fluorine Symposium in Estes Park, Colorado. Most of the ANL fluorine group attended this conference. Left behind at ANL were, John Malm, Howard Claassen and myself. Within this week we completed the synthesis and identification of XeF_4. During this work we also had evidence for the existence of a lower fluoride of xenon which was later identified as XeF_2. This work was published as a letter in *J. Am. Chem. Soc.* [10] in a record breaking three weeks in sharp contrast to the difficulties that Neil experienced. When he failed to get an acknowledgement of the receipt of his paper by *Nature*, he finally

withdrew it and published it in *Proc. Chem. Soc.* [8]. Maybe the editors of *Nature* had difficulties in appreciating the revolutionary discovery of Neil. Anyway, the publication of XeF_4 released an avalanche of publications in the field of Noble Gas Chemistry. The first conference on Noble Gas Chemistry [11] convened less than a year later at ANL. In the rush for priority to publish, many erroneous results were published. One example is the incorrect identification of the first krypton compound [12] by a group at Temple University as *KrF_4*. This compound was later identified by an ANL group [13] as *KrF_2*. Krypton tetrafluoride is still unknown. Other incorrect identifications were those of purported *XeF_5* by a group at the Ford Motor Company [14] later revised, however, to *$XeF_{5.96}$*, as well as a reported synthesis [15] of *XeF_8*. In all fairness it should be mentioned that the *first* synthesis of XeF_6 originated from that same fluorine research group at the Jozef Stefan Institute in Ljubljana [16]. There are other, less egregious examples. Mistakes were also made by theoretical chemists. One day we got a phone call from one telling us that he made a calculation which showed that XeF_4 is tetrahedral in shape. By this time it was already known that it was square planar from IR and Raman spectra. This work had not yet been published. The theoretician called back a short while later to acknowledge that he had made a mistake and revised calculations showed that it is indeed square planar. This is the stuff of which the scientific process is made. It is an inherently self-correcting process and as a whole these experiences cast no aspersions on the scientific process proper. Some other well-known examples of which most of you have heard would be the stories of polywater [17] and cold nuclear fusion [18]. These stories could be classified under what has been labeled by D. Rousseau as "pathological science" [19].

It goes without saying that we pursued intensively noble gas chemistry with work on XeO_4, $XeOF_4$, and ionic salts derived from the reactions of xenon and krypton fluorides and oxofluorides with Lewis acids and bases. Thus, we discovered the first KrF^+, $XeOF_3^+$, $XeOF_5^-$, XeF_5^+, XeF_7^- and XeF_8^{2-} salts.

Another interesting story connected with NG chemistry is the following. We received a phone call from a retired vice president of the American Can Company. He had the wherewithal to establish a laboratory in his basement where he tried to prepare the purest mercury possible. Why this interest in mercury? The can company used high current mercury switches for welding of seams in the cans. These switches would often foul up and the former vice president concluded that this was due to the presence of impurities in the mercury. He tried to purify mercury by sparking it in highly cleaned glass vessels under an atmosphere of NG. I don't remember which noble gas he used, but it was probably the cheapest and most accessible – argon. Anyway, the mercury in this sparked glass vessel had *no* meniscus. He even had printed leaflets touting this super pure mercury which he called 10^9 flat mercury in an attempt to market it. In the course of sparking, a tiny deposit developed on the walls of the glass vessels and he thought that these might be deposits of new NG compounds. We submitted this material to Martin Studier at ANL who had built a supersensitive time-of-flight mass spectrometer. The deposit turned out to be a mixture of metal and silicon oxides.

At about this time the first laser Raman spectrometers were developed and we investigated many fluorine compounds with this technique. One of the compounds that Howard Claassen and I looked at was vanadium pentafluoride [20]. By measuring Raman spectra as a function of temperature we were able to show that VF_5 is largely polymerized at room temperature. Later on I looked at the Raman spectra of NbF_5 and TaF_5 as a function of temperature. Unfortunately I covered only the temperature range from 90 °C to about 130 °C over which range there is no change in spectra [21]. My conclusion was that these compounds were not polymerized in the liquid state. *This was incorrect.* Some years later it was shown by the group of Ian Beattie [22] at the University of Southampton

using vapor density measurements and vibrational spectra at temperatures from 200 °C to 400 °C that these compounds were polymeric at temperatures of over 200 °C. So much for publishing prematurely!

In 1967 I moved from ANL to Jerusalem where I served as Professor of Chemistry at the Hebrew University. There I continued research in various aspects of fluorine chemistry, particularly reactions of oxides and salts in anhydrous hydrogen fluoride. As a result a number of new fluorides and oxofluorides were isolated including new oxonium salts.

Another subject I devoted time to was the impact of fluorine chemistry on the study of synthetic metals [23]. Synthetic metals are nonmetallic materials which exhibit some of the properties of metals such as high electrical conductivity and reflectivity. Some classes of synthetic metals are graphite intercalation compounds and doped polyacetylenes. At first I used powdered graphite in order to form intercalated graphite compounds with the purpose of storing them in bottles and using them easily as non-hazardous fluorinating agents. Using these intercalated fluorides a number of new organic fluorine compounds were identified [24]. Prof. John Fischer, from the University of Pennsylvania suggested to use highly oriented pyrolytic graphite (HOPG) as a substrate. This is essentially a form of graphite which is a single crystal along the *c*-axis but amorphous in the *ab*-plane. As such it lends itself to precise measurements of magnetic and electronic properties as a function of orientation [25] such as different magnetic suscept-ibility of intercalated OsF_6 depending on alignment in the magnetic field. One of the tools we used with much success in this work was the *Sartorius* Magnetic Suspension Balance (Fig. 2).

In this balance it was possible to follow weight changes in the course of reaction in the presence of corrosive gases such as
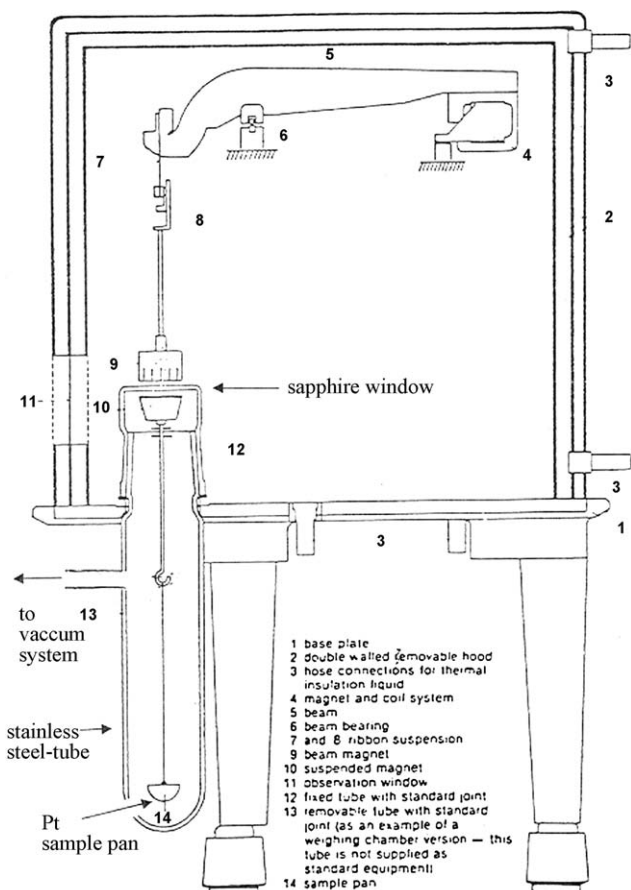

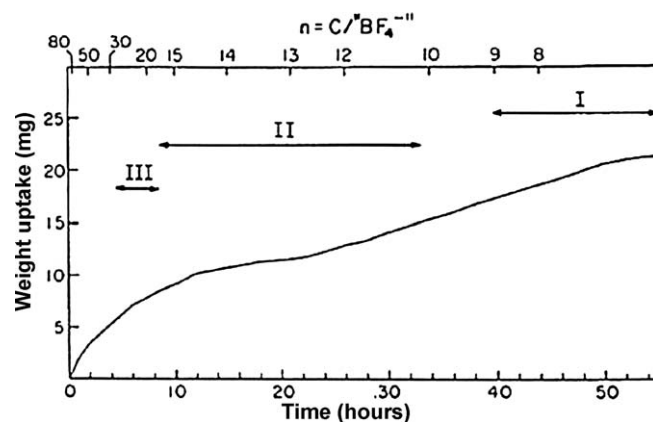**Fig. 2.** Sartorius Magnetic Suspension Balance.

Fig. 3. Weight increase as a function of time of a 22-mg sample of HOPG exposed to a 1:1 mixture of BF_3/F_2. Note the ranges in stoichiometry ratios where pure stages can be isolated.

fluorine or some of its volatile compounds. This was made possible by the complete separation of the reaction chamber from the weighing mechanism by magnets coupled via a sapphire window with a feedback mechanism for keeping the distance between the magnets constant. For example, I show the intercalation of HOPG with mixtures of BF_3 and fluorine [26] (Fig. 3).

This graph shows the weight changes as a function of time. At different times, particularly at or near inflection points in the slope, the sample was removed from the balance and the intercalation stage determined by X-ray diffraction and then subjected to continued exposure and so on. The nature of the intercalant was determined by solid-state ^{19}F NMR which showed that it consisted of mixtures of BF_3 and BF_4^-. Thus, we prepared a number of new intercalation compounds with HOPG. One of these compounds of note was the intercalation compound of AsF_5 into graphite [27], which had the stoichiometry C_8AsF_5. According to Bartlett [28] the reaction which occurs upon intercalation is $3AsF_5 + 2e^- \rightarrow 2AsF_6^- + AsF_3$.

Some arsenic trifluoride is indeed liberated, but the chemical behavior of the intercalated compound indicates also the presence of AsF_5. This intercalation compound, where the graphite was in the form of HOPG, had a sensationally high electric conductivity in the *ab*-plane. In terms of conductivity per weight it far exceeded that of copper. For a while it was thought that this intercalation compound had a future as completely replacing copper or other metallic conductors if only it could be fabricated into wires. There are even publications in which the graphite powder was contained in a copper tube which was swaged into wires after the intercalation. This hope did not materialize, because of technical difficulties and the fact that C_8AsF_5 was not that stable at room temperatures and higher.

The other synthetic metal we studied was polyacetylene doped with various fluorides. I won't go into this here except to mention that these doped compounds also showed vastly increased conductivities [29].

One more aspect of our work in fluorine chemistry was the fluorination of the then newly discovered buckminsterfullerenes. These compounds, of which the prototype was C_{60}, just begged to be fluorinated. The fully fluorinated one would be a spherical molecule, $C_{60}F_{60}$, the ideal lubricating compound possibly exceeding that of Teflon in lubricity. The fluorine group headed by John Holloway at the University of Leicester published a letter in *J. Chem. Soc. Chem. Commun.* [30] claiming to have prepared this compound, $C_{60}F_{60}$. Simultaneously we published a letter in *J. Am. Chem. Soc.* [31] in which we reported on the fluorination of C_{60}. However, we never managed to get a stoichiometry of F/C_{60} much larger than 50. The only evidence we ever had for this compound

Fig. 4. Moissan stamp.

Fig. 5. Of course the elements are earth, water, fire and air. But what about fluorine? Surely you can't ignore fluorine.

was a fleeting existence in mass spectra of fluorinated fullerenes. The state of this matter now seems to be that macro amounts of $C_{60}F_{60}$ have never been isolated and any stoichiometry of F/ $C_{60} > 48$ is unstable. In 1983 we hosted the 8th European Symposium on Fluorine Chemistry and in 1987 we organized a Symposium on Graphite Intercalation Compounds in Jerusalem. In 1986 convened in Paris a symposium in honor of the 100th Anniversary of the isolation of fluorine by Moissan – the Moissan Symposium. Among the many memorable papers I heard at this symposium was one by Karl Christe which described the synthesis of fluorine by chemical means. But the main reason I mention this symposium is another story. I heard that the French government in honor of this symposium issued a special postage stamp featuring a picture of Henri Moissan together with the first reaction of the isolation of fluorine (Fig. 4).

I went to a post office branch to buy some of these stamps and was told that they ran out of it. The same story occurred at another post office branch. Finally I located a post office where it was possible to buy this stamp. On this stamp is given the chemical reaction $H_2 + F_2 \rightarrow 2HF$. Nothing spectacular about this. Except it was the reverse of what Moissan had accomplished; namely, the reaction: $2HF \rightarrow H_2 + F_2$ by electrolysis of anhydrous HF. I came to the conclusion that the French government tried to withdraw this stamp from circulation because of a philatelic error. I told some other colleagues of this and they also rushed to buy this stamp. We thought we had made a philatelic scoop. We were wrong. Perhaps the designer of this stamp knew a little chemistry, but not enough. In summary, I would say that my work in chemistry has had its ups and downs but on the whole it has been a barrel of fun. I think my lifetime experience can be summarized in the following cartoon (Fig. 5) [32].

With this I wish to conclude by expressing my thanks to coworkers at the Argonne National Laboratory and elsewhere as well as the students I have worked with at the Hebrew University. And finally thanks also to the sponsors (Honeywell Co.) of the symposium for inviting me and granting me this honor.

References

[1] J.G.F. Druce, J. Chem. Soc. (1934) 1124.
[2] O. Ruff, W. Kwasnik, E. Ascher, Z. Anorg. Allgem. Chem. 209 (1932) 113.
[3] J.G. Malm, H. Selig, S. Fried, J. Am. Chem. Soc. 82 (1960) 1510.
[4] J.G. Malm, H. Selig, J. Inorg. Nucl. Chem. 20 (1961) 189.
[5] H. Selig, J.L. Chernick, J.G. Malm, J. Inorg. Nucl. Chem. 19 (1961) 377.
[6] H.H. Claassen, H. Selig, J.G. Malm, C.L. Chernick, B. Weinstock, J. Am. Chem. Soc. 83 (1961) 2390.
[7] B. Weinstock, H.H. Claassen, J.G. Malm, J. Am. Chem. Soc. 79 (1957) 5832.
[8] N. Bartlett, Proc. Chem. Soc. (1962) 218.
[9] N. Bartlett, N.K. Jha, Ref. [11] (1963) 23.
[10] H.H. Claassen, H. Selig, J.G. Malm, J. Am. Chem. Soc. 84 (1962) 3593.
[11] H.H. Hyman (Ed.), Noble Gas Compounds, University of Chicago Press, 1963.
[12] A.V. Grosse, A.D. Kirshenbaum, A.D. Streng, L.V. Streng, Science 139 (1963) 1048.
[13] F. Schreiner, J.G. Malm, J.C. Hindman, J. Am. Chem. Soc. 87 (1965) 25.
[14] B. Weinstock, Weaver and Knop, Ref. [11], 50.
[15] J. Slivnik, B. Volavsek, J. Marcel, V. Vracaj, A. Smalc, B. Frlec, Z. Zemljc, Croat. Chim. Acta 35 (1963) 81.
[16] J. Slivnik, B.S. Brcic, B. Volavsek, J. Marsel, V. Vrscaj, A. Smalc, B. Frlec, A. Zemljic, Croat. Chem. Acta 34 (1962) 253.
[17] F. Franks, Polywater, MIT Press, 1981.
[18] M. Fleischman, S. Pons, J. Electroanal. Chem. 261 (1989) 301.
[19] D. Rousseau, Am. Sci. 80 (1992) 54.
[20] H.H. Claassen, H. Selig, J. Chem. Phys. 44 (1966) 4039.
[21] H. Selig, A. Reis, E. Gasner, J. Inorg. Nucl. Chem. 30 (1968) 2087.
[22] Alexander, et al. J. Chem. Soc. Dalton (1972) 210.
[23] D. Vaknin, H. Selig, D. Davidov, J. Fluor. Chem. 32 (1986) 345.
[24] M. Rabinovitz, I. Agranat, H. Selig, C.H. Lin, L.B. Ebert, J. Chem. Res. (1977), 2353(M); 216(S).
[25] D. Vaknin, D. Davidov, H. Selig, V. Zevin, I. Felner, Y. Yeshurun, Phys. Rev. 31 (1985) 3212.
[26] H. Selig, D. Brusilovsky, J. Fluor. Chem. 57 (1992) 15.
[27] V. Münch, H. Selig, Synth. Met. 1 (1979) 407.
[28] N. Bartlett, B. McQuillan, A.S. Robertson, Mater. Res. Bull. 13 (1978) 1259.
[29] H. Selig, J.H. Holloway, A. Pron, D. Billaud, J. de Phys. 44 (C3) (1983) 179.
[30] J.H. Holloway, E.G. Hope, R. Taylor, G.J. Langley, A.G. Avent, T.J. Dennis, J.P. Hare, H.W. Kroto, D.R.M. Walton, J. Chem. Soc. Chem. Commun. (1991) 966.
[31] H. Selig, C. Lifshitz, T. Peres, J.E. Fischer, A.R. McGhie, W.J. Romanow, J.P. McCauley Jr., A.B. Smith, J. Am. Chem. Soc. 113 (1991) 5475.
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