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CHEMISTRY AT ITS MOST BEAUTIFUL

Pasteur's separation of enantiomers tops list of the most memorable discoveries in chemistry

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THE PREPARED MIND **Pasteur may have thought it tedious, but chemists regard his manual separation of enantiomers as the "most beautiful experiment." NATIONAL LIBRARY OF MEDICINE PHOTO**

The most beautiful experiment in the history of chemistry, according to a recent survey of C&EN readers, is Louis Pasteur's manual separation of sodium ammonium tartrate crystals into two sets of crystals that were mirror images of each other.

"The experiment was the effective beginning of stereochemistry and understanding molecules in three dimensions," comments Alan J. Rocke, professor of history at Case Western Reserve University, Cleveland.

Pasteur, a French scientist who coined the phrase "Chance favors only the prepared mind," used a magnifying glass and tweezers to separate the crystals. He published his first work on the subject in 1848. Subsequently, after several years of tedious work, he showed that solutions of each set of crystals rotated plane-polarized light an equal number of degrees but in opposite directions.

"Pasteur's separation of optical isomers opened an area of chemical structure particularly important to organic chemistry and biochemistry," remarks Carmen J. Giunta, associate professor of chemistry at Le Moyne College, Syracuse, N.Y.

Go To

THE TOP 10 AND MORE
Beautiful Experiments Ranked By Number Of Nominations & Historians

BEAUTY & CHEMISTRY
In The Eyes Of The Beholders

Releted Stories

Beauty In The Eye Of The Beholder
[C&EN, Nov. 18, 2002]

A Candle Burning Brightly
[C&EN, Sept. 11, 2000]

The Forgotten Chemist Who Changed The World
[C&EN, Jul. 2, 2001]

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E-mail the editor

The investigation was marked by "conceptual simplicity" and by "luck and determination," which give it "a human-interest appeal," Giunta continues. Pasteur's "determination is evident in his tedious manual separation of chiral crystals. Luck comes into play with the realization in hindsight that very few tartrate salts would have been amenable to Pasteur's separation strategy."

Peter J. Ramberg, assistant professor of history of science at Truman State University, Kirksville, Mo., observes that although the experiment is significant in establishing the relation between optical activity and molecular asymmetry, the popular conception that Pasteur was deliberately attempting to determine the relationship between crystalline form and optical activity is incorrect.

"Pasteur's project was to resolve some anomalies between the crystalline form of a series of tartrate and the number of waters of crystallization," Ramberg explains. "The property of optical activity entered Pasteur's work only near the end of a long series of experiments in conventional crystallography."

THE TOP 10 AND MORE **Beautiful Experiments Ranked By Number Of Nominations & Historians**	
1	Louis Pasteur's separation of tartrate enantiomers (1848)
2	Antoine Lavoisier's work on oxidation of metals, which led to the general theory of combustion and oxidation (ca. 1775)
3	Emil Fischer's determination of the configuration of glucose (ca. 1890)
4	Sir Humphry Davy's isolation, using electrolysis, of sodium and potassium (1807), and of magnesium, calcium, strontium, and barium (1808)
5	William Henry Perkin's synthesis of the dye mauve (1856)
6	Gustav Kirchhoff and Robert Bunsen's demonstration that metal compounds heated in a flame emit spectral lines characteristic of metal (1859)
7	Joseph Priestley's discovery of oxygen by heating "red calx"--mercury(II) oxide (1774)
8	Neil Bartlett's preparation of the first noble-gas compound, xenon hexafluoroplatinate, from platinum hexafluoride (1962)
9	Victor Grignard's discovery of the use of organomagnesium compounds in synthesis (ca. 1899)
10	Marie and Pierre Curie's discovery of polonium and radium (1898)
Other Shortlisted Experiments	
Hennig Brandt's discovery of phosphorus (1669)	
Henry Cavendish's production of water by exploding mixtures of hydrogen and air with an electric spark (1784)	
Francis Crick's and James Watson's determination of the double helix structure of DNA from X-ray diffraction studies (1953)	

Sir Edward Frankland's preparation of organometallic compounds (1852)
Fritz Haber's synthesis of ammonia using an iron catalyst (1909)
Charles Martin Hall's separation of aluminum from its ore (1888)
Wilhelm Körner's experiments to determine the relative positions of substituents on benzene (1874)
Stanley Miller and Harold Urey's simulation of production of prebiotic biochemical compounds such as amino acids by sparking a mixture of simple gases such as methane and ammonia (1953)
Edward Morley's determination of the atomic weight of oxygen (1895)
Lord Rayleigh and Sir William Ramsay's discovery of argon (1894)
Mikhail Tswett's first chromatographic separation of colored compounds (1903)
Count Alessandro Volta's invention of the electric battery using silver and zinc disks and a brine-soaked card (1799)
Alfred Werner's work on inorganic complexes of metals (ca. 1900)
Alexander Williamson's synthesis of ethers by reaction of sodium alkoxide with an alkyl halide (1850)
Friedrich Wöhler's preparation of urea from ammonium cyanate (1828)

EVEN SO, Pasteur's separation of enantiomers received more nominations than any other chemistry experiment. The nominations came in response to C&EN Editor-in-Chief Madeleine Jacobs' invitation to chemists around the world to nominate the 10 most beautiful--that is, elegantly simple but significant--chemistry experiments (C&EN, Nov. 18, 2002, page 5).

The 70 readers who responded nominated 55 experiments, of which 25 received two or more votes and just five received more than three votes. C&EN sent the shortlist of 25 experiments to a panel of science historians and chemists, inviting them to select their top 10. The panel included Rocke, Giunta, and Ramberg. C&EN compiled the top 10 list on the basis of readers' nominations and the panel's responses.

The discovery and isolation of chemical elements featured prominently in the top 10 and among nominations in the shortlist.

"Discoveries of elements can be beautiful," Giunta says. "Application of a new principle of technology to the problem of uncovering one or more of nature's building blocks has an elegance that illustrates how science builds on previous results.

"Besides the discovery of argon, I see Davy's discovery of potassium and sodium and the Curies' discovery of polonium and radium as beautiful and exemplary," he continues.

The work of English chemist Sir Humphry Davy is an elegant application of a new technology to separate compounds into their component parts, which previously were inseparable, according to Giunta. "Davy used a relatively new scientific tool--a battery that could reliably provide electrical current--to isolate sodium and potassium," he observes.

Peter Morris, principal curator for chemistry at the Science Museum, London, stresses that Davy isolated rather than discovered these elements. "I always argue that Davy did not actually discover them, as the elements were already known," Morris says. "For instance, Joseph Black had identified magnesium as a distinct element in 1755."

The isolation of radium, by Marie Curie and her husband Pierre, demonstrated a beauty of spirit, according to Giunta. "The principle leading to these discoveries was elegant," he says. "The isolation of radium after long work in arduous conditions displayed perseverance."

The Curies used fractional crystallization to isolate the elements from pitchblende, a uranium ore obtained as waste from mines. They carried out the separations in an old shed. Most of the work was done by Marie.

The two Curies shared the Nobel Prize in Physics in 1903 "in recognition of the extraordinary services they have rendered by their joint researches on the radiation phenomena discovered by Professor Henri Becquerel," according to the Nobel citation. Marie also won the Nobel Prize in Chemistry in 1911 "in recognition of her services to the advancement of chemistry by the discovery of the elements radium and polonium, by the isolation of radium and the study of the nature and compounds of this remarkable element."

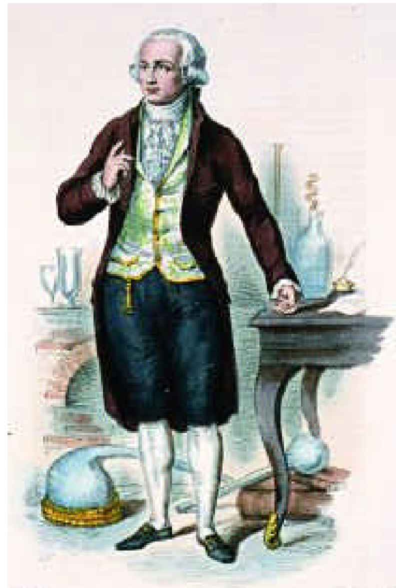
The discovery of oxygen by English scientist Joseph Priestley--number seven on the list--was designated as an International Historic Chemical Landmark jointly by the American Chemical Society and its British counterpart, the Royal Society of Chemistry, in England three years ago (C&EN, Sept. 11, 2000, page 34).

Priestley discovered that a gas, or "air" as he called it, was readily expelled on heating "red calx" of mercury--mercury(II) oxide. Priestley did not, however, identify the new gas as oxygen. It was named oxygen by French chemist Antoine Lavoisier, who repeated Priestley's experiment with mercury(II) oxide. Priestley shares the credit for discovering oxygen with Swedish pharmacist and chemist Carl Wilhelm Scheele, who isolated the gas by several methods, including heating various oxides and nitrates.

The development of atomic flame spectroscopy as an analytical technique by physicist Gustav Kirchhoff and chemist Robert Bunsen at the University of Heidelberg, Germany, also led to the discovery of elements. In 1860, the two scientists used the technique to show that cesium was present in samples of mineral water. They subsequently extracted the metal from the water. A year later, they discovered rubidium in the mineral lepidolite using the same technique.

Lord Rayleigh and Sir William Ramsay's discovery of argon was nominated by three readers but did not receive sufficient panel votes for the top 10. The preparation of the first noble gas compound did, however.

COORDINATION CHEMIST Neil Bartlett, now emeritus professor of chemistry at the University of California, Berkeley, prepared the compound when he was a faculty member at the University of British Columbia, Vancouver. He showed that platinum hexafluoride, a highly reactive blood-red compound, combines with xenon to form $Xe^{+}[PtF_6]^{-}$, a yellow-orange salt that is stable at room temperature.



METALIST **Lavoisier's work on the oxidation of metals garnered the number two spot because it made chemistry a quantitative science.**
NATIONAL LIBRARY OF MEDICINE PHOTO

What is beautiful about a chemistry experiment and what is not is highly subjective. Two readers, for example, voted for a discovery that has some distinctly ugly features--the discovery of phosphorus by German chemist Hennig Brandt.

"The elemental white phosphorus product is aesthetically beautiful--a waxy, glowing white mass," Giunta points out. "But Brandt had no coherent experimental intent that we are aware of, no expectation of what would happen, so there is no intellectual beauty in this story.

"Also, in some respects, the experiment was quite repulsive," he adds. "It involved the putrefaction and distillation of urine."

Brandt's discovery did not make it into the top 10.

Several panel members expressed reservations about perceiving the "beauty" of experiments in regard to the poll. "I'm simply not qualified to judge whether different experiments, over a 500-year period, were 'elegantly simple' by the standards of their day," comments panel member Arnold Thackray, president of the Chemical Heritage Foundation, Philadelphia. "But I do have a view of which experiments were 'beautiful' if, by beautiful, we mean holding profound significance to us today."

Morris goes even further, questioning the concept of a beautiful chemistry experiment. "I find these exercises inherently problematic, not least because I do not consider most of the events in your list to be an 'experiment,' let alone a beautiful one," he tells C&EN. "I do not think it is in the nature of chemistry to have 'beautiful experiments.' Beauty is more a function of mathematics and physics. Insofar as beauty can occur in chemistry, I think it belongs to synthesis, although elegant would be a better adjective. And there are hardly any syntheses on your list."

Ramberg, on the other hand, was struck by what he considered to be the predominance of syntheses and isolation techniques in the shortlist. However, he agrees with Morris that few of the shortlisted "events" can be considered experiments. "Many of them are accidental and therefore difficult to describe as an 'experiment' as such," he says.

An example of such an "experiment" is the discovery of the synthetic dye mauveine, also known as Perkin's mauve or aniline purple, by English chemist William Henry Perkin (C&EN, July 2, 2001, page 31). Perkin serendipitously prepared the dye while attempting to synthesize the antimalarial drug quinine from coal-tar extracts.

"There are very few experiments listed that were an explicit test of some specific theoretical chemical principle," Ramberg observes. "The predominance of synthesis in the shortlist may reflect the practice of chemistry itself, in which synthetic techniques are central, or it may also reflect the perceptions chemists have of past accomplishments in chemistry.

"Preparations and syntheses are always given prominence in textbooks, and therefore these stand out in chemists' minds as the classic experiments in chemistry," he continues. "Chemists may perceive the nature of a 'beautiful experiment' in a different way than physicists, who see them as a crucial test of a specific hypothesis."

Roald Hoffmann, chemistry professor at Cornell University and winner of the Nobel Prize in Chemistry in 1981, notes that the shortlist nominated by readers includes both single experiments and groups of experiments. "I have a lot of ambiguity about groups of experiments," he remarks. "On the one hand, I realize discovery, even by one person, is stepwise and painfully fragmented at times. But I think the group of experiments suggested has to be carefully examined, each by itself, and this is worth a substantive discussion, maybe a book!

"There is also drama in a single piece of work," Hoffmann adds, citing Bartlett's synthesis as an example. "Physicists, biologists, and the public at large tend to focus on single experiments. I don't know myself what is the answer, but I tend to come down on the side of single experiments."

The four highest ranked items in the top 10 are all bodies of work rather than single experiments. Pasteur's work on tartrate crystals continued for several years, for example, and Lavoisier carried out numerous experiments on the oxidation of metals.

"The experiments in which [Lavoisier] carefully weighed reactants and products of chemical reactions in order to account for all the transformations involved made chemistry a quantitative science, allying it with the beautiful realm of numbers," Giunta says. "Conceptual simplicity and elegance are evident in the application of conservation of mass to chemical transformations. And ingenuity is evident in the design of experimental apparatus to capture all of the relevant materials. I would single out his mercury/cinnabar experiments because of the pivotal role they played in his thinking about the role of oxygen in combustion."

THE DETERMINATION of the configuration of glucose by German chemist Emil Fischer is also an example of a body of work rather than a single experiment. "This was part of a large research project involving several smaller projects on the classification of the natural monosaccharides that gradually came together in 1891, when Fischer first proposed the configuration of glucose itself," Ramberg explains. "There was therefore no one specific experiment that 'determined' the configuration of glucose. This would be an example perhaps of 'beautiful chemical reasoning,' rather than a specific experiment."

SWEET SPOT Fischer rounds out the top three for determining the configuration of glucose. NATIONAL LIBRARY OF MEDICINE PHOTO

The discovery of alkylmagnesium halides (RMgX) by French organic chemist Victor Grignard is another example of a body of work rather than a single experiment. Grignard showed that solutions of alkyl halides in dry diethyl ether react with magnesium to form solutions known as Grignard reagents.

"Grignard made a large number of compounds with his reagents," Giunta notes.

Grignard reagents are essentially ionic. They contain covalent but highly polar carbon-magnesium bonds and can be regarded as carbanion donors. They are widely used in the synthesis of alkanes, alcohols, ketones, carboxylic acids, and other types of organic compounds.

Friedrich Wöhler's discovery that urea, an organic compound, can be prepared by heating ammonium cyanate, an inorganic compound, was among the top five nominations by C&EN readers. However, the panel gave it the thumbs-down, and it was therefore not included in the top 10.

"Professional historians of science have known, since 1944, that the story of Wöhler's synthesis of urea has been greatly distorted, and the revisionist version has been confirmed several times since 1944," Rocke explains. "First, Wöhler's reaction was simply a rearrangement of ammonium cyanate, which is not a very elegant experiment. Second, Wöhler's urea was not the first organic material to be prepared artificially. Third, committed vitalists disputed the synthesis on several grounds, for instance, by denying organic status to urea."

According to the vitalistic theory of organic chemistry, held by chemists in the 18th century, organic compounds could only be synthesized by means of a 'life force' in living cells. "By 1828, chemical vitalists were few and far between, and vitalism was well on the way out," Rocke says. "Despite what you read in the introductions to most organic chemistry textbooks, Wöhler did not destroy vitalism by this experiment, and he never claimed to have done so."

The determination of the double helix structure of DNA from X-ray diffraction studies by Francis H. C. Crick and James D. Watson also, perhaps surprisingly, did not make the top 10. It received just two nominations from C&EN readers, and most panel members voted against including it in the top 10. "It was brilliant work, but not an experiment in my book," Morris says.

Ramberg points out that the work was not a test of chemical principle. "This was a classic episode in structural elucidation using X-ray diffraction and model building," he says. "Crick and Watson applied well-established chemical and crystallographic principles to arrive at the structure, which answered an essentially biological question."

Inevitably, not every chemist will agree with the choice of the top 10 and their rankings. But one thing is for sure: The beauty of a chemistry experiment or body of work is in the eye of the chemist, or, as Pasteur may have said, "Chacun à son goût."

Top

BEAUTY & CHEMISTRY

In The Eyes Of The Beholders

Last November, this reporter asked C&EN readers to send in their nominations for "the most beautiful experiments in chemistry" (C&EN, Nov. 18, 2002, page 5). The unusual solicitation was prompted by a Sept. 24, 2002, ***New York Times*** article titled "Here They Are, Science's 10 Most Beautiful Experiments."

On closer reading of the article, it turned out that the experiments described were the 10 most beautiful ***physics*** experiments. They had been collected by Robert P. Crease, a member of the philosophy department at the State University of New York, Stony Brook, and historian at Brookhaven National Laboratory. He had asked readers of the international magazine ***Physics World*** to nominate the most beautiful experiments of all time. It shouldn't have surprised anyone that to a physicist, beauty is physics. A lot of C&EN readers were irritated, and so this current experiment began: Why not ask C&EN readers for their nominations of what constitutes beauty in science?

Nominators were asked to send a brief description of the experiment and who conducted it and to answer the question: What is the connection between its beauty and its scientific value? Not many of the 70 readers who responded actually followed these instructions, but C&EN Senior Correspondent Michael Freemantle was not put off by the challenge of compiling the list.

Chemistry's list has one thing in common with Crease's list: All the winners were solo, or nearly solo, achievements. No big science experiments made the list. Crease's original list has now become a book, "The Prism and the Pendulum: The Ten Most Beautiful Experiments in Science," to be published by Random House this fall. One supposes that book publishers assume that physics and science are synonymous. In any event, it is a very nice book, with a lengthy introductory essay on what makes an experiment beautiful and a nice epilogue about whether beauty can be found in the age of big science. Despite its narrow focus on physics, the book is well worth reading.

In keeping with this reporter's original pledge to readers, C&EN's 10 Most Beautiful Chemistry Experiments will now be shipped off to the ***New York Times.*** --MADELEINE JACOBS

Top

Home | Table of Contents | Today's Headlines | Business | Government & Policy | Science & Technology | cen-chemjobs.org

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