

Oesper Museum Booklets on
the History of Chemical Apparatus

No. 1

POLARIMETERS

William B. Jensen
University of Cincinnati

Photography by Jay Yocis



Oesper Collections
University of Cincinnati
2014

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SERIES INTRODUCTION

Like most museums, only about 25% of the holdings of the Oesper Collections in the History of Chemistry are on public display at a given time. In order to make the remaining 75% available in some form, it was decided to initiate a series of short museum booklets, each dedicated to a particular instrument or laboratory technique of historical importance to the science of chemistry. Each booklet would include not only photographs of both displayed and stored museum artifacts related to the subject at hand, but also a short discussion of the history of the instrument or technique and of its impact on the development of chemistry as a whole. Several of these booklets are expansions of short articles which have previously appeared in either the bimonthly series *Museum Notes*, which is posted on the Oesper website, or the series *Ask the Historian*, which appeared in the *Journal of Chemical Education* between 2003 and 2012.

William B. Jensen
Cincinnati, OH
April 2014

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The Discovery of Polarized Light

In 1669 the Dane, Erasmus Bartholinus (1625-1698), discovered that objects, when viewed through a crystal of a particular variety of clear calcium carbonate known as Iceland spar (figure 1), appeared double – a phenomenon now known as *double refraction*.¹ Unknown to Bartholinus at the time was the fact that the light



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Figure 1. A large mounted single crystal of Iceland spar (9.5" x 5.25" x 5") used to illustrate the phenomenon of double refraction, circa 1880. The significance of the paper crystal models will become apparent later.

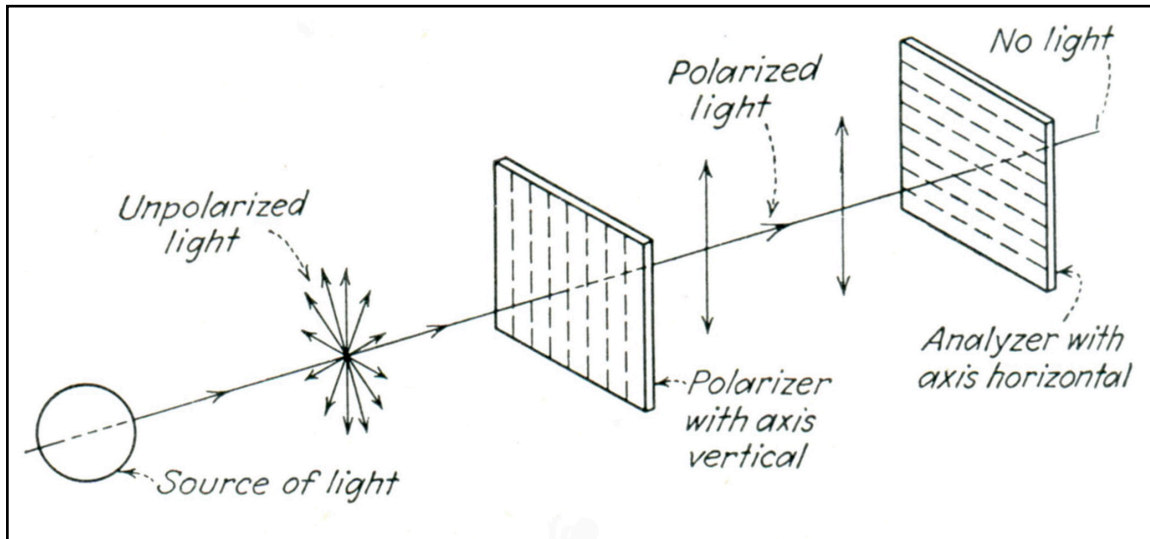


Figure 2. Nature of plane polarized light as envisioned by the wave model of light. The crystals of Iceland spar act like a picket fence that allows only one plane of light to pass. When the polarizer and analyzer crystals are at right angles, the light beam is extinguished.

passing through these crystals was also *polarized* – a phenomenon that was instead discovered by the French physicist, Etienne-Louis Malus (1775-1812), in 1809, along with the fact that light reflected from various surfaces was similarly polarized.²

A beam of light passing through two plates of glass looks the same to the human eye no matter how the two plates are rotated relative to one another. However, if a beam of polarized light, originating either from a reflecting surface or from passage through a crystal of Iceland spar (called the source or polarizer), is viewed through a second crystal of Iceland spar (called the analyzer), it is visible in its full intensity only if the planes of polarization for the two crystals are aligned. But if the analyzer crystal is gradually rotated relative to the polarizer crystal, the light intensity gradually decreases until it is extinguished when the planes of polarization for the source and analyzer are at right angles. It is as if whatever transmits the light beam no longer acts in all directions but is instead

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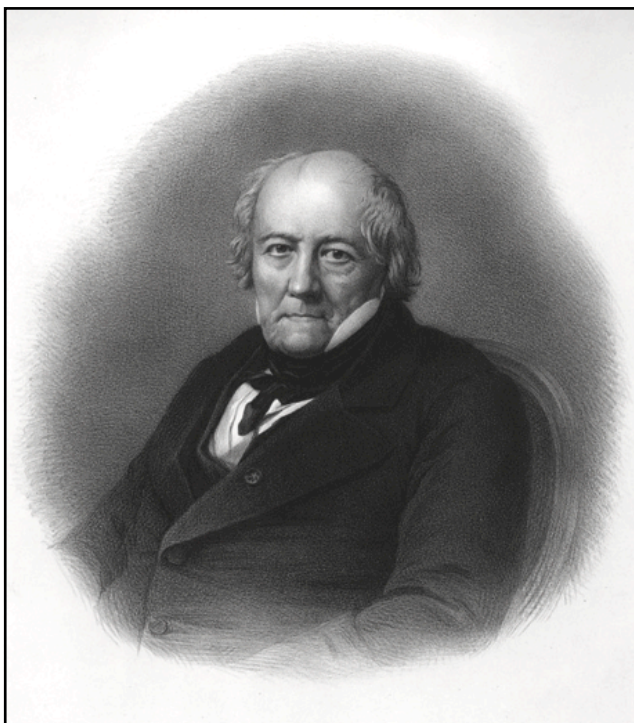


Figure 3. Jean-Baptiste Biot (1774-1862) inventor of the polarimeter.

confined to a single plane, though this change or polarization is undetectable to the unaided human eye (figure 2).

History of the Polarimeter

In 1811 the French physicist, François Arago (1786-1853), discovered that, when samples of certain transparent crystals, such as quartz, were placed between the polarizer and the analyzer, the angle at which the polarized light beam was extinguished was changed, suggesting that the plane of the polarized light from the source had been twisted a certain

number of degrees, either to the left or right, on passing through the sample.³ Even more important was the discovery in 1815 by the French physicist, Jean-Baptiste Biot (figure 3), that the same was true of certain organic liquids, such as oil of turpentine, and for the solutions of certain organic compounds, such as sugar.⁴ This ability of certain substances to twist the plane of a polarized light beam became known as *optical activity* and the measure of the number of degrees through which the plane was rotated as the *optical rotatory power* of the sample.

The instrument which Biot invented to study this phenomenon became known as a *polariscope*.^{4,5} In his early instruments Biot used reflected light as his source and placed his liquid samples and solutions in long tubes with transparent windows at each end (figure 4). He later added a circular wheel calibrated in degrees to the analyzer (figure 5) thus allowing one to quantitatively determine the angle of rotation for the sample, and thereby converting his simple polariscope into

a proper *polarimeter*.⁶ With this device, Biot discovered, between 1811 and 1860, all of the basic laws of polarimetry. Thus he found that the rotatory power of a substance depended not only on its chemical nature, but also on the thickness of the sample, the temperature,

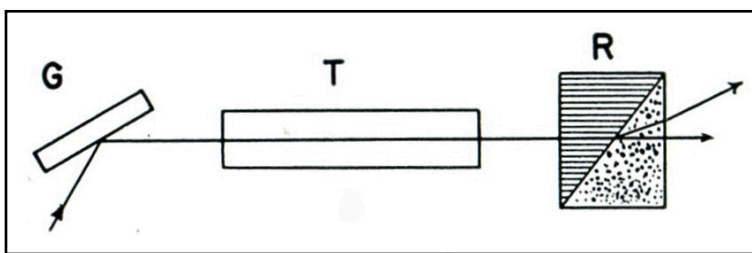


Figure 4. A schematic of Biot's original polariscope. The source is the polarized light produced by reflection of light off of a glass plate (G). The beam then passes through the sample tube (T) and on to a rotatable analyzer made of wedges of quartz and Iceland spar known as a Rochon prism (R).

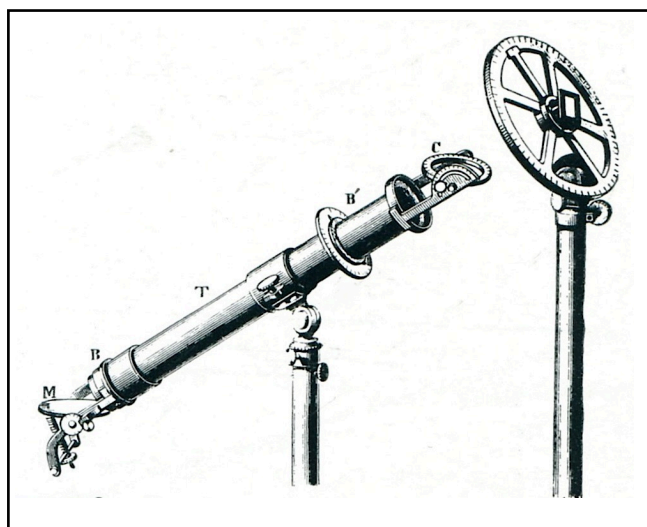


Figure 5. An early polarimeter designed by Biot. A black mirror (M) is the source for generating the polarized light beam by reflection. The tube containing liquid samples is in T and C is the mount for the study of solid samples. Note the addition of the circular scale with the analyzer in the center. As this analyzer is rotated an attached pointer moves along the circular scale, thus allowing one to quantitatively measure the optical rotary power of the sample.

the wavelength of the polarized light and, in the case of solutions, on both the concentration and the nature of the solvent. If the temperature (T) and wavelength (λ) are kept constant, this dependency, in the case of solutions, can be expressed by the simple equation:

$$\alpha = \alpha_D l c \quad [1]$$

where α is the observed rotation for the sample in degrees, l is the length of the sample tube, and c is the concentration. The proportionality constant, α_D , is called the *specific rotary power* of the sample and is equal to α when l was set at one decimeter, c at one

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gram of solute per mL of solution, the temperature at 20°C, and the wavelength of the polarized light equal to that of the yellow D-line of the sodium spectrum. If the sample corresponds to a pure liquid instead, c is replaced in equation 1 by the density (ρ) of the liquid. If the sample rotates the polarized light to the right, it is said to be *dextrorotatory* and α is assigned a positive value. If it rotates the polarized light to the left, it is said to be *levorotatory* and α is assigned a negative value.

In his original polarimeter Biot did not use a simple crystal of Iceland spar as his analyzer but rather a prism consisting of a wedge of spar glued to a complimentary wedge of rock crystal or quartz that was introduced around 1766 by the French astronomer, Alex-Marie de Rochon (1741-1817). The problem with using Iceland spar as either the source

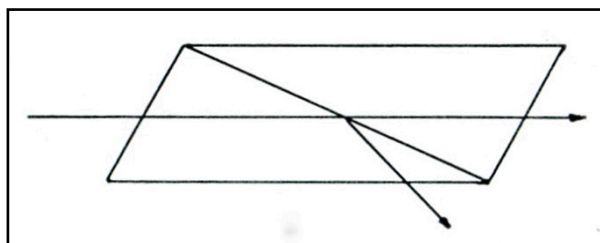


Figure 6. A Nicol prism made from two sections of Iceland spar indicating the divergence of the two refracted light rays.

or the analyzer was that it not only polarized the light, it also, as mentioned earlier, split it into two beams because of its ability to cause double refraction. A way of eliminating the resulting double image was finally discovered by the Scottish geologist, William Nicol (1770-1851), in 1829.⁷ He bisected a naturally occurring parallelepiped of Iceland spar along its shortest diagonal and then glued the two halves together as shown in figure 6. This so increased the angle of divergence between the two refracted beams that one of them was projected onto the interior wall of the polarimeter tube and lost while the other was projected down the center of the tube to the eye piece. In honor of its inventor, this device became known as a Nicol prism.

Using this innovation, the German chemist, Eilhard Mitscherlich (figure 7), introduced a modified polarimeter in 1844 for use with pure liquids and solutions, which employed a direct, rather than a reflected, light source, and in which both the polarizer and the analyzer were Nicol prisms (figure 8) – innovations which remained the basis of polarimeter design well into the 20th century.⁸

The Saccharimeter

One of the most important practical uses of the polarimeter was to monitor the concentration of sucrose solutions in the sugar industry. A solution of cane sugar or sucrose is optically active and has a specific rotatory power of +66.45 degrees. If we solve equation 1 for c :

$$c = \alpha / \alpha_D l \quad [2]$$

and fix the value of l along with the temperature and wavelength, then we have a direct proportionality between the concentration of our sugar solutions and their observed rotation:

$$c = k\alpha \quad [3]$$



Figure 7. Eilhard Mitscherlich (1794-1863) inventor of the most popular 19th-century form of the polarimeter.

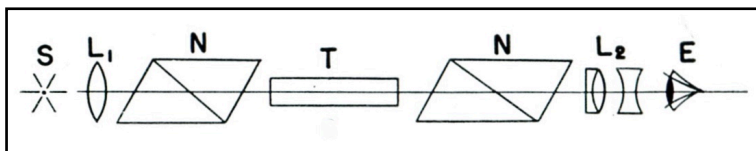


Figure 8. A schematic for Mitscherlich's modified polarimeter. A light source (S) is focused by means of a lens (L_1) on the Nicol prism (N) serving as the polarizer. The polarized light then passes through the sample tube (T) to a second rotatable Nicol prism which serves as the analyzer and the resulting light intensities are magnified by means of a second lens system (L_2) before reaching the eye.

where $k = (66.45l)^{-1}$ and we can now alter the scale on our polarimeter so as to directly read in concentration units instead of degrees of rotation. Indeed, since c is measured in units of gram/mL, if we set our scale at 100 for a

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pure sucrose solution, the scale reading will then directly tell us what percent by weight of an impure sample is also sucrose. A polarimeter altered in this fashion is called a *saccharimeter*.

There are, however, several more important differences between a standard polarimeter and a saccharimeter. Because sugar concentrations must be monitored continuously in a sugar mill and it was difficult for 19th-century chemists to maintain a constant and long lasting sodium flame, there was a demand for a polarimeter that could instead employ common polychromatic light sources. In addition,

the bright yellow of the sodium flame was hard on the eyes if used for prolonged periods. These problems were solved in 1845 with the introduction of the quartz wedge compensator by the French instrument maker Jean-Baptiste François Soleil (1798-1878).⁹

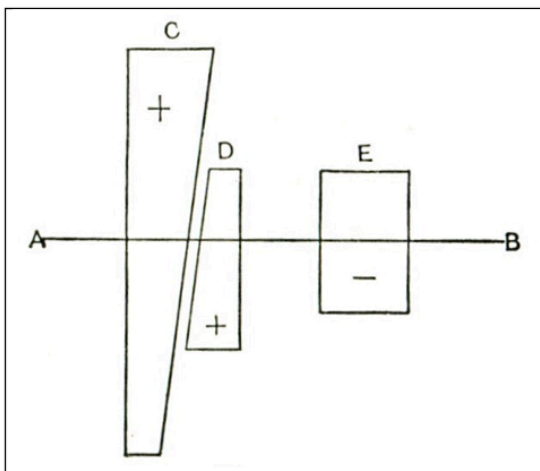


Figure 9. The principle of the quartz wedge compensator. C and D are wedges of dextrorotatory quartz and E is a crystal of levorotatory quartz. Details are described in the text.

The principle involved is illustrated in figure 9, where AB is the light path through the polarimeter, with the sample tube, polarizer and associated optics to the right (not shown), and the analyzer and associated optics to the left (not shown). C and D represent two wedges of dextrorotatory quartz which can be slid past one another so as to alter their com-

combined thickness in the light path, and E is a crystal of levorotatory quartz. With the sample cell empty, the light from the polarizer passes through E, where it is rotated to the left, and then through C and D, where it is rotated to the right. The combined thickness of C and D is then mechanically altered until it just cancels or compensates for the rotation produced by E.

When an optically active sucrose sample is then placed in the sample cell to the right of E, it rotates the polarized light to the right and thus partially undoes the

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left rotation from E. As a result, the overlap of C and D required to compensate for E is less than for the empty cell and the change in their overlap can be mechanically translated into a linear scale which gives the concentration of the sugar solution directly. In addition, this compensation works for all wavelengths and thus eliminates the necessity of using a monochromatic sodium light. All of this means that quartz-wedge saccharimeters are generally lacking both the large circular scales and the sodium light sources that are so characteristic of the conventional polarimeter.

Further Developments

In addition to the above developments, considerable effort was also expended on manipulating the optical image seen through the eye piece so as to make determination of the extinction point more accurate. By 1900 the most common of these devices were either the Lippich two-prism or three-prism systems (figure 10).

Starting in the 1970s, two further innovations radically changed the nature of the laboratory polarimeter. The first of these was the replacement of the Nicol prism by polarized plastic film. First patented in 1929 by Edwin Land and sold under the trade name of *Polaroid*, the original product consisted of aligned microscopic crystals of optically active iodoquinine sulfate embedded in a transparent film of nitrocellulose. Also known as *J-sheet*, this product was replaced in 1938 by a product known as *H-sheet*, which consisted of optically aligned polymer chains of polyvinyl alcohol doped with iodine. A third variation, known as *K-sheet*, was later introduced

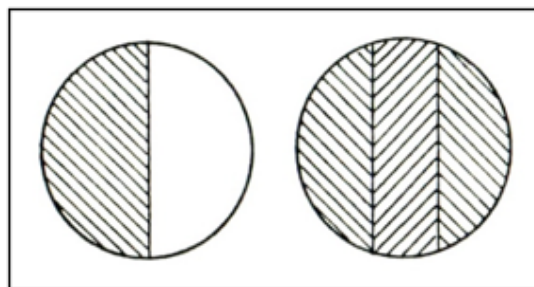


Figure 10. The optical fields produced by the Lippich two-prism (*left*) and three-prism (*right*) detection systems. For the two-prism system, the dark half becomes lighter and the light half darker as the analyzer is turned. The point at which the two halves are of equal intensity is the extinction point. For the three-prism detector the same principle applies relative to the central strip versus the two sections on either side.

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which consisted of optically aligned chains of polyvinylene.

The second major change was the replacement of the human eye with photo-cells coupled to a digital readout system of some sort. This initially consisted of an electrically driven mechanical scale but now takes the form of a liquid-crystal display. The net result is that the modern polarimeter has the appearance of an electronic “black box” which bears little physical resemblance to its 19th- and early 20th-century predecessors.

Museum Holdings

The following four sections deal with artifacts in the Oesper Collections relevant to the history of polarimeters, saccharimeters and related instruments. Regrettably the museum contains no 19th-century examples of these instruments and its earliest holdings date instead from around 1900. In order to maximize the image sizes, all descriptions and commentary for these sections have been confined to the figure captions.

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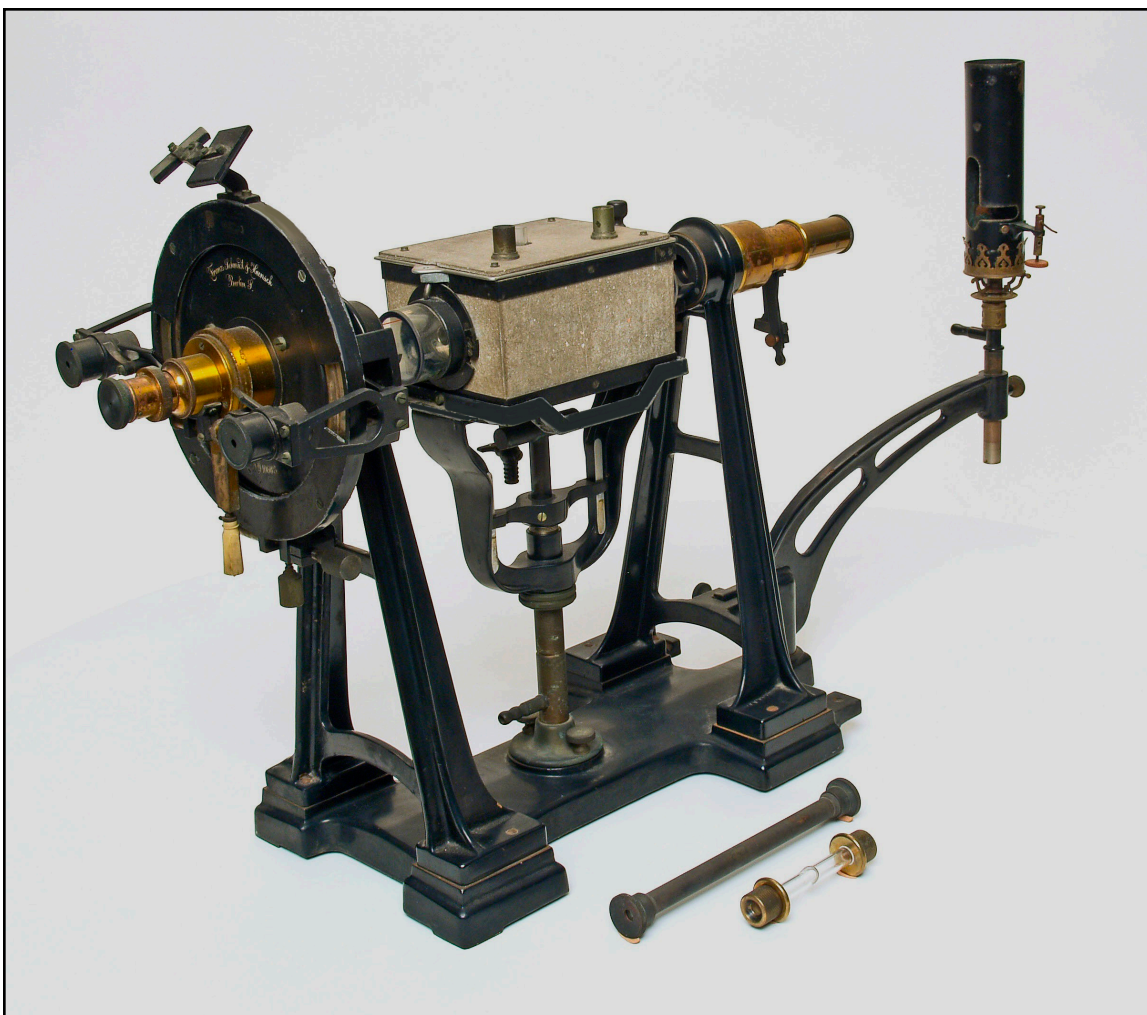
Polarimeters and Saccharimeters



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Figure 11. This is one of two examples owned by the museum of a circa 1900 polarimeter (22.5" x 17" x 9") made by F. Schmidt and Haensch of Berlin. A sodium flame serves as the light source and both the polarizer and rotatable analyzer are Nicol prisms. The analyzer and circular scale are rotated by means of the three projecting knobs on the eye piece, and the scale is read from the front by means of stationary verniers and the two magnifying lenses located to the left and right of the eyepiece. The extinction point is determined using a Lippich two-prism system. The "sight" at the far left is used to align the plane of the polarizer. The two instruments owned by the museum bear the identification numbers 7918 and 8422. The latter instrument differs from the former in having a double vernier opposite the left magnifying lens.

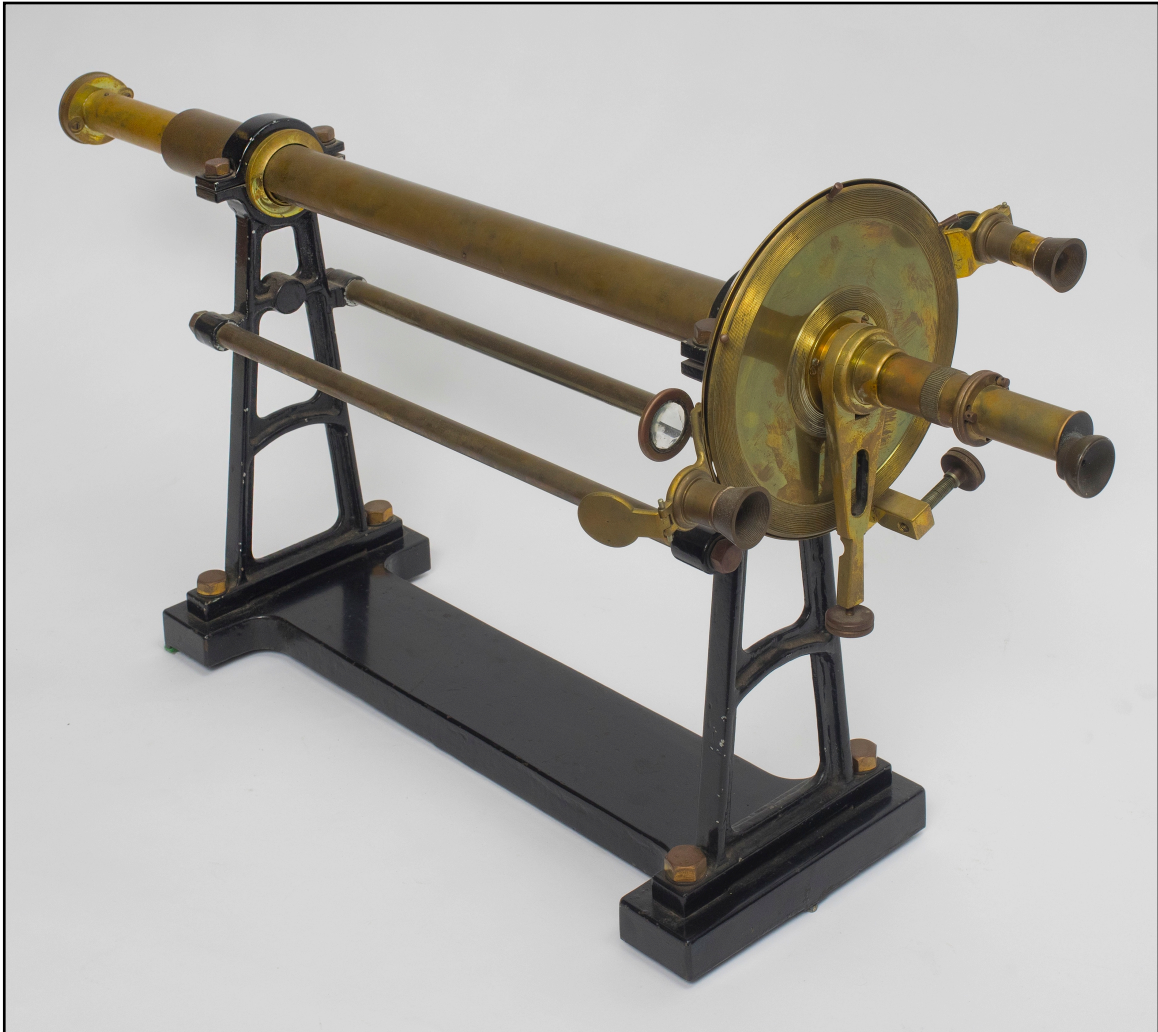
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Figure 12. A circa 1900 deluxe polarimeter (33"x 19.5" x 8.75") made by F. Schmidt and Haensch of Berlin with an adjustable constant temperature water bath for the polarimeter tubes and an attached sodium gas flame as the light source. The asbestos insulated aluminum box that serves as the water bath is heated by means of a second gas burner located directly below it and has openings in its lid for a thermometer and stirrer. The circular scale is enclosed and is read from the front via stationary verniers and two cutouts in its casing immediately opposite the two magnifying lenses on either side of the eyepiece. The front plate of the scale housing bears the instrument identification number 10608.

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Figure 13. An extra-long, circa 1914 polarimeter (35.5" x 17" x 10") made by Bellingham and Stanley of London. A sodium flame serves as the light source and both the polarizer and rotatable analyzer are Nicol prisms. The circular scale is completely encased and is read from the back side via two cutouts using the two magnifying lenses located to the left and right of the eyepiece, fixed verniers, and a system of mirrors. The scale and analyzer are rotated using six small knobs located along the outer circumference of the scale.

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Figure 14. A circa 1920 saccharimeter (23.5" x 17" x 11.5") made by F. Pellin of Paris for the Arthur Thomas Company of Philadelphia.¹⁰ It uses a polychromatic light source with a potassium dichromate filter and a quartz-wedge compensator that allows one to read the sugar concentration directly off a linear scale – whence the absence of a circular scale. Instead, the half circle plate to the left of the cell compartment was apparently intended to serve as a light shield.

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Figure 15. A circa 1930 Mitscherlich-style polarimeter (18.5" x 15.5" x 4.75") made by the firm of Rudolf Winkel of Göttingen Germany. A sodium vapor lamp serves as the light source. The circular scale and analyzer are rotated by means of the three knobs projecting from the eyepiece and the former is read by means of a stationary vernier located at the top. Both the polarizer and analyzer are Nicol prisms and detection is based on the Lippich two-prism or half-shadow system. The instrument identification number is 7189.

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Figure 16. A circa 1960 full circle polarimeter (15.5" x 8" x 4.25") made by Kern of Aarau Switzerland. A sodium lamp serves as the light source, which, thanks to the mirror, can be placed to one side rather than directly behind the instrument. Both the polarizer and rotatable analyzer are Nicol prisms. The outer stationary circular scale is read from the front by means of a single magnifying lens which is rotated, along with the vernier and analyzer, by means of the lever to the lower right of the eyepiece. The extinction point is determined using a Lippich three-prism system.

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Figure 17. One of two examples owned by the museum of a circa 1970 student model SR6 polarimeter (15.75" x 8.5" x 4.5") made by the firm of Stieg and Reuter of Bad Homburg, West Germany. They come with detachable sodium lamps, and appear to use polaroid sheet rather than Nicol prisms for both the polarizer and analyzer. They also employ the half-shade principle for detecting the extinction point. The stationary semi-circular scale is read from the front by means of a magnifying lens and a vernier which rotate with the analyzer and are controlled by means of the lever located beneath the eye piece. The two instruments owned by the museum bear the instrument identification numbers 4403 and 3812 and differ in the color of their bases.

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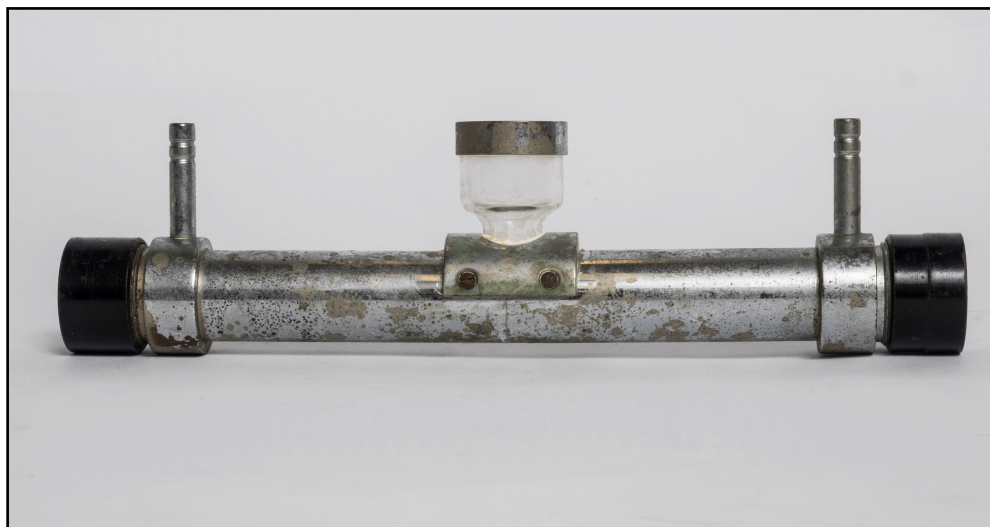
Sample Tubes



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Figure 18. A selection of polarimeter tubes. They range in size from 8.25" x 1" to 4.25" x 1". Some are encased in metal, some have tinted glass, and some have a side opening for adding the sample and/or monitoring the temperature. The caps on the older tubes are metal whereas those on the newer tubes are plastic.

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Figure 19. A polarimeter tube (8.5" x 2" x 1") with a metal water jacket for regulation of the sample temperature.

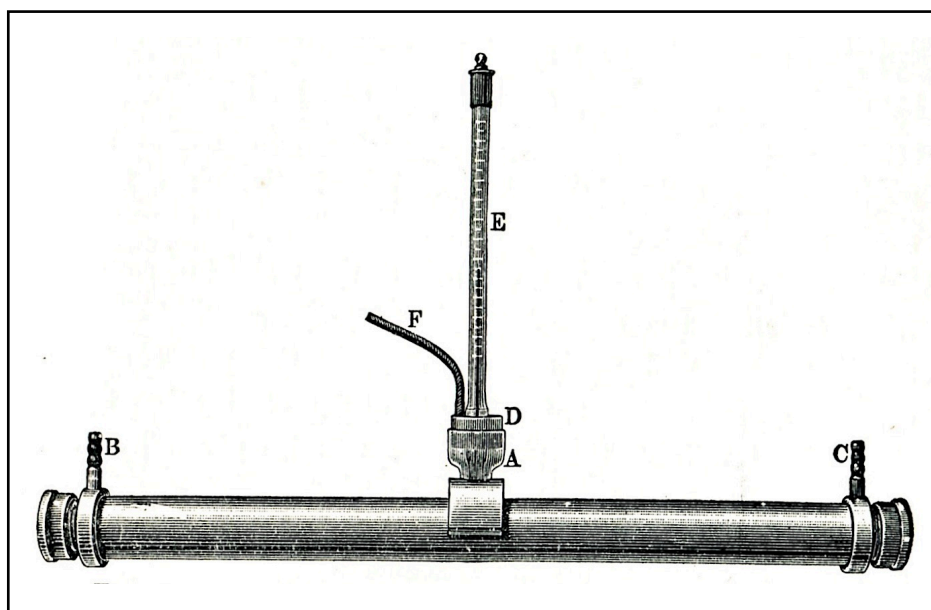
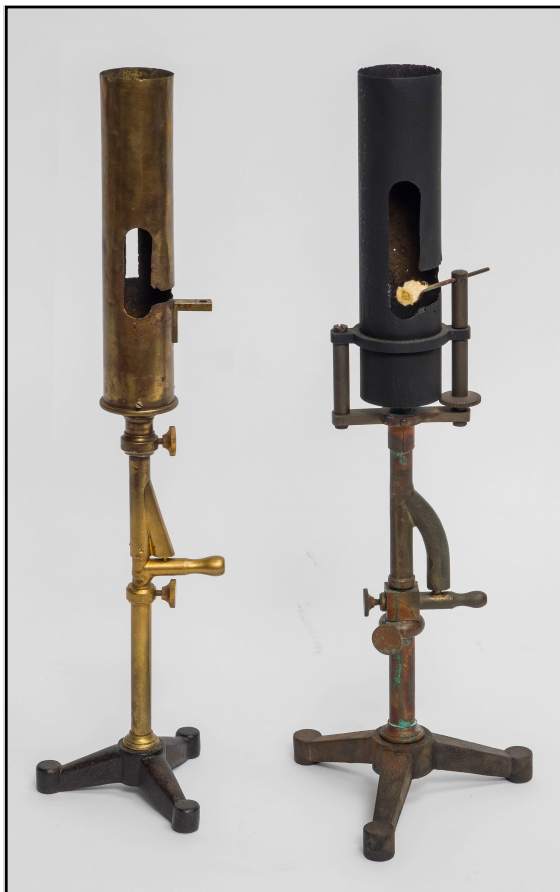


Figure 20. A period etching of the jacked polarimeter tube shown in figure 19 as given in G. W. Rolf, *The Polariscope in the Chemical Laboratory*, Macmillan: New York, NY, 1905, p. 93. E is the thermometer, F is an air vent, D is a rubber stopper, B and C are the inlets and outlets for the circulating water and/or steam.

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Light Sources



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Figure 21 (left). A pair of circa 1900 sodium light gas burners (left: 16.5" x 4" x 4"; right: 16.5" x 5" x 5"). The yellow sodium flame is obtained by rotating an asbestos or pumice plug soaked in a solution of sodium chloride into the gas flame. A similar burner is attached to the polarimeter in figure 12. The burner on the left appears to have been modified to act as a luminous light source for use with a saccharimeter rather than a polarimeter.



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Figure 22 (right). A circa 1940 sodium vapor lamp and power source (power source: 6" x 6" x 5"; lamp & stand: 13" x 8" x 4"). The power source indicates that it was manufactured by George W. Gates & Co. of Franklin Square, Long Island, NY. Electric sodium vapor lamps did not become commercially available until the late 1930s.

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Figure 23 (*left*). A circa 1950 sodium vapor lamp and power source (power source: 6" x 6" x 5.75"; lamp & stand: 14" x 8" x 5"). No manufacturer information is indicated on either the lamp or the power source.

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Figure 24 (*right*). A circa 1960 sodium vapor lamp and power source (power source: 15" x 8" x 5.5"; lamp & stand: 15" x 8" x 5"). The power source indicates that it was manufactured by O. C. Rudolph & Sons, Inc. of Fairfield, NJ, as Model No. 90.



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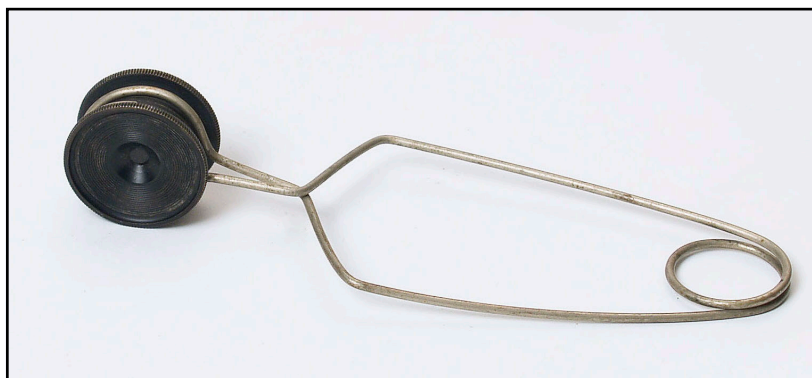


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Figure 25. (*left*). A circa 1980 sodium vapor lamp and power source (power source: 10.5" x 7.5" x 4.75"; lamp & stand: 16"x 14" x 3"). No manufacturer information is indicated on either the lamp or the power source.

Related Instruments

Figure 26 (*right*). A circa 1920 pair of wire tongs (5.75" x 2" x 1") containing a pair of polarizing tourmaline crystals set in rotatable painted brass disks and used for viewing gems and minerals. First described by K. M. Marx in 1827.



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Figure 27 (*left*). A circa 1910 polarizing microscope (13" x 6" x 4.5") made by E. Leitz of Wetzlar Germany. It is essentially a vertical polarimeter for viewing thin cross-sections of minerals and rocks rather than liquids, as in the case of conventional horizontal polarimeters. Rather than rotating the analyzer (located in the tube) one rotates the circular sample stage. This has a scale on its outer rim and a fixed vernier to one side (not visible). It can be used for rapid identification of the various minerals in rock samples.

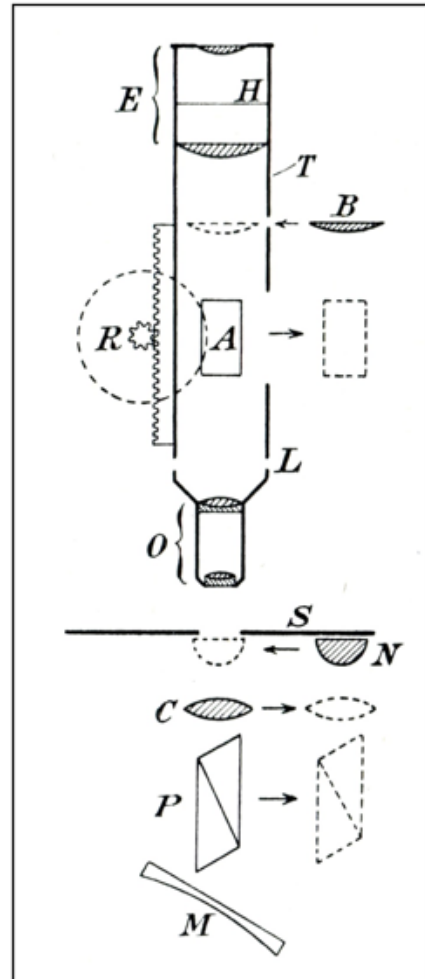


Figure 28 (*right*). A side-view schematic of a classical polarizing microscope.¹¹ E is the eyepiece, T is the tube, R is the focus knob, O is the objective, S is the stage, and M is the mirror. A is the analyzer and P is the polarizer, both of which can be slide in and out of the optical field along with various supporting lenses (B, N and C).

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The Polarimeter's Significance in the History of Chemistry

The year 1848 saw the publication of a landmark paper in the history of chemistry by the French chemist and microbiologist, Louis Pasteur (figure 29), in which the polarimeter played a key role.¹² Pasteur was studying the relationship between the dissymmetry of hemihedral crystals and their optical activity. Dissymmetric crystals often come in two forms, known as *right-handed* and *left-handed*, which are nonsuperimposable mirror images of one another. As early as 1820 the British physicist, John Herschel, had shown that crystals of right-handed quartz rotated polarized light to the right, whereas crystals of left-handed quartz rotated it to the left.¹³ Pasteur was working with an optically inactive racemic form of the salt sodium ammonium tartrate [$\text{Na}(\text{NH}_4)(\text{C}_4\text{H}_4\text{O}_6)$]. Upon carefully examining the crystals



Figure 29. Louis Pasteur
(1822-1895)

of a freshly prepared batch of this compound, he discovered that not all of them were identical. Rather they consisted of a mixture of left- and right-handed nonsuperimposable hemihedral crystals (figure 30) like those found in quartz.

These he sorted out under a microscope and, when he tested solutions of each in his polarimeter, he found that the solution of the right-handed crystals rotated the polarized light to the right and that of the left-handed crystals rotated it an equal number of degrees to the left. The reason this compound had appeared to be optically inactive was that it was in

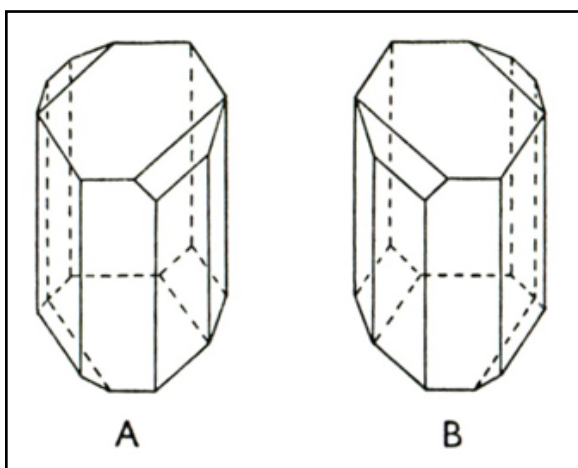


Figure 30. Drawings of left- and right-handed sodium ammonium tartrate crystals (A and B). Paper models of A and B also appear in figure 1 in front of the large mounted crystal of Iceland spar.

molecular arrangement of the molecules within the crystals, which was destroyed when the crystals were dissolved, that of the tartrates had to reside instead within the structure of the molecules themselves and therefore persisted after dissolution.¹⁴

Now instead of studying the correlation between optical activity and the dissymmetry of crystals, as Pasteur had, the focus shifted – especially after the rise of classical structure theory in the late 1860s – to a study of the correlation between optical activity and the dissymmetry of molecules as expressed in their structural formulas. A pioneer in

fact a 50/50 mixture of optically active dextro and levo crystals whose equal, but opposite, optical activities perfectly cancelled one another.

Why this result wasn't just a simple confirmation of Herschel's earlier result with quartz was the fact that the optical activity of quartz vanished when its crystals were dissolved, whereas that of the tartrate crystals persisted. This meant that, whereas the dissymmetry responsible for the optical activity of quartz resided in the inter-



Figure 31. Joseph Achille Le Bel (1847-1930)

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this new field of study was the French chemist, Joseph Achille Le Bel (figure 31). In 1874 he published a paper in which he proposed two rules that would allow one to predict whether a given compound and its various derivatives were optically active based on a consideration of their two-dimensional structural formulas.¹⁵ Essentially it stated that any carbon atom, within the molecule, that was attached to four different kinds of atoms or groups of atoms, would give rise to optical activity provided that one of the groups was not a mirror image of the carbon atom in question together with the remaining three groups. Le Bel also noted, almost in passing, that the necessary dissymmetry required for optical activity could be accounted for if the four substituents about the optically active carbon center were arranged three-dimensionally at the corners of an asymmetric tetrahedron.

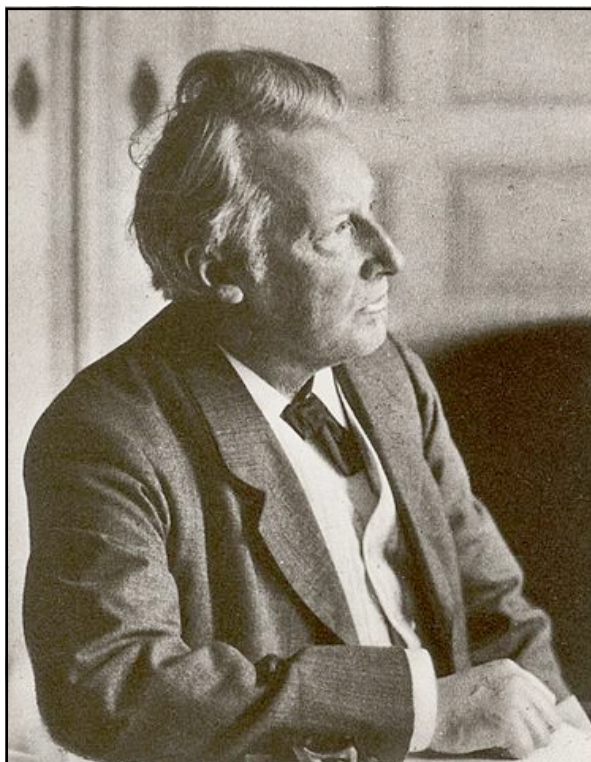


Figure 32. Jacobus Henricus van't Hoff (1852-1911)

That same year, a young, 22-year old, Dutch chemist named Jacobus Henricus van't Hoff (figure 32) privately published a small pamphlet in which he advocated the conversion of two-dimensional structural formulas into three-dimensional formulas via the assumption that the four bonds around each carbon atom were directed towards the corners of a tetrahedron.¹⁶ Like Le Bel, he recognized that, if the four bonds were connected to four different kinds of atoms or groups of atoms, the resulting tetrahedron would be asymmetric and could give rise to optical activity. However, unlike Le Bel, he also used the tetrahedral carbon atom to rationalize other kinds of isomerism and also drew actual three dimensional structural

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formulas. In so doing, van't Hoff's hypothesis of the tetrahedral carbon atom, which was only implicit in Le Bel's work, became the basis of a new chemical speciality now known as *stereochemistry*, after a suggestion first made by the German chemist, Victor Meyer, in 1890.¹⁷

One of the first tasks of this new discipline was to determine whether optical activity was unique to the compounds of carbon, and soon chemists were also reporting optically active compounds of such elements as sulfur, selenium, tin, silicon and nitrogen. By 1907 sufficient results had accumulated so as to be made the basis of a small specialist monograph by Scholtz.¹⁸ The majority of these compounds, like those of carbon, involved tetrahedral coordination, and this gave rise to the further question of whether optically active compounds could be prepared with geometries other than tetrahedral. The answer came in 1911 when Alfred



Figure 33. Alfred Werner
(1866-1919)

Werner (figure 33), the founder of modern coordination chemistry, reported an optically active octahedral complex for cobalt.¹⁹ The collection of Werner's papers, edited by Kauffman,¹⁹ contains a photograph of the polarimeter used by Werner in this work, which appears to be identical to the instrument shown in figure 11.

The field of stereochemistry was not the only area of chemistry in which the polarimeter played a significant role. In 1850, two years after the publication of Pasteur's seminal paper, the German physicist, Ludwig Ferdinand Wilhelmy (1812-1864), used the polarimeter to establish the first quantitative rate law, thereby laying the foundations for the field of chemical kinetics.²⁰ The chemical reaction which Wilhelmy studied was the acid-catalyzed hydrolytic

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cleavage of the disaccharide, sucrose, into its component monosaccharides – glucose and fructose:



All three of these sugars are optically active, with the specific rotatory power of sucrose being $+66.45^\circ$, that of glucose being $+52.5^\circ$, and that of fructose being -92.4° . This means that, as the reaction proceeds, the specific optical rotation of the reaction mixture will go from a value of $+66.45$, at the beginning of the reaction, to a value of $-39.9^\circ = (+52.5^\circ + -92.4^\circ)$ at completion. Since the rotation gradually changes sign or inverts as the reaction proceeds, this reaction is often described as the “inversion” of sugar. By measuring the change in rotation as a function of time and variations in the initial concentrations of both the sucrose and the acid catalyst, Wilhelmy was able to establish the quantitative rate law:

$$-dZ/dT = MZS \quad [5]$$

where Z is the concentration of the sucrose (*Zucker* in German), S is the concentration of the acid catalyst (*Säure* in German), M is the rate constant, and T is time. Since reaction rates depend on concentrations, it is necessary to monitor the changes in this parameter over time using physical means rather than chemical means and, for this particular reaction, the polarimeter proved to be the ideal choice.

Several other 19th-century chemists employed the polarimeter to study the laws of mass action and equilibrium using reactions involving optically active alkaloids of various kinds, including John Hall Gladstone in the 1850s, John Hewitt Jellet²¹ and Biot²² in the 1860s, and W. Will and Georg Bredig²³ in the 1880s. Jellet's work, in particular, was considered important enough by Wilhelm Ostwald to be translated into German and republished as part of his famous reprint series *Klassiker der exakten Wissenschaften*.²⁴ Since Wilhemy's pioneering work was unknown to chemists until brought to their attention by Ostwald in the 1880s,

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these additional uses of the polarimeter to study chemical reactivity were apparently arrived at independently of that work.

By the last quarter of the 19th-century the polarimeter had firmly established itself as an indispensable instrument in both industrial and academic chemical laboratories and, as such, it soon became the subject of a series of specialist monographs dealing with both its construction and various chemical applications.²⁵⁻²⁸

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6. I am assuming that the distinction between a polariscope and a polarimeter is the same as that between a spectroscope and a spectrometer, namely that the former allows you to view optical rotation whereas the latter also allows you to quantitatively measure it. In actual fact the literature seldom makes this distinction. All of the 19th and early 20th century literature, including apparatus catalogs, invariably uses the term po-

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lariscope to describe all forms of the instrument, whereas the more recent literature invariably uses the term polarimeter.

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10. This instrument is something of a puzzle, since stylistically it would appear to date from the 1880s. However, the engraving on the light shield indicates that it was sold by the Arthur H. Thomas Co. of Philadelphia, and it is listed in the 1921 edition of the company's catalog. Its maker, Félix Pellin, joined his father's Parisian instrument company in 1900, though he did not become sole owner until 1927. Either the company was willing to relabel and sell older back stock or it was extremely lax in updating its designs. If so, this is not the first example we have encountered in the museum of older laboratory items being relabeled and sold 30-50 years after they were manufactured. For an etching of the instrument, see *Laboratory Apparatus and Reagents*, Arthur H. Thomas Co: Philadelphia, PA, 1921, p. 502. For background on the Pellins, see P. Brenni, "19th Century French Scientific Instrument Makers: XIII: Soleil, Duboscq, and Their Successors," *Bull. Sci. Instr. Soc.*, **1996**, 51, 7-16.

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