One Hundred Years of Photochemistry#

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In 1973 at the International Conference of Photochemistry in Jerusalem I had casual conversation with Otto Strausz about olden times. From my perspective I generally characterize olden times as a period before television, Kleenex, and scotch tape. With reference to photochemistry, I characterize it as the period before the casual use of mass spectrometers for analysis and before the inventions of the Beckmann spectrophotometer and gas chromatography: the times when analysis was done, if it was done, by the Blacet-Leighton method of gas microanalysis and quantitative spectroscopy, depended on a series of procedures culminating in the ultimate torture of getting the H-D curve of a photographic plate.

Professor Strausz seems to have been intrigued by our conversation and, later in planning for the next conference in Edmonton, asked me to give a talk on the history of photochemistry. We agreed that the talk would not be in the nature of a research paper, such as might be presented by an historian of science, but rather would reflect my personal views and experience. We further agreed that it would not go beyond 1950. There were two reasons for this: a neat package, more-or-less a century of American photochemistry; 1950 is about the time of the start of a new era with the invention of flash photolysis in 1949, the massive intrusion of organic chemistry into the field, and the rapid development of excited state chemistry together with the application of an increasingly sophisticated spectroscopy.

In the fall of 1978, Professor Strausz invited me to write up the talk for publication in the Inter-American Photochemical Society Newsletter. I agreed to do so and was able to prepare a manuscript only a few years later than I promised. The talk was primarily a slide show delivered at the conclusion of the conference banquet. The article below is a reconstruction from the slides and some fragmentary notes.

Calvert and Pitts (Photochemistry, 1966) define photochemistry as "The study...deals with a unique type of chemical reactions. It is concerned with the 'bimolecular' interaction of a light quantum and a molecule and the subsequent chemical and physical changes which result from this interaction. Light is always one of the reactants in a photochemical system." The underlining of always is clearly intended to emphasize the importance of light.

At the Eleventh Informal Conference on Photochemistry at Vanderbilt University honoring Professor Frances E. Blacet, I said that photochemistry began in 1868. The evidence I provided was the Seal of the University of California (Slide 1). Further research has uncovered a possible alternative: as early as October in the year 4004 B.C. according to an article, Genesis, in the Old Testament. (Bishop James Usher in his biblical chronology, gives the third day, the creation of light, as October 1, but this seems to be based on old data probably not reliable to more than ± 15 days.) The relevant passage is "Yehi Or" (Slide 2) For the benefit of those of you who do not read Hebrew, I offer the following transliteration: vayomer elohim yehi or. This event has been widely accepted:, see for example, the 1508 A.D. depiction by Michelango in the Sistine Chapel (Slide 3)

This article appeared earlier some years ago in IAPS Newsletter. When I contacted Professor Volman for an historical article I became aware of it and considered reprinting the article would be valuable considering that several articles along these lines have appeared recently.

Slide 1: Seal of the University of California: Let There Be Light, 1868.

וַיֹּאמֶר אֱלֹהִים יְהִי אוֹר

4004 BC

Slide 2: Genesis, Old Testament: And God said "Yehi or."

Although most of us accept the Calvert-Pitts definition, there are revisionists. Beginning in 1966, *J. Am. Chem. Soc.*, **88**, 5532, Howard Zimmerman published the first paper of a series, still going on, under the general title "Photochemistry Without Light." If photochemistry can be conducted in the dark, perhaps the beginning date should be about 400 A.D., the fall of the Roman Empire and the start of the Dark Ages.

Below I give the names and dates of scientists associated with photochemistry landmarks prior to 1950:

Photochemistry Landmarks

1777	Scheele	1912	Einstein
1801	Cruickshank	1913	Bodenstein
1809	Dalton	1925	Franck
1817	Grotthus	1925	Taylor
1841	Draper	1941	Lewis
1910	Warburg	1949	Norrish-Porter

Slide 3: Micenlangelo Fresco, Sistine Vatican, Rome, 1508-12: God Separates Light From Darkness.

Scheele (1777) - J. P. Simons (Photochemistry and Spectroscopy, 1971) writes: "The first record of any inquiry into the effect of varying conditions on a photochemical reaction, rather than the mere recording of 'natural phenomena', was made by the Swedish chemist Scheele in 1777, who observed that violet light was the most effective in darkening silver chloride".

Cruickshank (1801) - First observations on the photochemical reaction between hydrogen and chlorine, a reaction of great importance in the development of photochemistry.

Dalton (1809) - The observation of an induction period in the photochemical hydrogen-chlorine reaction.

Grotthus (1817) - Elementary formulation of the first law of photochemistry; i.e., that only absorbed light can cause photochemical change.

Draper (1841) - Rediscovery of the first law, now known as the Grotthus-Draper Law, by relating light intensity to rate in the hydrogen-chlorine reaction.

Warburg (1910) - The first quantum yield determination.

Einstein (1912) - The second law of photochemistry, the Einstein Photochemical Equivalence Law.

Bodenstein (1913) - The proposal of the atom-chain reactions.

Franck (1925) - The principle of adiabatic absorption and the development of the potential energy surface.

Taylor (1925) - The proposal of free-radical-chain reactions.

Lewis (1941) - The proposal of the triplet state

Norrish-Porter (1949) - Flash photolysis.

[Note added: The reader may wonder why it is not Stark (1910)-Einstein Law or why Planck (1902) - quantum theory is omitted. Let him/her wonder.]

John Draper was the first American Photochemist. Born in England in 1811, in 1832 he emigrated to the United States and became, in 1836, Professor of Chemistry and Physics at Hampden-Sidney College; afterwards, in 1839, he was appointed Professor of Chemistry and Physiology at New York University. Draper was the first President of the American Chemical Society founded in 1876 (Slide 4).

Draper's name is associated with a number of important developments in photochemistry: the Grotthus-Draper Law (the "first law of photochemistry"); the Draper Effect; and Draper's Law. Less well known are his feats in photography: he is responsible for the oldest surviving photo portrait -- a picture of his sister taken in 1840 with a 65 second exposure; in the same year he took the first photograph of the moon.

Slide 4: Photograph of John W. Draper, First President of the American Chemical Society

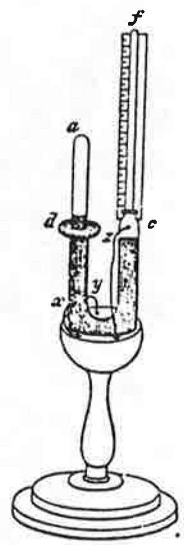
In 1817 Grotthus formulated the "first law" in primitive fashion: "the substance which responds most markedly to a given colored light shows in its natural state the complementary color to this light." The importance of this statement was lost until Draper, from a study of the H_2-Cl_2 reaction, wrote "This quality gained by the chlorine arises from its having absorbed tithonic rays corresponding in refrangibility to the indigo." (Tithonic" derives from Tithanos in Greek mythology, who "shrunk in old age.")

Draper's Law and the Draper effect also derive from studies of the H_2-Cl_2 reaction. Indeed the studies of Cruickshank, 1801, on this system represent the start of modern photochemistry. With a mixture of two volumes of moist chlorine and one volume of hydrogen, Crucikshank found complete reaction in 24 hours. In 1809 Gay Lussac and Thenard found no reaction after 8 days in the dark and fast reaction or explosion in sunlight. It was this system which in 1809 led to Dalton's discovery of photochemical induction: "the gases after being put together seemed to have no effect, when suddenly the mixture began to diminish with rapidity -- till in 2 or 3 minutes nearly the whole had disappeared."

With reference to the H_2-Cl_2 reaction, Noyes and Leighton (The Photochemistry of Gases, 1941) state: "The first work of any importance was performed by Draper in 1844." This date seems a little late as his satement of the "first law" was made in 1841. Equal in importance to the "first law" was Draper's Law. From the faulty premise that there were two forms of chlorine, ordinary chlorine, ß, and a species produced by light, α, -- "I infer that chlorine is one of those allotropic bodies having a double form of existence" -- Draper concluded that the "amount of combination is, in general, proportional to the time with constant illumination," an expression of a relationship between rate and intensity. Although explicable from principles well known at the time, the Draper effect nevertheless had a significant impact on later experimentalists. Draper carried out his experiments over water. In the initial stage he observed an increase of pressure of the gases; this was followed by a period during which the pressure remained constant; and finally there was an overall pressure decrease. Obviously the observations were due to heating from the exothermicity of the reaction followed by cooling and absorption of the HCl product in the water.

In Draper's quantitative research on intensity relationships in the H_2-Cl_2 system he utilized an apparatus which he called a "tithanometer" (Slide 5). This consisted of a glass U tube partially filled with a hydrochloric acid solution. Hydrogen and chlorine were produced electrolytically in situ in one arm of the tube and the reaction was monitored by the changes in liquid levels. The first to use the term "actinometer" were Bunsen and Roscoe in 1857 for their apparatus similar to that of Draper's but operating at constant pressure. Although these developments were the immediate precursors to a succession of increasingly sophisticated actinometric systems, the first chemical photometer was proposed in 1787 by de Saussure based on the light induced evolution of oxygen from chlorine water.

Not nearly as important a figure as Draper in American photochemistry -- his name is attached to no phenomena -- is Albert R. Leeds. Nevertheless, after Draper he is the next American to contribute significantly to photochemistry in the early years. Leeds, born in 1844, was Professor of Chemistry at Stevens Institute in Hoboken, New Jersey. He was closely associated with Draper in the American Chemical Society, serving as head of the publication committee when the Society was founded and three years later as vice president.



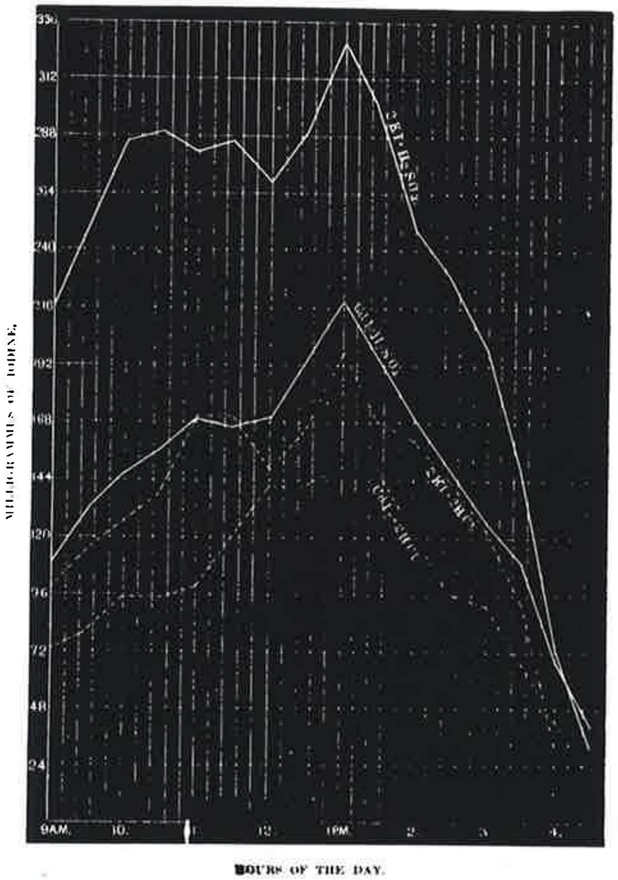
DRAPER'S
TITHONOMETER.

Slide 5: Drapers Tithanometer: Photometer Based on the Hydrogen-Chlorine Reaction

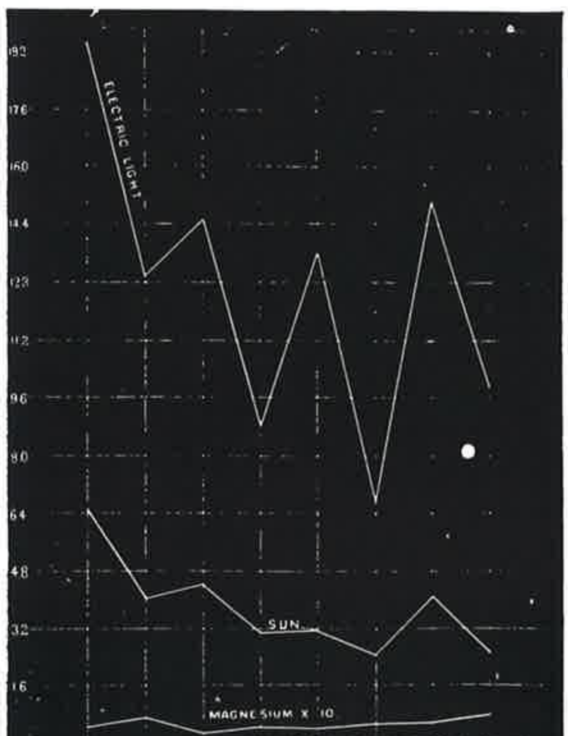
Leed's paper "Influence of Light Upon the Decomposition of Iodides", J. Am. Chem. Soc., 1, 65 (1879), was the first photochemical article to appear in the journal. The effect of sunlight at various times of the day on the rate of decomposition of solutions of potassium and cadmium iodide was shown (Slide 6). A comparison of the intensity of various light sources -- electric light (carbon arc operating on electricity from a steam powered dynamo), sun, a magnesium ribbon lamp run by clock work -- as determined by iodine production from various iodides was shown (Slide 7).

Without doubt the most important photochemistry meeting ever held was a Discussion of the Faraday Society, "Photochemical Reactions in Liquids and Gases", at Oxford in 1925. The meeting was in two parts, "Einstein's Law of Photochemistry Equivalence" and "The Mechanism of Photochemical Reactions". By 1925 quantum theory was thoroughly incorporated in science and the idea that the Einstein Law applied to the act of light absorption was well understood. Nevertheless, there were enough subtleties to warrant a discussion of the subject and to have Plotnikow argue against acceptance of the law. After 1925 the photochemical equivalence law ceased to be a viable issue for argument. The paper at this meeting which has had the most impact was Franck's "Elementary Processes of Photochemical Reactions", a delineation of his ideas on the adiabatic dissociation of molecules by light absorption. R. G. W. Norrish, talked on "The Role of Water in the Photosynthesis of Hydrogen Chloride" and W. A. Noyes delivered a paper on "The Formation of Polar Compounds by Photochemical Reactions".

Slide 6: First Photochemical article in the Journal of the American Chemical Society, 1879, A. R. Leeds: Effect of Daylight Times on Iodide Decomposition.



Slide 7: Effect of various light sources on iodise decomposition



Faraday Society Discussion 1925

I. Einstein's Law Photochemical Equivalence	II. The Mechanism of Photochemical Reaction
Allmand (London)	Bodenstein (Berlin)
Weigert (Leipzig)	Franck (Gottingen)
Stern (Hamburg)	Bown (Oxford)
Plotnikow (Zagreb)	Taylor (Princeton)
Dhar (Allahabad)	Noyes (Chicago)
Rideal (Cambridge)	Norrish (Cambridge)

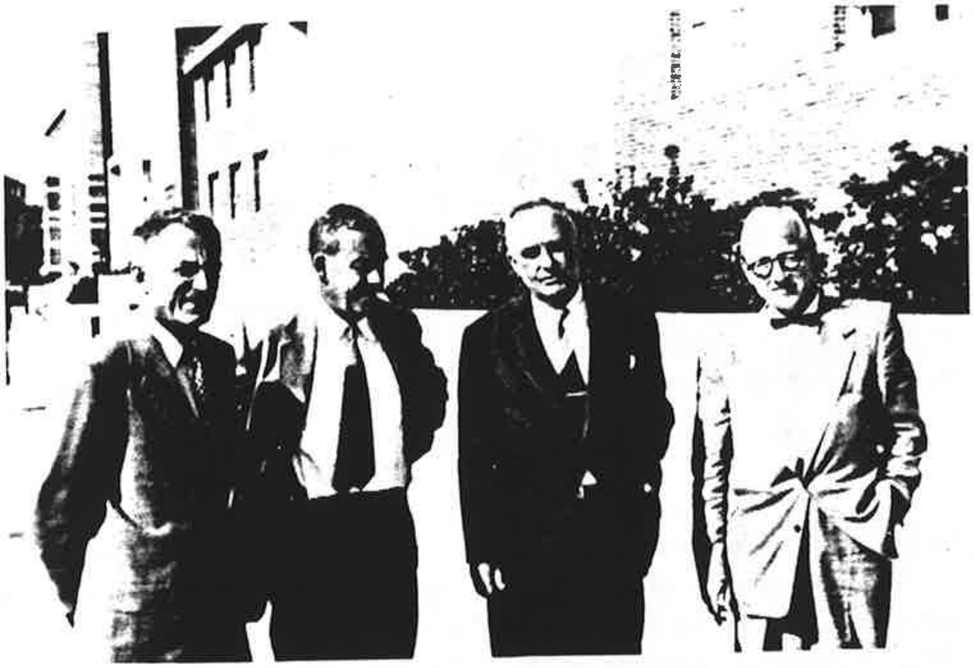
Ten years later the American Chemical Society sponsored a symposium on kinetics, April 1935, and one on photochemistry, August 1935. The names of persons who would be identified as photochemists, particularly in 1935, on the kinetics symposium program and all of the participants on the photochemistry symposium are given below. By 1935 the principles of the relationship between spectra and primary process were well understood, and photochemists were to a large extent interested in the mechanism of secondary process. For many the distinction between photochemist and kineticist was a matter of taste.

ACS Symposia

Kinetics of Reaction April, 1935	Photochemistry August, 1935
Taylor	Leighton
Kistiakowsky	Bates
Rice	Rodebush
Daniels	Dickinson
	Rollefson
	Franck

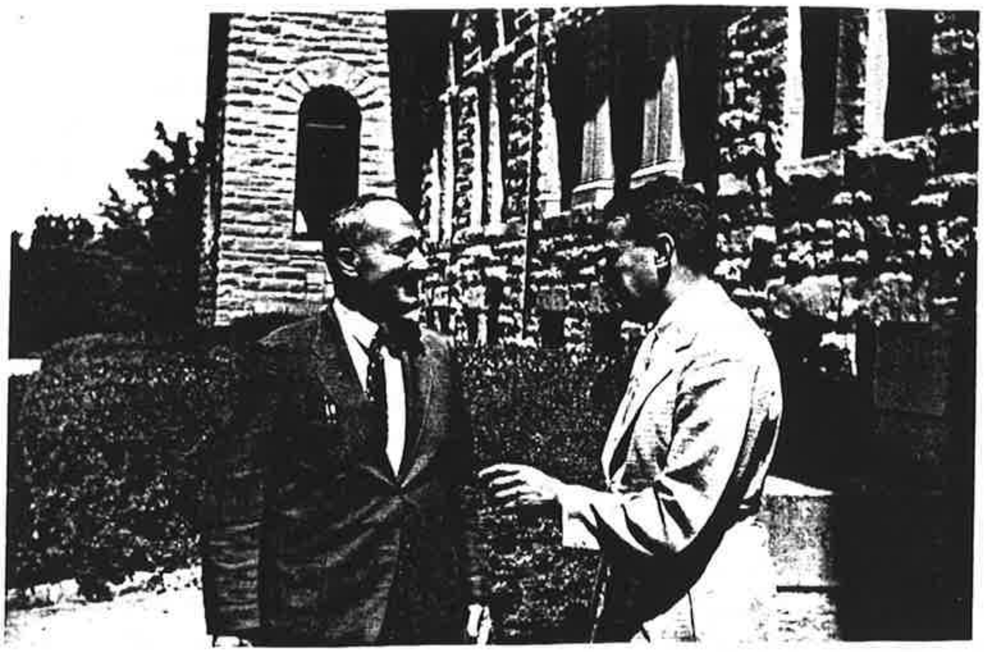
The meeting we are attending "VIII International Conference on Photochemistry" is one of a series of which the first, "Reunion de Photochimie", was sponsored by Professor Paul Goldfinger in Brussels in June, 1962. The idea of having an international meeting was developed during a meeting of the Fifth Informal Conference on Photochemistry held here, University of Alberta, in June 1961, which Professor Goldfinger attended. The series of "Informal" meetings was initiated by Professor Francis Blacet in 1952 at the University of California, Los Angeles (Slide 8). These meetings are a United States - Canadian series, but over the years a significant and increasing number of participants have come from overseas.

The legitimate precursor to both of the above series, meetings without society sponsorship or with limited society sponsorship, was that held at Stanford University in the summer of 1938 during my first year as a graduate student. At that time Philip Leighton, Paul Cross, and Richard Ogg were members of the Chemistry Faculty in photochemistry, spectroscopy, and kinetics. Francis Blacet and James Frank were

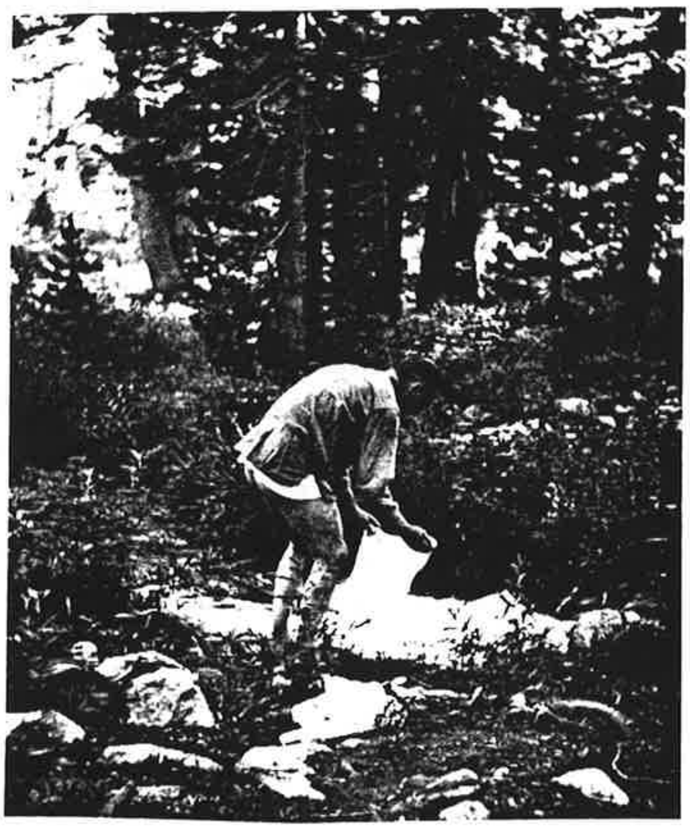


Slide 8: The First Informal Conference on Photochemistry (U.S.—Canadian): Francis Blacet, Edward Steacie, Albert Noyes and Harry Gunning.

Slide 9: The 1938 Stanford Photochemistry Meeting: George Kistakowsky



Slide 10: The 1938 Stanford Photochemistry Meeting: James Franck and Edward Teller.



Slide 11: The 1938 Stanford Photochemistry Meeting: Albert Noyes "Notorius Photochemist Exposed".

Visiting Professors for the Summer Quarter. Albert Noyes was at Stanford during much of the summer collaborating with Philip Leighton on "The Photochemistry of Gases". Also during this period a distinguished group of scientists working on photosynthesis, primarily biologists, were in residence associated with the Carnegie Institution of Washington Laboratory at Stanford and Stanford's Marine Biology Station at Pacific Grove. Professor Leighton had planned a photochemical conference and a number of other photochemists, to supplement the nucleus on hand, participated. A partial list of these follows (the names come from memory as no written record has yet been uncovered): Farrington Daniels, George Kistiakowsky, John Leermakers, Gerhard Rollefson, Oscar Rice, Edward Teller, Edward Wiig, Roscoe Dickison, Bryce Crawford. In my opinion the most important discussion at the meeting centered on the analysis of space and time light intermittency, a presentation by Roscoe Dickison. An elegant treatment of the subject based on this discussion was incorporated in "The Photochemistry of Gases". Prior to 1938, very little use had been made of intermittent light effects; since 1938 application based on intermittence have played a leading role in the development of photochemistry.

Finally, I should like to note American Photochemists born in or before 1900 from whom many of us directly derive our photochemical inheritance. I have limited the list to those I have known or know personally. Nevertheless, it contains all, or at least almost all, of the scientists in this category whose names would logically come to the fore.

J. Franck	1882	P. A. Leighton	1897
J. S. Forbes	1882	W. A. Noyes, Jr.	1898
W. H. Rodebush	1887	F. E. Blacet	1899
F. Daniels	1889	G. R. Rollefson	1900
H. S. Taylor	1890	K. W. R. Steacie	1900
R. G. Dickinson	1894	G. B. Kistiakowsky	1900

In my own experience I had done photochemical research in the laboratories of four of this group: in 1935-1938 as an undergraduate and as a M.A. candidate with Francis Blacet at U.C.L.A.; in 1938-1940 as a Ph.D candidate with Philip Leighton at Stanford; in 1945-1946 on O.S.R.D. research with Worth Rodebush at the University of Ilinois; and in 1949-1950 as a Guggenheim Fellow with George Kistakowsky at Harvard. To get a Nobel Prize winner in the list, I also note that I took a course from James Franck. (Readers of Robert Merton, the Columbia sociologist of science, will recognize the above as an OTSOG --- "on the shoulders of giants".). It gives me at least the minimum of "on-paper" credentials to present this history.