THE HISTORY OF OZONE. IV. THE ISOLATION OF PURE OZONE AND DETERMINATION OF ITS PHYSICAL PROPERTIES (1)

Mordecai B. Rubin, Technion- Israel Institute of Technology

Introduction

Ozone is a devilish molecule, seemingly created specifically to validate the existence of the Law of Inanimate Malice (2). The procedures for its preparation give relatively low yields in admixture with the starting material, air, or oxygen. It is highly toxic even at very low concentrations and often violently explosive at high concentrations. It is thermally unstable, decomposing at a measurable rate at room temperature, and also extremely reactive. Its reactions include oxidation of many metals (including mercury) and of many organic compounds (including rubber) often with extreme rapidity at temperatures at or below that of Dry ice. Thus it combines difficulty in preparation and handling with hazardous behavior, instability and toxicity. Historically, even such a simple task as lubrication of stopcocks presented a problem; sulfuric acid was used in many cases as a lubricant until ozone-resistant fluorocarbon greases were developed many years later.

In view of the difficulties, it is not surprising that 25 years elapsed from the discovery of ozone by C. F. Schönbein (3) in 1840 to the determination of its molecular formula by Soret in 1865 and confirmation in 1868 (4). In 1845 Schönbein commented (5) that the problem of determining ozone's constitution would be enormously simplified if sufficiently low temperature could be achieved to permit its isolation in the liquid or solid state. This report describes the subsequent achievement of that goal, isolation of pure liquid and solid ozone, and the determination of their physical properties. It should be noted, however, that the simplifications hoped for by Schönbein were not necessarily forthcoming as will be shown. The results of spectroscopic investigations and the long struggle to establish the structure of the ozone molecule will be presented in a separate article.

Liquid Ozone

Thomas Andrews, the discoverer of critical pressure of gases, attempted (6) to liquefy ozone by cooling an ozone-oxygen mixture with dry ice, but the temperature was not sufficiently low. The first successful experiment of this type was reported in 1882 by Hautefille and Chappuis (7) by using Cailletet's apparatus after the successful development in 1877 of techniques for liquefying low-boiling gases by Cailletet and by Pictet. In 1880 Hautefille and Chappuis had succeeded in obtaining ozone as a blue gas (8) and then as a liquid mixed with solid carbon dioxide (9). The blue color of ozone prompted Chappuis to continue with a detailed study (10) of its absorption spectrum in the visible region but no work was reported at that time on other properties of ozone.

Five years later, Olszewski reported (11) that ozone could be condensed from a mixture with oxygen by cooling at atmospheric pressure with liquid oxygen (bp -183° C). He estimated the boiling point of ozone to be -106° C. Attempts to crystallize ozone by further cooling were not successful. Olszewski's paper also included the first report of an explosion with ozone. When ozone

came into contact with ethylene (both at very low temperature), a violent explosion occurred shattering the apparatus and pulverizing the glass. Perhaps because of this experience, no further work on liquid ozone was reported from the Cracow laboratory. Eleven years elapsed before the next report appeared when Troost (12), in 1898, obtained liquid ozone by condensation with liquid oxygen. He redetermined the boiling point using a calibrated iron-constantan thermocouple in the headspace of a tube containing liquid ozone undergoing free warming. His value for the boiling point was -119° C, 13° lower than that of Olszewski; the currently accepted value (see below) is halfway between the two. Troost also encountered the explosion problem, in this case an explosion when the thermocouple, previously cooled in liquid oxygen, was immersed in the liquid ozone itself. Five years later, Goldstein (13) described a simple apparatus for producing small quantities of liquid ozone. An evacuated quartz apparatus with a cold finger cooled in liquid air was filled with a few mm pressure of oxygen and subjected to an external discharge from an induction coil. Within seconds the tube became luminous and the pressure sank to about 0.1 mm Hg; small quantities of liquid could be obtained by repeated operation.

The explosion hazard has dogged workers interested in the properties of liquid ozone through the years. In 1956 Hughes (14) wrote: "To prevent a possible serious accident in case of an explosion, only a few hundredths of a gram were produced at one time. Fortunately, there were no explosions." A. Ladenburg (15) prepared about 5 ml of apparently pure liquid ozone for boiling point determination and wrote that it was not possible to find a recognizable piece of the apparatus after the violence of the explosion which occurred; he abandoned his attempts. E. Ladenburg and Lehmann (16) reported a considerable number of violent explosions in their work on ultraviolet-visible spectra of liquid ozone. Explosions have even been observed (17) with solidified ozone at liquid hydrogen temperature (-250° C). Most workers have employed the precautions described by Hughes (14), namely working with small amounts of ozone, whatever preparative method was employed. The reasons for the frequent explosions are unclear. Some workers have attributed them to impurities, particularly traces of organic compounds, in the apparatus used or in the oxygen taken as starting material for preparation of ozone. Further, it seems essential to avoid any sudden changes in physical state or environment, such as rapid changes of temperature, physical shock, and so on. Typical of the problems involved in working with ozone, it was necessary to prevent appreciable amounts of ozone from reaching mechanical vacuum pumps, otherwise explosions occurred in the pumps. Tubes containing soda lime were sometimes used to protect various sections of apparatus from ozone; sulfuric acid manometers were used alone or coupled with mercury manometers. Karrer and Wulf (18) used a water aspirator as vacuum pump, and another group (19) used a trap packed with sections of glass tubing and heated to 450° C to decompose any ozone before it reached the pumping system. Riesenfeld and Schwab (20) commented in 1922: "By avoiding even the slightest traces of catalysts for ozone decomposition (ether, for example), rapid increases in pressure, or warming, we have so far never had an explosion of liquid ozone;" it might further be noted that very small amounts of pure ozone were collected in their work. This was echoed later by Jenkins (21) in a 1959 article devoted to the handling of liquid ozone,which should be required reading for anyone dealing with this treacherous substance.

Given the considerable difference (about 70° C) in boiling points between oxygen and ozone, the abovementioned scientists assumed that the deep blue liquid that they obtained consisted of pure ozone, and none of them seem to have made any attempt to establish the validity of this assumption. In the event, it turned out to be severely incorrect, and pure ozone was not obtained until 1922, over 80 years after Schönbein's discovery and 40 years after ozone was first liquefied. Moeller's 1922 book (22) gives only the two boiling points mentioned above and values, determined on gas mixtures, for the heat of formation, solubility in water, and density of ozone.

The first serious study in which pure ozone was prepared and a number of its physical properties determined came from the laboratory of E. H. Riesenfeld (17, 20, 23, 24, 25, 26, 30) at the University of Berlin during the period 1922-26. Karrer and Wulf (18) also reported pure liquid ozone in 1922 but were dogged by frequent explosions at various stages of their procedure. For example, while the system could be evacuated with a mechanical vacuum pump in the absence of ozone, the presence of ozone caused explosions in the pump making it desirable to use a water aspirator for pumping, as mentioned above. The vacuum was supplemented by a large reservoir which was evacuated to a high vacuum, then closed off, and opened when it was desired to reduce the vacuum obtainable with the aspirator. Probably because of these difficulties, Karrer and Wulf determined

only the molecular weight by the vapor density method obtaining a value of 47.3 ± 0.8 while Riesenfeld and Schwab (23, 26) obtained the value 47.9 ±1.4. Both groups confirmed the results of earlier work done with ozone in low percent ozone-oxygen mixtures. Karrer and Wulf only returned to liquid ozone research five years later.

Riesenfeld, who had been an active investigator of various aspects of ozone chemistry for about ten years, introduced his 1922 work on pure, liquid ozone by explaining that the recent availability of micro methods for determining physical constants of liquids made it feasible to investigate the behavior of pure ozone using very small amounts of substance thereby minimizing the hazards involved. A detailed description of the procedure used (24, 26) is instructive and illustrates the various precautions required because of ozone's devilish nature.

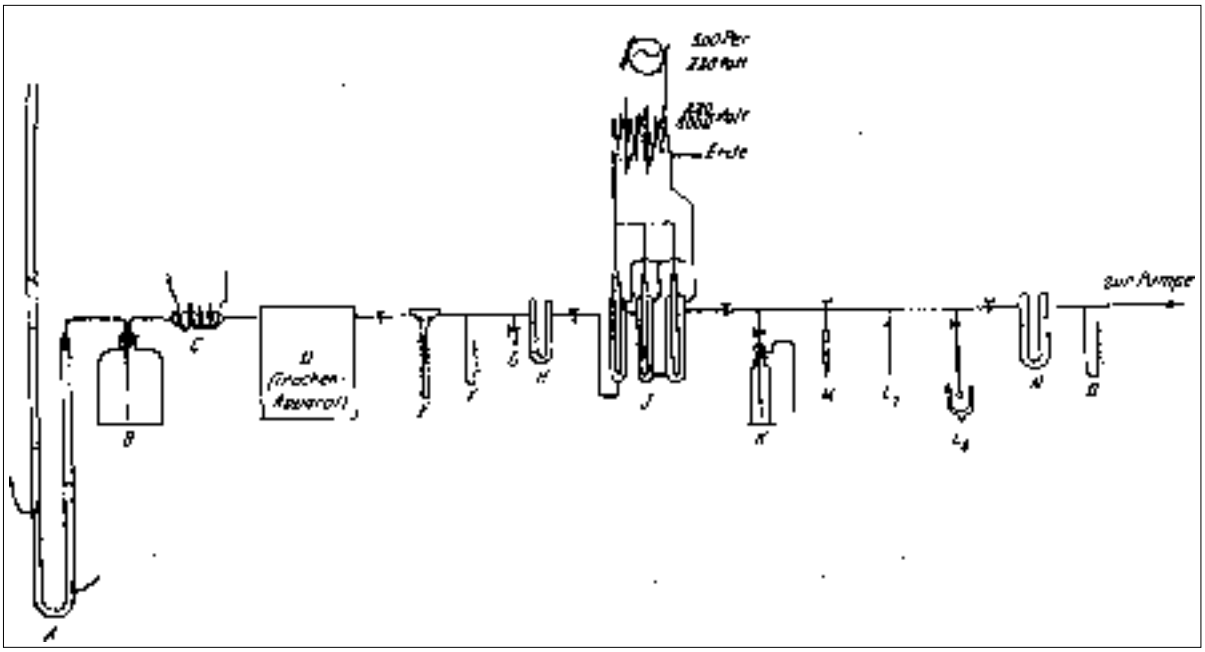

Figure. Apparatus for preparing pure ozone according to H. Riesenfeld and G. M. Schwab, *Ber*., **1922**, *55*, 2088-99; G.-M. Schwab, Z. *Phys. Chem*., **1924**, *110*, 599-625.

The diagram of the apparatus, reproduced from the original drawing (24), is shown in the Figure. It begins with electrolysis (A) of water to generate oxygen, which was collected in (B) and then passed through a heated tube (C, 300° C) to destroy any hydrogen or organic compounds present as well as any ozone formed in the electrolysis (this would attack the mercury manometer following). It was then passed through a drying apparatus (D) containing conc. sulfuric acid and phosphorus pentoxide. The rates of flow and pressure were measured with flowmeter E and manometer F. The pure, dry oxygen at a small positive pressure was passed through three Berthelot tubes (J), operating at 8000 V and 500 Hz, which produced 10-15% ozone in oxygen. Samples of gas could be collected for analysis from vessel K, and excess gas could be vented to the atmosphere through tube M, which was filled with soda lime to destroy ozone before it entered the laboratory environment. A two-phase, blue-colored system condensed when the gas mixture was passed into capillary tubes (L_1-L_6) previously sealed at one end and cooled with liquid air. These were followed by U-tube N filled with soda lime to destroy ozone, thereby protecting the pumping system and the manometer (O). The part of the system containing the liquid ozone-oxygen mixture (M-O) could then be isolated, connected to the vacuum pump, and manipulated as desired.

Ladenburg had noted in 1898 (15) that the condensed liquid from cooling ozone-oxygen mixtures with liquid oxygen contained an appreciable amount of a lower boiling component (oxygen), but the observation of a two-phase system in the capillary tubes L_1-L_6 was

Table. Physical Properties of Ozone

Property	Riesenfeld Results (ref.)	Handbook Chemistry & Physics (orig. ref.)
Melting Pt. (°C)	-251 (a, b, c, d)	-194 ± 0.5 (f)
Boiling Pt. (°C)	-112.3 (a, b, d, f	-111.9 (g)
Critical Temp (°C)	-5 (c,d,f); -10 (a, b)	-12 (g)
Crit. Pressure (atm)	65 (a), 67(c)	54/6 (g)
Crit. Density, (g/ml)	0.537 (a, c, d)	
(cc gas/mol)	89.4	
Liquid Density(-183° C (g/ml))	1.71 (a, d, h)	1.571 (i)
Crit Temp (°C); liquid O_2-O_3 mixture	-158 (b, d)	-180 (j, k)
Heat of Vaporization (cal/mol)	0 K: 3500 (d);-112° C: 2547 (d)	

References: (a) Ref. 17; (b) Ref. 20; (c) Ref. 23; (d) Ref. 24; (e) Ref. 44; (f) Ref. 26; (g) A. C. Jenkins and C. M. Birdsall, "The Vapor Pressures and Critical Constants of Pure Ozone," *J. Chem. Phys.*, **1952**, 20, 1158-1161; h) C. Brown and K. D. Franson, "Manometric Determination of the Density of Liquid Ozone," *J. Chem. Phys.*, **1953**, *21*, 917-919; (i) R. I. Brabets and J. M. McDonough, "Density of Liquid Ozone." *J. Chem. Phys*., **1957**, *27*, 880-882; (j) C. K Hersh, A. W. Berger, and J. R. C. Brown, "Physical Properties of Liquid Ozone-oxygen Mixtures: Density, Viscosity, and Surface Tension," *Advances in Chemistry Series*, No. 21, American Chemical Society, Washington, DC, 1959, 22-27; (k) A. C. Jenkins, F. S. DiPaolo, and C. M. Birdsall, "The System Ozone-oxygen," *J. Chem. Phys*., **1955**, *23*, 2049-2054.

unexpected. This was shown in the Riesenfeld work to be due to the formation (23) of two immiscible layers with the lower layer consisting of 30% oxygen dissolved in ozone and the upper layer of 30% ozone dissolved in oxygen. The composition varied with temperature; the critical temperature for this two-phase phenomenon was shown to be -158° C. Brown, Hersh, and Berger (19) confirmed these results in 1955 but obtained a value of -180° C for the critical temperature. When a vacuum was applied to the two-phase system cooled in liquid air, the volume decreased and eventually a single phase was observed accompanied by a decrease in pressure to less than 1 mm mercury. The tubes L_1-L_6, each containing a few drops of deep blue liquid, could then be sealed off and used for subsequent measurement. This blue residue, presumed to be pure ozone, was analyzed by collecting a small volume in a bulb cooled in liquid air which was then sealed and transferred to a second apparatus where it was broken under a 2-5% potassium iodide solution buffered with boric acid. The volume of oxygen produced was measured and the aqueous solution titrated with sodium thiosulfate. These measurements indicated that the blue liquid consisted of approximately 95% ozone, the 5% discrepancy being attributed to thermal decomposition of ozone and errors introduced by the manipulations involved.

The Riesenfeld group reported the boiling point, liquid density at various pressures, critical pressure, heat of vaporization of liquid ozone, and the melting point of the solid (see below). Their values are listed in the Table together with the values given in recent editions (27) of the *Handbook of Chemistry and Physics*. Most of these were taken from summary articles by Streng (28) and by Hersh (29). An examination of the table shows that, with the exception of the boiling point, the micro techniques of the 1920s left something to be desired so far as accuracy of measurement was concerned.

Beja (25) determined the vapor pressure over the temperature range -108.5 to -169° C in 1923 and Spangenberg (30) extended these measurements to -183° C in 1926. Temperature control in these experiments employed a mercury block cooled by hydrogen gas; the block temperature was measured with a platinum resistance thermometer and taken to be the temperature of the liquid. Spangenberg obtained the following expression (30) for the vapor pressure of ozone as a function of temperature (T/K):

$$\log p\ (\text{mm}) =$$

$$-809.5/T + 1.75 \times \log T - 0.01116 \times T + 5.850$$

Incidental to the work of the Riesenfeld group was the conclusion (23, 24) that no significant amount of a heavier allotrope of oxygen, such as Harries' oxozone (O_4, MW 64, see Ref. 1) was present in the product from action of silent discharge on oxygen. According to Harries, ozone generated by silent discharge contained about 30% of oxozone. Such a product would have been expected to have a significantly higher boiling point than O_3 and would vary considerably in other properties as well, but no variations in properties were observed as a function of the extent of distillation. Further support for the absence of oxozone derived from the reproducibility of the physical constants obtained by different workers. Briner and Biederman (31) reached the same conclusion ten years later using samples of ozone obtained by silent discharge at various frequencies.

Condensation of ozone-oxygen mixtures from silent discharge, using liquid air or liquid oxygen as coolant, became a standard procedure for obtaining liquid mixtures in later years. Pure ozone was then obtaining by pumping on the liquid oxygen cooled ozone-oxygen mixture until a very low pressure was achieved; more careful investigators used trap-to-trap distillation and pumping. In many cases (21, 32) it was assumed, on the basis of vapor pressure measurements alone, that the product was pure ozone without confirming this by any analytical procedure. Magnetic susceptibility (see below) was a very sensitive criterion of purity. The values for a considerable number of properties of ozone were determined and can be found in the standard reference sources mentioned earlier. These values have remained unchanged for several decades. Thermodynamic properties were determined in large part from spectroscopic measurements.

Two properties, the dipole moment and the magnetic susceptibility of ozone, are of special interest. The dipole moment, which was very important in the long debate on the structure of the ozone molecule, was first reported in 1939 by Lewis and Smyth (33), who used conventional methods on the liquid ozone-oxygen mixture obtained from condensation of the product of silent discharge with liquid oxygen. They obtained a value of 0.49 D, ruling out linear and symmetrical triangular structures for ozone. Trambarulo and co-workers (34) obtained a similar value (0.53 ± 0.02 D) using spectroscopic data.

The unusual magnetic properties of dioxygen prompted investigations of this property of ozone as early as 1881. In that year both Becquerel (35) and Schumeister (36) reported investigations of the mixture of ozone and oxygen gases produced by silent discharge on oxygen. They were unable to obtain reliable numerical values but both reported that ozone had a specific paramagnetism approximately three times that of oxygen! This surprising result lay dormant in the literature for over 45 years until 1927 when Wulf (37) reported results which led him to conclude that "the numerical value of the volume susceptibility of ozone is but a small fraction of that of oxygen" and suggested that ozone might even be diamagnetic. Vaidyanathan (38) reached the same conclusion one year later. These observations led to further investigations on liquid ozone and ozone-oxygen mixtures at low temperatures by Lainé (39) in 1933 and 1934. He concluded that the specific susceptibility of liquid ozone at temperatures in the region of liquid air was approximately $+1.5 \times 10^{-7}$ compared to a value of $+2406 \times 10^{-7}$ for oxygen under similar conditions. The large difference allowed the determination of very small concentrations of oxygen in ozone and permitted Lainé to establish that a sample of liquid ozone kept at liquid air temperature for 10 hours had changed by less than 1/50,000 in oxygen. Laine's results were accepted by Brown, Hersh, and Berger (27), who determined the magnetic susceptibility of ozone-oxygen mixtures using an Alnico magnet cooled in liquid oxygen or liquid nitrogen.

It should also be noted that a 1953 report (40) that a maximum temperature, -105° C, occurs at about 80 % ozone concentration in the temperature-composition diagram for ozone-oxygen mixtures, could not be reproduced. The incorrect reported maximum was attributed (41) to improper design of the measuring apparatus.

Liquid ozone acquired special interest as a possible replacement, wholly or in part, for the liquid oxygen used in rocket engines since such replacement would increase the amount of energy available per unit weight. This interest made funding available for the spurt of activity in research on liquid ozone during the 1950s and early 1960s. It was also responsible for the appearance of a considerable number of patents on the dubious attractions of a variety of stabilizers for liquid ozone. To the best of our knowledge, no practical application has been made of any of these stabilizers.

Solid Ozone

The first report of pure, solid ozone also came from the Riesenfeld laboratory in 1922. Schwab (24, 26) de-

scribed *very gradual* cooling of liquid ozone by slow immersion in a liquid hydrogen (-253° C) bath and obtained a blue-black crystalline mass. Time-temperature curves on slow warming, measured in two experiments with a thermocouple in the solid, gave plateaus at 22.4 and 21.2 K which were inferred to be due to melting; the average value was 21.8 K (-251° C). The explosion hazard was also present in this and other work with solid ozone despite the extremely low temperatures involved. Both Schwab and Streng and Gross in 1959 (42) encountered violent explosions upon rapid cooling of liquid ozone, thus demonstrating once again the sensitivity of ozone to any drastic change in physical surroundings. Research on solid ozone has been very limited, perhaps because of the extreme hazards involved in preparing and working with this substance.

Probably the most striking result in solid ozone research was reported by Marx and Ibberson (43) in 2001. Condensation of gaseous ozone at 10-20 K gave solid ozone, which was used for X-ray and neutron powder diffraction analysis. The solid had a bent structure with an O-O-O angle of 117.9°, in good agreement with the gas phase structure! Measurement of the unit cell dimensions over the range 5-54 K provided no evidence for a phase transition, which might explain the discrepancy between the currently accepted melting point of -193° C and Schwab's earlier value of -251° C; the latter was probably an artifact of the measuring technique.

This value, mp -251° C, remained unchallenged for over 30 years. Many reports described use of liquid nitrogen (bp -196° C,) to condense *liquid* ozone from ozone-oxygen mixtures. However, during this period, a number of investigators (42, 44, 45) encountered solid material under these conditions. In 1954 Brown, Berger, and Hersh (44) reported a solid in some of their experiments when distilling ozone into a liquid nitrogen cooled U-tube for manometric measurements. The smooth flow of the condensing liquid halted and application of helium pressure (up to 1 atm) had no effect. Slow immersion of liquid ozone into nitrogen at its triple point (-210° C) invariably led to the formation of a solid which was stable indefinitely at the temperature of liquid nitrogen. "Color photographs and visual observation strongly suggested a crystalline material." Warming the liquid nitrogen bath at a rate of 0.06 °C/min by slow addition of liquid oxygen resulted in melting beginning at -193.4° C which was complete at -192.5° C (average value -193° C). It is clear that liquid ozone readily supercools since numerous measurements have been made on liquid ozone at liquid nitrogen temperature (-196° C). The formation of a supercooled liquid or an amorphous form of solid ozone was also observed by Hanson and Mauersberger upon condensation of ozone at liquid nitrogen temperature; this was converted to a crystalline form upon cooling to about -203° C.

In 1959 Streng and Grosse went on to determine the density of the solid using the known densities of the liquid at various temperatures for calibration. They measured the height of columns of solid ozone at various temperatures and calculated the free space by measuring the amount of nitrogen that could be added. Molar volumes were 27.8 for the solid and 29.75 cm^3 for the liquid, giving a value of +7.1% for the volume expansion on melting.

Hanson and Mauersberger (45), who had determined the vapor pressure of liquid ozone at temperatures in the region of liquid argon, used the same technique to determine the vapor pressures of the two solid forms of ozone. The unique feature of their 1986 method was connection of the vapor pressure apparatus to a mass spectrometer to determine the percent of oxygen present in the vapor section. This allowed correction for thermal decomposition of ozone (or any other source of oxygen) during the course of the measurement. They obtained the following linear relationship between pressure and the reciprocal of temperature (T/K) for the crystalline form of ozone:

$$P(\text{torr}) = 10.460 - 1021.6/T$$

For example, the vapor pressure of ozone at -205° C (68 K) is 1×10^{-5} mm, from which the latent heat of sublimation was calculated to be 97.4 cal/g.

Broida et al (46) suggested that ozone is trapped as the solid in the polar caps of Mars.

Summary

The isolation of pure ozone and the investigation of its properties turned out to be a hazardous endeavor requiring great care from the investigator. Over 80 years elapsed between C. F. Schönbein's discovery of ozone in 1840 and the isolation of pure liquid ozone. While it might have been thought that having the pure substance in hand would simplify research, the difficulties involved in obtaining and handling the pure substance were substantial. Only by avoiding impurities, working with small quantities of substance, and minimizing changes in physical state was it possible to handle ozone with a reasonable degree of safety. Interest in the use of ozone

to wholly or partially replace liquid oxygen as a rocket fuel prompted considerable research on liquid ozone and liquid ozone-oxygen mixtures in the period after World War II, but the hazards of liquid ozone appear to have defeated this.

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ABOUT THE AUTHOR

Mordecai B. Rubin is Emeritus Professor of Chemistry in the Department of Chemistry, Technion-Israel Institute of Technology, Haifa, Israel 32000 (chrubin@tx.technion.ac.il). A major research interest for many years was organic photochemistry. He still teaches a one-semester course in the history of chemistry each year. Retirement is like a permanent sabbatical. As a young man, many years ago, he developed an apparatus for small-scale ozonolysis, which was dubbed the Rubin ozonator.