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SUMMARY OF PAPERS

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Part I – 150 Years of Fine Balance Making (*Printed Book & PDF version*)
- Historical
- Technical
- Commercial
- Associated Companies Brief Histories

Part II – The Collector's Vade-Mecum (*PDF only*)
Part III – Valedictory Observations (*Both*) & Appendices (*PDF only*)

Mr Oliver claims that the work is a culmination of more than twenty-five years effort, much of it full-time; also that his researches made use of several hitherto untapped sources, including interviews with many former Oertling staff. The decision to leave all of part II and most of part III out of the printed book was, cost considerations apart, motivated by a desire to make the printed book accessible to the more general reader of science history, whilst still meeting his objective of producing "An Encyclopaedia of Everything Oertling" to satisfy collectors and serious students. I am neither a scientific instrument historian, nor a balance collector, and hence I read the book purely out of general interest, albeit as someone old enough to have used several examples of both 'traditional' two-pan and 'modern' single-pan balances, in my time, including, in 1966, a beautiful old, but, pristine brass five-place balance that I can still call to mind very vividly. I can thus only comment on the book from the point of view of an ordinary chemist having a general interest in science history. I would say nevertheless that Mr Oliver looks to have succeeded in making the work dual purpose, inasmuch that I had little difficulty in reading Part I, even if I only scanned Parts II and III. The printed book does rather look a little formidable at first sight, with its 600 or so A4 pages and near 3Kg weight, except that it is printed in a large font (12 Pt Georgia), with what looks like 1.5 line spacing, making it very undemanding on the eye. The other decision Mr Oliver has taken in order to make the book accessible is to offer it at the affordably low price of £30. At that price it might not matter too much to some purchasers if the Collectors Vade-Mecum is irrelevant and if, say, the Commercial section was to be of less interest than the Historical or Technical, as I confess it was to me.

The story of Mr Oertling and his company to be found in part I is likely to appeal to almost anyone interested in the history of chemistry, given all that the balances have enabled over the years and given their attractiveness as artefacts. I found the parts I read, by which I mean Part I, the Valedictory Observations and some selected appendices to be well-written and very readable, not least because of Mr Oliver's admirably economical and to-the-point style, with its use of short sentences wherever possible.

Mr Oliver is to be congratulated on the huge effort needed to collate and present as much is and can be known about Oertling and his dynasty, legacy and company, in my view. I say 'as can be known' because it seems that two significant archives, one family and one company, were lost or destroyed in the mid-twentieth century, something that even someone as dogged as Mr Oliver could do little about.

From a personal perspective, I was interested to see that, like me, Mr Oliver is a Graduate of the Royal Institute of Chemistry: an increasingly rare breed who suffered the ordeal of a four-day practical examination, in which we very likely used Oertling balances, although they could have been Mettler, I suppose, as it is too long ago for me to remember.

Richard Buscall

The book is available directly from the author barry.oliver@keme.co.uk – price £30 plus P&P. A two-page flyer can be found here:

http://stanton-instruments.co.uk/A5%20Flyer%20-%20Oertling%20Book.pdf

RSCHG MEETING REPORTS

The Handed World - 150 Years of Molecular Chirality

Wednesday 13 October 2021, RSC Library, Burlington House, Piccadilly

This meeting, postponed from 2020 because of Covid, celebrated the sesquicentenary (150 years) of molecular chirality. The RSC Historical Group could have chosen some years on either side; *our* sesquicentenary is of an idiosyncratic weighted average of events from 1860 (Pasteur) to 1874 (van't Hoff and Le Bel). The meeting was inspired in 2017 by Alan Dronsfield's observation that 2019 would be the sesquicentenary of Paterno's ball-and-stick representations of molecules including tetrahedral carbon (discussed below in this report). The postponement of the meeting from 2020 because of Covid did, however, make 2021 the precise sesquicentenary year of the publication of Lewis Carroll's *Through the Looking-glass, and What Alice Found There*. In this (published on 27 December 1871, not in "1872" as indicated inside the book), shortly before Alice jumps through the "Looking-glass" from the chimney-piece, addressing her cat Kitty, she speculates: "Perhaps Looking-glass milk isn't good to drink", and she may be right at least in relation to the sugar lactose in the milk. In addition, the postponement meant that the meeting took place exactly a week after the award of the 2021 Nobel Prize in Chemistry to Benjamin List and David MacMillan "for the development of asymmetric organocatalysis".

The Historical Group was pleased to welcome two members of the Lewis Carroll Society, one of whom, Dr Jane Skelly, a biochemist and editor of the scholarly journal *The Carrollian*, chaired the second of the three sessions of the day.

A list of seventy-six relevant historical characters is available at: https://www.researchinip.com/20211013/0.2histfigs.pdf

Introduction to the Day

Dr Michael Jewess (RSC Historical Group, Chair of the Meeting Organising Committee)

Chemists in the nineteenth century achieved great feats of inductive reasoning. From purely macroscopic observations they drew conclusions that were confirmed in the twentieth century by means of observations on the atomic scale, for instance by X-ray crystallography. From Dalton early in the nineteenth century to Cannizzaro in 1860, reasoning from combining ratios, chemists concluded that molecules comprised known atoms in known numbers bound closely together. From 1860 to 1874, reasoning from optical activity, they created a picture of molecules in 3-dimensional space with known or knowable geometries. In particular, they concluded that a molecule in which a carbon atom was bonded tetrahedrally to four different groups could exist in two mirror-image forms. Each form was unsuperimposable on the other no matter how it was moved about in space, the phenomenon we now describe as molecular chirality. Consistently with Alice's speculation, chirality matters to life; biological processes often, though not always, rely on and generate molecules in just one of two chiral forms.

Discovery of the Phenomenon of Polarisation of Light

Prof. John Steeds, FRS (University of Bristol)

Over a period of 250 years, experiment led to our current understanding that light propagates in the form of transverse waves. The chief pioneers whose work was discussed were as follows: Hooke, Newton, Bartholinus, Christiaan Huygens, Malus, Arago, Fresnel, Foucault, Fizeau, Breguet and Maxwell. The key steps that led to this conclusion were described, together with the reasons why this conclusion took so long in coming. Not only was Newton with his great authority in favour of a corpuscular theory of light, but also observations with polarised light (no interference when two beams linearly polarised at right angles were recombined) seemed to be against the wave theory so long as one imagined the waves to be longitudinal rather than transverse.

The three commonly used ways of generating plane polarized light (absorption, reflection, and birefringence) were discussed together with their use in creating left- or right-handed circularly polarized light. A particularly successful polariser operating by absorption is "Polaroid" invented and commercialised by the American Edwin Henry Land (1909-1991), who consciously modelled it on "herepathite" studied by the English physician William Bird Herepath (1828-1868).

Optical Activity – A Century of Perplexity

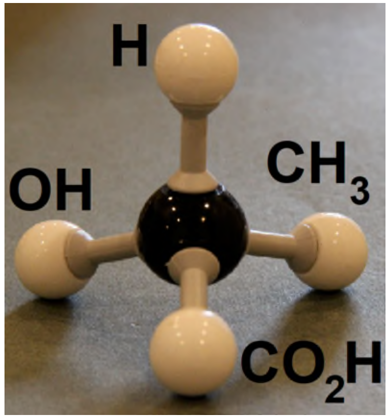
Prof. Alan Dronsfield (University of Derby)

In 1809 Etienne Malus discovered that light reflected off a crystal of quartz was, to use today's terminology, plane polarised. When this light was passed through a crystal of quartz, the light was rotated, sometimes in one direction, sometimes in the other and the direction of rotation was a characteristic of the crystal's shape. Inexplicably (at the time) when the quartz was melted and allowed to resolidify this power to rotate light was lost. This was the first of many perplexities associated with the phenomenon of optical activity. Quartz's behaviour was in contrast with that of barley sugar that showed the ability to rotate the light in the solid state, when molten, when allowed to resolidify and when dissolved in water to form a syrup. Further examples were soon identified which showed barley sugar behaviour, including a few which exhibited rotatory power even in the vapour state.

It was a further perplexity that laboratory-synthesised chemicals were always optically inactive. Those that were active were obtained from Nature. The behaviour of the two types of (visually different) quartz crystal pointed to a difference in underlying morphology or molecular structure, but this could not be extended to the molecular level until chemists agreed on what constituted a molecule, and further, how one was made up of constituent atoms and bonds. Alexander Crum Brown suggested molecular representations very close to today's structural formulae and Auguste Hofmann used croquet ball models in his lectures, but only constructed his molecules in two dimensions. There is some evidence that Auguste Kekulé advanced the notion of the tetrahedral carbon atom, but he left it to his disciples to promulgate the idea. Emanuele Paterno drew 3D structures identical to those we use today, but did not connect them to optical activity. This was left to the seminal (and independent) work of Le Bel and van't Hoff, from whom we get the notion of the "asymmetric carbon atom" and the idea that molecules whose mirror images are non-superimposable should display optical rotation in opposite directions. The applicability of these ideas was rapidly and extensively tested. Did the asymmetric atom have to be carbon? Could the idea of non-superimposable object and mirror image be applied to species that did not contain a formal "asymmetric" central atom? Can enantiomers exist for molecules that contain no carbon atoms at all?

Prof. Dronsfield concluded by looking at the history of attempts to achieve enantiomeric excesses by conducting syntheses in the presence of magnetic fields, including some of his own work in the 1990s. He then reviewed "fraudulent" chemistry more generally – including, in a light-hearted vein, that conducted in Adolf Baeyer's laboratory, around 1890.

Dramatis Personae: Jean Baptiste Biot, 1774-1862; Louis Pasteur, 1822-1895; Alexander Crum Brown, 1838-1922; Joseph Achille Le Bel, 1847-1930; Jacobus Henricus van't Hoff, 1852-1911; William Jackson Pope, 1870-1939; Alfred Werner, 1866-1919; Eberhard Breitmaier, 1931- present.



If, of the four H atoms of methane (white balls), three are replaced by different groups so as to form a lactic acid molecule, there are two ways of doing this: to form the molecule shown above, and to form its mirror image. Courtesy Michael Jewess.

From *d* and *l* to *R* and *S:* Discovery of Absolute Configuration

Prof. Henry Rzepa (Imperial College)

The main actor in the prologue to this story is Emil Fischer, who in the 1890s set out on an odyssey to prove by chemical synthesis van't Hoff and Le Bel's famous 1874 hypothesis that for an organic molecule containing *n* asymmetric carbon atoms (carbons bearing four different substituents in a tetrahedral arrangement), there could be up to 2^n three-dimensional stereoisomers. This in turn led to the development of Fischer's famous notation, a map-like projection from three into two dimensions applied to the carbon backbone of the linear forms of glucose and its fifteen stereoisomeric forms ($2^4 = 16$), of which Fischer actually made twelve. Historical accounts however rarely note Fischer's remarkable proof in 1914 that if two different substituents on a tetra-substituted asymmetric carbon are transposed by chemical transformations without breaking any of the bonds to that carbon to produce a non-superimposable stereoisomer (a process equivalent to reflection of the three dimensional structure of the molecule in a mirror), the sign of the measured optical rotation (known as $[\alpha]_D$) inverts but its numerical value is unchanged. Fischer thus set a formidable challenge; how to link the signed value of $[\alpha]_D$ measured for an asymmetric molecule with the one or other of its mirror image forms. This became known as the problem of absolute configuration and is encapsulated in his reference molecule for sugars, D-(+)-glyceraldehyde. Here D is the (modern) notation for the absolute configuration of one of the mirror image forms (L being the other) and (+) is the sign of its measured optical rotation at the wavelength of sodium D-line (589 nm). Fischer's association of D with (+) was a pure guess. But how to prove this guess was correct?

Having thus set the scene, the main act of Prof. Rzepa's talk told of attempts by three later actors to respond to this challenge. The first notable attempt was by Werner Kuhn in 1936 and the next a most intriguing and largely unheralded effort in 1937 by John Kirkwood, both using the new theories of quantum mechanics which had been introduced well after Fischer's guess. The final denouement in 1951 was by Johannes Bijvoet using experimental crystallography and which finally proved Fischer's guess to be correct. Nowadays, the latter receives most of the credit, but was it an erroneous sign in his (1937) equations that resulted in Kirkwood's theoretical attempt being scuppered? Or was it that chemists (unlike physicists, *viz* Einstein predicting gravitational waves or Dirac predicting the positron) were not yet ready to trust theoretical over experimental verification? In his 1937 analysis, Kirkwood candidly sets out an important uncertainty in his linkage between the sign of $[\alpha]_D$ and absolute configuration as being the flexible shape or conformation of the molecules. In this he prepared the stage for players such as Derek Barton in 1948 to formulate a Nobel prize-winning area of chemistry, conformational analysis. Only in 1952, a few months after Bijvoet's work, did Kirkwood report a way of side-stepping the conformational ambiguities of his original choice of molecule with a more rigid system, thus (independently of Bijvoet) verifying Fischer's guess. Bijvoet's assignment of absolute configuration to sugars, and by inference to amino acids, was rapidly accepted and in turn set the stage for two further Nobel-worthy scientific advances to be made at around the same time, the three-dimensional helical structures of some proteins and of DNA by respectively Pauling and Watson and Crick. Both discoveries relied on the absolute configurations of amino acids and sugars to infer, *inter alia*, the right-handed nature of the helical motifs in both proteins and DNA.

The epilogue to Prof. Rzepa's talk noted that although Fischer's stereochemical notation was a great advance, it applied only to sugars and was also associated with much confusion (such as two quite different meanings of the *d*/*l* notations). This problem was soon solved with articles written between 1951-56 by Cahn, Ingold, and Prelog (known affectionately as CIP). These changes in nomenclature, along with advances in representing the stereochemistry of molecules using line diagrams with perspective after the 1950s, mean that confidently comparing pre-1950s literature with modern CIP notations remains a challenge, especially when writing talks such as this one! The reader can see one part of this story retold at DOI: 10.14469/hpc/6368 with more detail.

The cast: Emil Fischer, 1852-1919; John Kirkwood, 1907 – 1959; Johannes Bijvoet, 1892 – 1980; Derek Barton, 1918 – 1998; Linus Pauling, 1901- 1994; Francis Crick, 1916 - 2004 and James Watson, 1928 – present; Robert Cahn, 1899 - 1981 and Christopher Ingold, 1893 - 1970 and Vladimir Prelog, 1906 - 1999 (CIP).

Molecular and Supramolecular Chirality

Prof. Giuliano Siligardi (Diamond Light Source Ltd)

This talk gave an overview view of chirality, both in molecular and supramolecular terms, the tools to measure it, and the people who laid the foundations.

A molecule is said to be optically active or chiral or dissymmetric if it is not superimposable on its mirror image as firstly described in 1848 by Louis Pasteur (1822-1895). The configuration of D sugars and the L amino acids, the building blocks of terrestrial life identified by Fischer (1852-1919) recipient of 1902 Nobel Prize in Chemistry, have higher stability than their respective enantiomers (mirror images) due to parity-violating of the electroweak force established in 1956 by Lee and Yang, for which they were awarded the Nobel Prize in Physics (1957). This different stability, amplified through the vast timescale of the universe, has led to the terrestrial homochirality.

Chiral molecules rotate the plane of polarization of linearly polarized light, the variation with the rotation with wavelength being known as optical rotatory dispersion (ORD). Chiral molecules also absorb differentially the left and right circularly polarized light (CPL), this phenomenon being known as circular dichroism (CD). Modern CD instruments modulating the CPL with photo-elastic modulators can also measure ORD with appropriate modifications (Velluz, Grosjean and Legrand, 1965).

For small, flexible chiral molecules, the optical activity from electronic and vibrational CD must be calculated using quantum mechanical theory for all the stable conformations present in solution. This is now the method to assign the absolute configuration of therapeutic drugs as recommended by the Food and Drug Administration. For larger molecules like proteins, nucleic acids and chiral polymers, this is still difficult and expensive to accomplish. As the function and activity of proteins are directly related to their structure, the ability to characterise their conformational behaviour in solution as a function of environment (temperature, solvent and drug binding interactions) is invaluable information that can be used to verify the correctness of molecular modelling *in silico.* This combination is guiding the basic research that, when successful, has led to commercial applications. The pharmaceutical industry is an important example.

Supramolecular chirality is a younger research field of self-assembly of even larger systems that are observed in the solid state for organic optoelectronic and photovoltaic materials, nanocrystalline cellulose, and artificial retina that, if dissymmetric, can be studied with chiroptical spectroscopic techniques. Like for molecular chirality, the physical properties of materials are optimised if the supramolecular chirality is homogeneous. For example, the efficiency of optoelectronic and photovoltaic devices is maximised for specimens prepared with homogeneous supramolecular chirality.

However, these systems are more complex than those in solution because for solid-state the observed CD can have linear dichroism (LD), linear and circular birefringence (LB and CB) contributions hampering any CD analysis. Using the Mueller matrix calculus for manipulating the polarization states of light (Mueller, 1900-1965) these contributions can be extracted and quantified enabling the imaging of optical activity in the visible region pioneered by B. Kahr (2003) and in the UV region with the novel Mueller Matric Polarimeter (MMP) recently installed at B23 beamline of Diamond Light Source. Only with the MMP tool, the homogeneity of supramolecular chirality can be assessed and measured at higher spatial resolution guiding the optimization of the parameters to achieve reproducible specimens, which is the sine qua non for any commercial application.

"Perhaps Looking-glass milk isn't good to drink". From *Through the Looking-glass, and What Alice Found There*, by Lewis Carroll (1832-1898), illustration by John Tenniel (1820-1914).

Does the Right Hand Know What the Left Hand is Doing? - Chirality in Real Life

Dr Ian Blagbrough (University of Bath)

Dr Blagbrough has an active interdisciplinary research group working in phytochemistry. This requires an understanding of the application of different aspects of handedness. Today it has been set out clearly and elegantly, unambiguously and without room for contradiction that an optically active molecule is chiral and non-superimposable on its mirror image, as first described in 1848 by Louis Pasteur (1822-1895). Thus, the reflection of its three dimensional structure in a vanity mirror affords a different molecule, its enantiomer, which displays optical rotation equally, but in the opposite direction. This led on to the crucial building blocks of terrestrial life being determined as D-sugars and L-amino acids by Emil Fischer (1852-1919) in the 1890s. That such molecules have higher stability than their respective enantiomers is deeply significant for their biological activity. The plethora of chiral natural products and the importance of molecules arising from the pharmaceutical industry provide simple and then more complicated examples. Of course, handedness without receptors (proteins, DNA, RNA), did not speak to the conundrum that laboratory synthesized molecules were always optically inactive. Those that were active were isolated natural products. What of the molecule displaying handedness not only at chiral carbon atoms, but by its three dimensional helical structure, e.g. proteins (Linus Pauling), DNA (Francis Crick and James Watson)? Such natural helices were initially determined to be right-handed, but then left-handed examples were shown. This interconversion was (perhaps of course) shown to be biologically important.

The chemical cast: barley sugar, glucose, fructose, sucrose, lactate, alanine, glutathione, LLD-ACV, penicillins, cefalosporins, monobactams, microcystins, brevetoxin, oranges and lemons, spearmint and dill, thalidomide, ibuprofen, dexibuprofen, handedness in DNA with respect to RH and LH helices for packing and unpacking.

The players: poisonous plants, beneficial plants, bacteria, fungi, algae, venomous animals.

Michael Jewess and John Hudson

RSCHG WEBINAR REPORTS

A Century of Global Synthetic Ammonia: 1921-2021 – Anthony S. Travis (September 2021)

Following the tremendous success of BASF's Haber-Bosch process for synthetic ammonia during World War I, great efforts were made outside of Germany to introduce similar processes. After the cessation of hostilities, as BASF was in no mood to license its strategically important process these efforts intensified. The first success was achieved by the Italian chemist Luigi Casale, who in April 1921