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Henry Enfield Roscoe

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Abstract Henry Enfield Roscoe (1833–1915), together with Robert Bunsen, his mentor, carried on fundamental research in photochemistry, determining its laws and quantitative effects. His most important studies were on the chemistry of vanadium, uranium, tungsten, and molybdenum, their oxides and oxychlorides, carrying on, for the first time, their synthesis and separation. He also did important studies on public heath. His academic activities transformed Owens College (Victoria University) into the leading chemistry school in Britain.

PALABRAS CLAVE
Fotoquímica;
Vanadio;
Tungsten;
Niobio;
Salud pública;
Educación

Henry Enfield Roscoe

Resumen Henry Enfield Roscoe (1833-1915), con la colaboración de Robert Bunsen, su mentor, realizó estudios fundamentales sobre fotoquímica, fijando sus leyes, y la determinación cuantitativa de sus efectos. Sus trabajos mas importantes fueron sobre la química del vanadio, uranio, tungsteno, y molibdeno, sus óxidos y oxicloruros, realizando, por primera vez, su síntesis y separación. Asimismo, efectuó estudios importantes sobre salud pública. Sus actividades pedagógicas transformaron a Owens College (Victoria University) en la escuela líder de química en Inglaterra.

Life and career

Henry Enfield, the eldest son of Henry Roscoe (1800–1836) and Maria Fletcher (1798–1885), was born in London on January 7, 1833. His only sister, Harriet, was born in 1836. His forebears were nonconformists, mainly Presbyterian or Unitarian.[1] His father, a Liverpool barrister, had moved to

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[1] English Dissenters or Nonconformists, were English Christians who separated from the Church of England and opposed State interference in religious matters. They were called so because they refused to take the Anglican Communion or to conform to the

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London in 1819 to seek his fortune in the bar, and after retiring very early, was appointed Judge of the Court of Passage in Liverpool (1834). He died in 1836, at the age of thirty-seven, leaving the family in financial stress. His mother, who had artistic gifts, improved the family income by teaching watercolor painting at a girl's school. Henry thought that he was going to be a physician but his uncle Richard Roscoe strongly discouraged his mother from allowing him to do so, explaining that medicine was a very difficult career, which probably would kill her son. In 1842 the family moved to Liverpool and Henry entered the High School of the Liverpool Institute for Boys, a non-classical school, divided in a higher and a lower class, the higher for boys of a better class, and the lower school for tradesmen's sons and boys of the lower class. The school was uncommon in having a chemical laboratory in which the students worked and learned chemistry. The chemistry teacher was William Henry Balmain (1818–1880), the discoverer of Balmain's luminous paint and boron nitride, and from him Henry developed his interest for chemistry. Roscoe's mother encouraged him by letting him use a room as a laboratory. He succeeded in purchasing enough apparatus to perform most of the common chemical experiments and thus entertain his cousins and friends by giving them animated lectures. He made gun cotton soon after its discovery by Christian Friedrich Schönbein (1799–1868, discoverer of ozone) and used it to fire a small cannon (Roscoe, 1906; Thorpe, 1916b).

In 1848, after seven years at high school, Roscoe, was admitted to University College, London, at that time the academic and research institution in England open to men who were refused admittance to the older Universities on religious grounds. The brilliant classes of Thomas Graham (1805–1869) impressed him so much that he decided to follow chemistry as a career. At the beginning of his second year of studies he joined the Birkbeck Chemical Laboratory, directed by Alexander William Williamson (1824–1904), who shortly thereafter let him carry original research. After succeeding to Graham's chair, Williamson appointed Roscoe his assistant in the general chemistry class for the winter session of 1855–1856 (Roscoe, 1906; Thorpe, 1916b).

In 1853, Roscoe received his Bachelor of Arts degree with Honors in chemistry and traveled to Heidelberg to work with Robert Wilhelm Bunsen (1811–1899). Bunsen taught Roscoe quantitative techniques and gas analysis and encouraged him in original research. One of his first quantitative projects was on silicate analysis, which led to a first paper, published with Eduard Schönfeld (1828–1891), about the composition of certain samples of gneiss (a common and widely distributed type of rock formed by high-grade regional metamorphic processes from pre-existing formations that were originally either igneous or sedimentary rocks) (Roscoe & Schönfeld, 1854). In addition, Roscoe translated into English Bunsen's book on Gasometry (Bunsen & Roscoe, 1857). At the end of his second year Roscoe passed his doctor's oral examination *summa cum laude* and then begun, together with Bunsen, in their famous studies in photochemistry, which occupied much of his time and energy during the next eight years (Bunsen & Roscoe, 1855, 1856, 1857a, 1857a, 1857a, 1859, 1863; Roscoe, 1906).

In 1856 Roscoe returned to London and established a private laboratory in Bedford Place, employing William Dittmar (1833–1892) as his assistant. He also began teaching at an army school at Eltham and did analytical work on the air of dwellings for a Departmental Committee. He analyzed the air of the soldiers sleeping rooms in Wellington Barracks when the men were in bed, visited many schoolrooms, as well as artisan's residences, and determined the amount of CO_2 contained in the air of a crowded theater (Roscoe, 1858, 1906).

In 1857, Edward Frankland (1825–1899), first professor of chemistry at the recently established Owens College of Manchester, resigned and Roscoe applied and was accepted for the position. Roscoe closed his London laboratory and began his new duties, taking Dittmar with him as his assistant (Roscoe, 1906).

Owens College had opened in 1851 but when Roscoe joined it there were only thirty-four students; the College had reached such level of discredit that Roscoe was even refused lodgings when the landlord learned of his affiliation. He reformed the chemical curriculum and gave it a solid reputation. As a result of his, efforts Owens College became the leading chemistry school in the country (Roscoe, 1906; Thorpe, 1916a, 1916b).

The blockade of Confederate ports by the Union, during American Civil War, with the consequent interruption of baled cotton imports, generated a serious social and economical crisis to the textile industry of North West England. The resulting Cotton Famine (1861–1865) resulted in Lancashire's cotton mills running out of raw cotton to process, high unemployment, and the region going from high prosperity to poverty and famine. In order to try to help improve the despair of the working class, Roscoe and some of his friends developed the idea of providing the unemployed with intellectual recreation, and initiative, which turned to be a resounding success. Roscoe and his friends gave more than one hundred presentations on musical, scientific, geographical, and other subjects to audiences averaging over 4000 a week (Roscoe, 1906). The success of these first attempts stimulated Roscoe to initiate the *Science Lectures for the People*, which were given for eleven years by many famous scientists, among them the biologists Thomas Henry Huxley (1825–1895) and William Benjamin Carpenter (1813–1885), the mathematician and physicist William Spottiswoode (1825–1883), the physicist John Tyndall (1820–1893), and the astronomer William Huggins (1824–1910). Eventually the eleven series of lectures were collected and printed in Manchester as *Science Lectures for the People* and sold at a penny each (Roscoe & Williamson, 1877; Thorpe, 1916b). All these activities led to the foundation of the Working Men's College in Manchester (Roscoe, 1906).

Roscoe stayed as head of the Chemical department of Owens College until his election as Member of Parliament for the Southern Division of Manchester in 1885, when he resigned the Professorship of Chemistry.

In 1863 Roscoe married Lucy Potter (?-1910). They had a son, Edmund, and two daughters, Margaret and Dora. Edmund passed away when he was an undergraduate student

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tenets of the restored Church of England. After the Toleration Act was passed in 1689, Dissenters were permitted to hold services in licensed meetinghouses, and to maintain their own preachers in England and Wales.

at Magdalen College. Oxford. On December 18, 1915, Roscoe had a heart attack and passed away; he was buried beside his wife at Brookwood cemetery.

Roscoe's main research activities were in inorganic chemistry. His first important work, on the laws of photochemical actions, was conducted with Bunsen during the years 1855–1862. In them they established the foundations of comparative photochemistry, the determination of its laws, and development of an actinometer, based on the reaction of chlorine and hydrogen under light, which allowed a precise quantitative analysis of the action of light. Bunsen and Roscoe demonstrated that the amount of photochemical action produced by a constant source varied inversely as the square of the distance and that the absorption varied directly as the intensity. They also measured the chemical action of the parts of the solar spectrum, describing the existence of several maximums of chemical intensity. His most important research was on vanadium and its compounds. He was the first to develop a process for preparing pure metallic vanadium and showing that the substance, which had previously passed for the metal was contaminated with oxygen. In so doing he corrected Berzelius's value for the atomic mass. Roscoe was awarded the 1868 Bakerian Lecture for this work. He also carried out researches on niobium, tungsten, uranium, and their oxides and oxychlorides, on perchloric acid, and the solubility of ammonia and chlorine in water (Thorpe, 1916a, 1916b).

Honors and awards

Roscoe received many awards and honors on account of his scientific, educational, and industrial contributions. He was awarded the Royal Medal of the Royal Society (1873) ''for his various chemical researches, more especially for his investigations of the chemical action of light and of the combinations of vanadium'' and delivered the Bakerian Lectures[2] for 1865 and 1868. His 1865 Bakerian lecture was about a method of meteorological registration of the chemical action of daylight (Roscoe, 1865), and the 1868 one about vanadium and the determination of its atomic mass (Roscoe, 1868). He was awarded the Dalton Medal of the Philosophical Society of Manchester and the Elliot Cresson Gold Medal of the Franklin Institute (1912). He was elected a corresponding member of the Académie des Sciences and an honorary member of the American Philosophical Society of Philadelphia, the New York Academy of Sciences, the Chemical Society of Berlin, the Bunsen Gessellschaft, of the Verein für Naturwissenschaft of Brunswick, the Royal Society of Sciences of Göttingen, and the Royal Accad. Lincei of Rome, among others. In 1883 Oxford University conferred him an honorary degree of doctor of civil law, and Dublin (1878), Cambridge (1883), Montreal (1884), and Glasgow (1901) a honorary degree of Doctor of Laws (LL.D.). Roscoe was elected into the Royal Society in 1863 and served twice as its Vice-President. He was one of the original members of the Society of Chemical Industry and became its first president. He joined the Chemical Society in 1855 and served as its Vice-President, and President. Between 1896 and 1902 he became vice-chancellor of the University of London. He played a main role in the founding and direction of British Institute of Preventive Medicine (today, The Lister Institute of Preventive Medicine) in Chelsea, modeled upon the Institut Pasteur in Paris, and served as a Carnegie trustee after 1901. In 1909 he was selected for the Privy Council.

In 1884 Roscoe was knighted ''in acknowledgement of his distinguished service on the Technical Education Commission''. He served as a Liberal Member of Parliament from 1885 until his defeat in the election of 1895.

Scientific career

Roscoe published over 150 papers, reports, conferences, and books. His *Lessons in Elementary Chemistry* (Roscoe, 1866b) and *Chemistry* in the Science Primer Series for Macmillan (Roscoe & Williamson, 1877) were widely adopted and translated into nine languages. His comprehensive *Treatise on Chemistry* (Roscoe & Schorlemmer, 1877-1884), written with Carl Schorlemmer (1834–1892), appeared in 1877–1884. His lectures before the Society of Apothecaries, published as *Spectrum Analysis* (Roscoe & Schuster, 1869), went through several editions. Roscoe also wrote a biography of Dalton and *A New View of the Origin of Dalton's Atomic Theory* (Roscoe, 1895, Roscoe & Harden, 1896), in collaboration with Arthur Harden (1865–1940, 1916 Nobel Prize for Chemistry), and an *Autobiography* (Roscoe, 1906).

Photochemistry

In 1809 Joseph-Louis Gay-Lussac (1778–1850) and Louis-Jacques Thénard (1777–1857) reported their study of the influence of light on the reaction between equal volumes of chlorine and hydrogen. The change in color of the gases enabled them to follow the course of combination over several days in hazy sunshine, keeping meanwhile another mixture of the reactants in the dark as a control. Their results indicated that in bright sunlight the gases reacted violently, shattering the flasks used; with a less intense light the combination proceeded more slowly. The mixture lost its color, and converted into HCl, readily soluble in water (Gay-Lussac & Thenard, 1809). In 1843, John William Draper (1811–1882) used this property to construct an actinometer (which he named *tithonometer*) for measuring the chemical force of the *tithonic rays*, which were found at a maximum in the violet space, and from there gradually faded away to each end of the spectrum (Draper, 1843). Draper became convinced that light affected the chlorine alone, converting it from a passive to an active state (Draper, 1844).

Bunsen conceived the idea of making this reaction the basis of a method of measuring the relative amount and activity of the light rays, responsible for the chemical change. Bunsen and Roscoe realized that Draper's tithonometer had too many defects that prevented a very precise measurement of the effects of light on a chemical reaction. The most important defect was that the pressure

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[2] The Bakerian Lecture is the Royal Society's leading lecture in the physical sciences. It originated in 1775 through a bequest by Henry Baker (1698–1774) of £100 for an oration or discourse which was to be spoken or read yearly by one of the Fellows of the Society ''on such part of natural history or experimental philosophy, at such time and in such manner as the President and Council of the Society for the time being shall please to order and appoint''.

in the apparatus varied during the experiment, affecting the solubility of chlorine and the composition of the gas. After many fruitless experiments, Bunsen and Roscoe succeeded in constructing an apparatus which obviated the defects of Draper's tithonometer and allowed not only accurate comparative determinations, but also reduced the chemical action of light to an absolute measurement. Their actinometer consisted of a half-blackened flat glass bulb (which they named the *insolation vessel*), half-filled with chlorine water, which also partly filled a horizontal index tube. After a mixture of equal volumes of chlorine and hydrogen, obtained by the electrolysis of HCl with carbon electrodes, was passed through the apparatus for a long time, the bulb was then exposed to light from coal gas, passed through a tube of water. The HCl formed dissolved in the chlorine water in the bulb and the liquid in the index-tube moved toward the bulb at a measured rate (Bunsen & Roscoe, 1856, 1857a).

Their results indicated that in the beginning there was no combination of the gases: ''The first action of light on electrolytic chlorine detonating gas is accompanied by a phenomenon of a highly peculiar kind. . .*photochemical induction*. The chemical action does not appear in its full strength at the moment of first illumination with completely constant illuminating power but is first vanishing, or nearly vanishing, small, then increases gradually, reaching a maximum first after an appreciable time and then remains constant. . .This peculiar action of the light determined the method, which must be followed in the measurement of the chemical rays. The observations can never be made use until the successive differences have become constant.'' An important result was that the amount of chemical action produced by light from a constant source varied inversely as the square of the distance (Bunsen & Roscoe, 1857a).

In their second paper (Bunsen & Roscoe, 1857b), Bunsen and Roscoe discussed the question of chemical induction, which they defined as ''the act by which the resistance to combination is diminished and the combining power thus brought into greater activity''. According to Draper, chlorine, on exposure to light, underwent an allotropic transformation, permanent for several weeks, which differed from ordinary chlorine by possessing a greater combining power (Draper, 1843). Bunsen and Roscoe proved that Draper was mistaken; the true cause of the phenomenon was photochemical induction. Their experiments showed that the time that elapsed from the first insolation until the first traces of photochemical induction became visible, and until the maximum action was attained, was according to circumstance extremely different. One of the main conditions that modified the induction was related to be volume of the gas exposed to light; photochemical induction was retarded when the mass of gas insolated increased. The action of light rapidly decreased with the depth of the insolated gas and the combining power of the mixture of chlorine and hydrogen diminished in the dark or on exposure to a smaller amount of light.

Bunsen and Roscoe went on to prove that addition of a very small quantity of a foreign gas in the normal mixture considerably increased the resistance to combination in the dark. Thus, the maximum induction of a chlorine and hydrogen mixture containing only 3/1000 more hydrogen than the 1:1 ratio, decreased from 43.47 to 16.40. Bunsen and Roscoe hypothesized that the diminution in action was not caused by the dilution with hydrogen but from a catalytic action proceeding from its particles. Addition of small amounts of other gases was even more striking. For example, dilution with 5/1000 volumes of oxygen caused the maximum induction to decrease from 100 to 2.7, and addition of 0.13% of HCl exerted no perceptible action on the induction.

The next research was related to the laws that regulate photochemical reaction after the induction was completed (Bunsen & Roscoe, 1857c). Bunsen and Roscoe proved that the absorption of the chemical rays in passing through a medium varied directly as the intensity of the light, and that the amount transmitted varied proportionately with the density of the absorbing medium. Hence, it was immaterial, as regards the amount of light, in what order various absorbing media were placed between the source of light and the measuring instrument. Bunsen and Roscoe found that for a given amount of chemical action effected in the mixture of chlorine and hydrogen, an equivalent quantity of light was absorbed, and that the coefficients of extinction of pure chlorine for chemical rays from various sources of light were very different.

The next was to obtain a convenient constant source of light, which could be used as a general and absolute standard of comparison for the chemical action of light (Bunsen & Roscoe, 1859). According to Bunsen and Roscoe the flames of ordinary candles or lamps, the intensity of the light evolved by a heated wire, etc., were subject to variation in their optical and chemical illuminating power, a fact which prevented their employment when high accuracy was needed. The amount of light radiating from a flame not only depended on the mass and constitution of the illuminating material, but even more on the particular circumstances under which the combustion was effected. Bunsen and Roscoe found that burning a gas issuing from a very small opening resulted in a flame having the form of a very obtuse cone and burning steadily. On the basis of these results, they defined the *standard flame* as that produced by the free combustion in atmospheric air of carbon monoxide issuing at the rate of $5\,\mathrm{cm}^3/\mathrm{s}$ (at standard conditions), from a circular platinum burner 7 mm in diameter under a pressure differing very slightly from that of the atmosphere. The *photometric unit* was now defined as the amount of action produced in one minute by the standard flame placed at one m. The chemical unit of light was taken as the amount of action, which the standard flame at the distance of one meter effected on the normal mixture of chlorine and hydrogen in one minute, and one chemical degree of light was defined as ten thousand chemical units.

Using these definitions, Bunsen and Roscoe determined the quantitative relations of the chemical action effected by direct and diffused sunlight, to investigate the laws, which regulate the distribution on the earth's surface of the chemical activity emanating from the sun, and to measure the chemical action of the constituent parts of the solar spectrum. The greatest action was observed between the lines G in the violet and H in the violet, while another maximum was found to be near the line I in the ultra violet. Toward the least refrangible end of the spectrum the action became imperceptible about the line D in the orange, but at the other end of the spectrum the action was found to extend as far as Stokes's line U, or to a distance from the line H greater than the total length of the ordinary visible spectrum (Bunsen & Roscoe, 1859; Thorpe, 1916a, 1916b).

Bunsen and Roscoe (Bunsen & Roscoe, 1863) confirmed their findings by passing sunlight through a number of round holes of accurately measured diameter in a metal cap and receiving the images at such a distance that the visual angle of the openings was smaller than that of the sun. The photochemical effect was measured on a strip of sensitive silver chloride paper, blackened by a pendulum apparatus, by determining the point where the shade of the strip coincided with the unalterable point. The reciprocal of the times, which corresponded to those of equal shade, gave the intensity of the light, expressed in the defined units. This procedure allowed construction of an instrument capable of measuring the chemical action of light effected at any point on the earth's surface by the total sunlight and diffuse daylight, under the most widely varying circumstances of climate and atmospheric condition (Bunsen & Roscoe, 1863).

In 1864 Roscoe described a method of meteorological registration of the chemical action of total daylight based on a modification of that originaly used by Bunsen and himself. The account of this method was described in the Bakerian Lecture for 1865 (Roscoe, 1865). The paper illustrated the results of consecutive observations on each day for nearly a month at about midsummer, and compared the chemical action of light at Manchester at the winter and summer solstices, and the vernal and autumnal equinoxes (Thorpe, 1916a, 1916b).

Inorganic chemistry

Vanadium

By the mid of the nineteenth century, very little was known about vanadium. The element had been discovered in 1801 by Spanish mineralogist Manuel Andres del Río (1764–1849) at the School of Mines in Mexico City (and named panchromium, later erythronium) while analyzing a lead-containing mineral from the Purísima del Carmen mine in Zimapán, Mexico, and in 1830 by the Swedish chemist Nils Gabriel Sefström (1787–1845) at the School of Mines in Falun. Jöns Jacob Berzelius (1779–1848) proved that both elements were the same. Since it gave a number of brilliantly colored salt, Berzelius named it vanadium from Vanadis, the cognomen of the Norse goddess Freya, alluding to her beauty.

Most of the work on vanadium and its compounds had been done by Berzelius, who prepared what he thought was the metal and formulated the highest (acidic) oxide as VO_3, resembling CrO_3 (Berzelius, 1831). Berzelius based his conclusion on his findings that vanadic acid underwent a constant loss of weight when reduced with hydrogen at red heat and the action of chlorine on this reduced oxide. By reducing vanadic acid in a hydrogen stream, he determined the atomic mass of vanadium as 68.5 ($O = 8$) (Roscoe, 1868, 1869, 1870).

Roscoe was drawn into investigating vanadium by a twist of fate, which led to his most important contribution to inorganic chemistry and to many honors and awards. As told in his first publication on the subject (Roscoe, 1868, 1869), in 1865 he was asked to visit the copper mines at Mottram St. Andrews near Alderley Edge in Cheshire, where copper occurs together with a large number of other metals, notably cobalt, in the Lower Keuper Sandstone of the Trias. The process of extraction consisted in treating the ore first with HCl and then with bleaching liquor and milk of lime. This resulted in dissolution of all the nickel and cobalt, and part of the copper, and precipitation of the lead, iron, arsenic, part of the copper, and vanadium. The manager of the mine believed that the lime precipitate contained about 10% copper, but when it was dissolved in acid and the copper precipitated with zinc, the solution still retained a bright blue color, which was assumed to be copper in a peculiar condition, inasmuch as it was not precipitated by zinc. Roscoe realized at once that this could not be copper but that that the blue color was probably due to the presence of the very rare metal vanadium. He asked the manager to send him some of the solution to test, and found his suspicions confirmed. He then obtained a large quantity of the lime precipitate, which contained about 2% of vanadium, together with lead, arsenic, iron, lime, and sulfuric and phosphoric acid. Roscoe and his assistant Edward Thorpe (1845–1925) developed a method by which the vanadium was extracted as an ammonium vanadate, which on heating yielded vanadic acid (Roscoe, 1868). They prepared several pounds of ammonium vanadate from the liquors, and went on to investigate vanadium compounds. Roscoe and Thorpe reduced their vanadic acid with hydrogen, as done by Berzelius, and concluded that the true formula of vanadic acid was V_2O_5 (when $O = 16$) and the true atomic mass of vanadium 51.3. To explain the discrepancy with Berzelius' results they hypothesized that the substance supposed by Berzelius to be vanadium was actually not the metal but an oxide with atomic weight 67.3. Roscoe and Thorpe had learned that the presence of the slightest trace of phosphorus prevented the complete reduction of the vanadium pentoxide to trioxide in hydrogen. Luck played in the hands of Thorpe: by accident he found in the cellars of the Royal Society a sample of ammonium vanadate sent by Berzelius to Michael Faraday in 1831. Analysis of the sample showed the presence of a considerable amount of phosphorus (Roscoe, 1868).

Roscoe when on to prepare metallic vanadium a large number of its oxides and oxychlorides (V_2O_2, V_2O_3, V_2O_4, V_2O_5, VOCl, $VOCl_2$, $VOCl_3$, $V_2O_2Cl_2$, $V_2O_2Cl_4$, and $V_2O_2Cl_6$), vanadates, divanadates, and the mono and dinitrides, as well as determine some of their physical and chemical properties of the solids, and their solutions (Roscoe, 1870). In order to try to obtain the metal in its free state, he followed Berzelius' procedure (Berzelius, 1831) of exploding by heat a mixture of the fused pentoxide and excess sodium. The explosion produced a black powder, which was then washed with water until free from alkali. The washed black powder glittered when suspended in water and on oxidation only gained 16%, showing that it contained more oxygen than the trioxide. All variations of the above method ended in a black powder consisting of mixed oxides. After much experimenting Roscoe found that the only way to produce metallic vanadium was to reduce a chloride, free of oxygen, in an atmosphere of perfectly pure hydrogen (Roscoe, 1870). Roscoe described his metallic vanadium as a light whitish gray-colored non-magnetic powder of specific gravity 5.5, which did not oxidize or even tarnish in the air at atmospheric pressure, and did not decompose water at room temperature. Slowly heated in a current of air it glowed brightly forming first a brown oxide (V_2O or V_2O_2), then the black trioxide, the blue tetroxide, and finally, the pentoxide. Cold or hot HCl and cold sulfuric acid did not attack it. With nitric acid of all concentrations it oxidized with violence, forming a blue liquid. In his third publication on vanadium (Roscoe, 1870), Roscoe continued his study of the properties and reactions of metallic vanadium, describing the preparation of vanadium oxytribromide, oxydibromide, sodium orthovanadate ($Na_3VO_4{\cdot}16H_2O$), sodium pyrovanadate ($Na_4V_2O_7{\cdot}18H_2O$), barium pyrovanadate lead pyrovanadate, silver orthovanadate, silver and pyrovanadate.

In his first paper (Roscoe, 1868) also discussed the fact that the vanadium compounds seemed to be an exception to the isomorphism concepts then prevalent. Carl Friedrich August Rammelsberg (1813–1899) had reported that the mineral vanadinite was isomorphous with apatite, pyromorphite, and mimetesite, minerals consisting of calcium phosphatofluoride, lead phosphatochloride, and lead arsenatochloride, analogously constituted minerals containing phosphorus and arsenic (Rammelsberg, 1856). Roscoe had found that by the action of a reducing agent it was possible to obtain a solution of a vanadium oxide which on reoxidation to vanadic acid appeared to require as much oxygen as Berzelius's vanadium, regarded as metal, would have needed. This fact, combined with the finding that the sample analyzed by Berzelius was found to contain phosphoryl, allowed establishing the chemical affinity of vanadium to phosphorus, arsenic, and the other members of the trivalent group. This conclusion may be considered the chief outcome of Roscoe's first paper: Vanadium, phosphorus and arsenic replace one another in all proportions, and minerals containing vanadium crystallize in the same form as, or are isomorphous with those containing phosphorus and arsenic. Although vanadium and phosphorus are then closely allied, addition of a small amount of phosphorus to vanadium changes altogether the properties of the former. Thus if phosphoric acid is added to vanadic acid, the impressive crystals of the latter are changed into a dark, pitch-like, non-crystalline mass (Roscoe, 1906).

Involvement of Roscoe with vanadium ended with a short communication ''On Two New Vanadium Minerals'' (Roscoe, 1877) and a lecture on ''Recent Discoveries about Vanadium'' at the Royal Institution (Thorpe, 1916a, 1916b).

An interesting point is that in his autobiography (Roscoe, 1906) reports his belief that ''a good deal of my subsequent ill health was due to working on this subject in the old laboratory. I was obliged to use rooms, which were not intended for such purposes, and breathing the bad air due to the presence of products of combustion, chlorine, and other horrors had certainly a deleterious effect upon me. ''Today we know that vanadium uptake through air may cause bronchitis and pneumonia, irritation of lungs, throat, eyes, and nasal cavities. Wheeze and dyspnea are commonly reported in workers exposed to vanadium pentoxide dust and fume. Solutions of vanadium compounds have a marked toxic effect in laboratory animals.''

Other metals

Roscoe studied tungsten and its compounds and described for the first time the existence of the pentachloride WCl_5 and the pentabromide WBr_5 (Roscoe, 1872). He found the hexachloride WCl_6 to be less stable than the pentachloride WCl_5; on heating, it decomposed yielding an abnormal vapor density. The pentachloride did not undergo any change on boiling and gave a normal vapor density. In 1874 Roscoe reported the synthesis of uranium pentachloride, mixed with the tetrachloride, by passing an excess of dry chlorine over a heated mixture of charcoal with any oxide of uranium or with the hexachloride, UO_2Cl_2 (Roscoe, 1874). Uranium hexachloride was found to exist on two forms according if it was produced slowly or quickly. With a slow stream of chlorine, the pentachloride formed long dark needle-shaped crystals, which reflected the light with a green metallic luster, but were ruby-red color when viewed by transmitted light. The pentachloride deposited in the form of a light brown powder when the chlorine stream was rapid. Uranium pentachloride could not be volatilized without partial decomposition; it yielded the tetrachloride and free chlorine when heated alone or in an atmosphere of chlorine or carbon dioxide.

Roscoe used the Greenland mineral columbite, to prepare columbium (niobium),[3] niobium pentoxide, niobium trichloride, niobium pentachloride, and niobium oxychloride. Metallic niobium was obtained as a bright steel-gray, shining, metallic crust, by passing pentachloride vapors mixed with hydrogen, repeatedly through a red-hot glass tube. On heating, vapors of niobium pentachloride decomposed into the trichloride (unknown before) and free chlorine. The trichloride thus formed had the remarkable property of decomposing carbon dioxide when heated in that gas with the formation of niobium oxychloride, $NbOCl_3$ and carbon monoxide, a reaction not exhibited by any other metallic chloride (Roscoe, 1878a).

Roscoe also determined the vapor densities of the chlorides of lead and thallium, which he showed to possess a normal density (no decomposition) (Roscoe, 1878b). In 1878 Marc Delafontaine's (Delafontaine, 1878) reported the presence of a new rare-earth metal, *philippium*, in the mineral samarskite obtained from North Carolina. Roscoe proved that philippium was actually a mixture of yttrium and terbium (Roscoe, 1882a, 1882b).

In 1882 Roscoe sent to the French Academy a note on a redetermination of the atomic mass of carbon by the method of Dumas and Stas, using Cape diamonds, and obtained the value 12.002 ($O = 16$) as the mean of six experiments (Roscoe, 1882c). Roscoe and Shuster also showed that that the spectrum of the CO_2 furnished by the South African diamond was identical with that furnished by other forms of carbon (Thorpe, 1916a, 1916b)

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[3] Charles Hatchett (1765–1847) reported a new element similar to tantalum in 1801, and named it columbium. In 1809 William Hyde Wollaston (1766–1828) wrongly concluded that tantalum and columbium were identical. Heinrich Rose (1795–1864) determined in 1846 that tantalum ores contain a second element, which he named niobium. In 1864 and 1865 it was found that niobium and columbium were the same element (as distinguished from tantalum). The name of the element was officially adopted as niobium in 1949.

Perchloric acid and its compounds

At the time of Roscoe, very little was known about the composition of potassium perchlorate, it was thought to contain about 46 wt.% oxygen and was represented by the formula $KClO_4$: the anhydride Cl_2O_7 had not been isolated, and the composition of only one or two of its salts had been published. Roscoe, with the help Schorlemmer, made a fairly complete investigation of perchloric acid and its hydrates and a number of its salts (Roscoe, 1861b, 1862a, 1866a). They first prepared aqueous perchloric acid by distilling a mixture of potassium chlorate with a saturated solution of hydrofluosilic acid; the liberated chloric acid decomposed and escaped as a gas, whilst aqueous perchloric acid remained in the liquid. The aqueous acid was found to be a colorless heavy oily liquid, having an almost identical aspect to that of concentrated sulfuric acid (Roscoe, 1861b, 1862b). Roscoe prepared pure perchloric acid by distilling the aqueous solution with four times its weight of very concentrated sulfuric acid. Contact with a carbonized material (charcoal, paper, or wood) caused an explosive combustion, ''which in violence did not fell short of the detonation produced by the sudden decomposition of nitrogen chloride.'' When the acid was heated, it begun to decompose at 75 °C and after 92 °C it gave dense white fumes turning into a dark brown liquid. The acid was used to prepare its monohydrate and the perchlorates of ammonia, iron, mercury, lead, as well as copper ammonio-perchlorate (Roscoe, 1861b).

The monohydrate was prepared by carefully adding water to the perchloric acid under continuous cooling. The monohydrate solidified at room temperature to long silky needle-shaped crystals, which fumed strongly in the air and melted at about 50 °C, most rapidly absorbing moisture, and immediately deliquescing on exposure. The synthesis of perchlorate of ammonium, ammonio-perchlorate of copper, ferrous perchlorate, mercurous perchlorate, and perchlorate of lead were also discussed (Roscoe, 1861b).

In a following publication (Roscoe, 1862b) Roscoe described the preparation of perchloric ether by distilling a mixture of barium perchlorate with barium sulfovinate (ethyl sulfate). The dry perchloric ether was found to decompose explosively when poured from one vessel to another, or when its particles were in any way slightly shaken; hence Roscoe recommended taking the greatest care when working with this compound. In contact with water, the ether was much more stable, and could be shaken, or even distilled, without explosion. At 755 mmHg its boiling point under a thin layer of water, was 74 °C (Roscoe, 1862b).

The finding that thallium and ammonium sulfates were isomorphs, led Roscoe to study the possibility that the same phenomenon was shared by the perchlorates of thallium, potassium and ammonium (Roscoe, 1866a). He prepared thallium perchlorate by dissolving the metal in aqueous perchloric acid and also, by the double decomposition of thallium sulfate and barium perchlorate. The salt appeared as colorless transparent rhombic crystals having a density of 4.844 at 15.5 °C, and formula $TlClO_4$.

Physics

At the beginning of the 19th century Dalton and Henry hypothesized that the solubility of a gas dissolved in a liquid was proportional to the pressure (Wisniak, 2001). Bunsen tested this hypothesis experimentally and found it to be true for the solubility of a large number of non-reactive gases in water at different temperatures (H_2, O_2, N_2, CO, CO_2, CH_4, ethane, ethylene, and air) (Bunsen, 1855). According to Bunsen, deviations from Henry's law will occur at pressures and temperatures near the critical point and in cases in which chemical attractions between the gas and the solvent are present. Schönfeld also found the law to be true for aqueous solutions of SO_2, even at temperatures, which approached the point were the oxide forms a hydrate with the solvent. Roscoe used the absorptiometer developed by Bunsen to determine the relation, which exists between chlorine and water at temperatures approaching that at which the hydrate of chlorine is formed (Roscoe, 1856). Since Schönfeld had already determined the Bunsen absorption coefficient of chlorine in water, Roscoe restricted his work to the examination of gases of known composition containing chlorine. One of such mixtures was that evolved by the electrolysis of concentrated HCl. Experiments on the solubility of this gas in water, done in the dark (to avoid chemical reaction) and at different temperatures, showed that the amounts of chlorine absorbed differed considerably from the amount which should be contained if the gas had followed Henry's law. Roscoe attributed the difference to a reaction between chlorine and water, forming HCl and hypochlorous acid. The same deviations were found for a mixture of chlorine and CO_2.

In a following work, Roscoe and Dittmar studied by Bunsen's methods, the absorption of hydrochloric acid and ammonia in water (Roscoe & Dittmar, 1860) and found that these gases did not obey Dalton and Henry's law below 60 °C. Similar results were obtained for solutions of ammonia in water. The quantity of ammonia absorbed by water at 0 °C was far from being proportional to the pressure. The amount of absorbed ammonia was found to vary much more considerably with change in temperature than was the case with HCl. An additional important result was that Roscoe and Dittmar found that the composition of a constant boiling solution of hydrochloric acid varied with the pressure and hence it could not be regarded as a chemical compound (Roscoe & Dittmar, 1860).

It was known that on boiling at constant pressure, aqueous solutions of acids such as HCl, HBr, HI, HF, HNO_3, and H_2SO_4 of varying concentrations attained a fixed composition. This fact had led many scientists to believe in the formation of a definite compound between water and the acid (hydrate). Roscoe believed this explanation to be incorrect and that the actual reason was physical and not chemical; the phenomenon was due to a particular relation between the composition of the mixture and the vapor pressure of the components (Roscoe, 1861a). Thus, he found that aqueous solutions of different initial compositions, achieved on boiling at 735 mmHg, a constant temperature of 120.5 °C and composition 68 wt.% acid. This composition could not be represented by any simple atomic relation, for example, the formula $HNO_3 + 3H_2O$ requiring 70 wt.% of acid. Distillation at lower pressures showed that both the composition and temperature of the constant mixture varied. Similar results were obtained with aqueous solutions of HCl, HBr, HI, HF, and H_2SO_4. The composition of the hydrated acid on boiling was found to be entirely dependent on the pressure at which it is heated, a strong solution losing acid, and a weak solution lowing water until the residue on each case acquires a constant composition, depending on the pressure under which it is boiled.

The attentive reader will realize that Roscoe was describing what today we call azeotropism, a term which was coined by John Wade and William Merriman in 1911, from the Greek α, a privative, and $\zeta\varepsilon\omega$, to boil (Wade & Merriman, 1911).

Aqueous solutions of perchloric acid, formic acid, and acetic acids were found to behave in the same manner (Roscoe, 1861b, 1862b). At 760 mmHg, aqueous solutions of formic acid achieved a constant composition of 77.5 wt.% acid and a constant boiling point of 107.1 °C, independent of the initial composition being higher or lower than 77.5 wt.%. Aqueous acetic acid, distilled under atmospheric pressure, or higher and lower pressures, was found to split up into water and glacial acid. The same result was obtained by distilling under pressures both greater and less than that of the atmosphere.

Experiments were carried out to investigate the absorption of hydrochloric acid and ammonia by water. At a temperature of 0 °C, the amount of HCl absorbed by water changed but very slightly with pressure, a variation of pressure from 1 m to 0.5 m resulting in a decrease in the quantity of absorbed gas of only 8.7% instead of 50%. The laws regulating the absorption of HCl in water were totally different from those obeyed by other gases. The quantity of ammonia absorbed by water at 0° was far from being proportional to the pressure. For equal increments of pressure up to about 760 mmHg of mercury, the corresponding increments of absorbed ammonia continually decreased, but above this point the amount of dissolved gas increased in a more rapid ratio than the pressure (Roscoe & Dittmar, 1860).

Most of the aqueous acids, and especially hydrochloric, hydrobromic, hydriodic, hydrofluoric, nitric, and sulfuric acids, of very different concentrations, not only attained a fixed composition when boiled under the ordinary atmospheric pressure, but the liquids thus prepared were definite chemical compounds of acid and water. The composition of nitric acid, sulfuric acid, hydrochloric acid, hydrobromic acid, hydriodic acid, and hydrofluoric acid were presented in detail (Roscoe, 1861a).

Public health

Roscoe worked for a Departmental Committee on Ventilation and showed that air can pass through dry brickwork in buildings. In 1876 he was appointed to the Noxious Vapors Commission chaired by Henry Austin Bruce (Lord Aberdare, 1815–1895) in order to investigate the environmental pollution caused by ''alkali works, cement works, chemical manure works, coke ovens, copper works of all descriptions, glass, lead and metal works, potteries and salt works''. The commission concluded that ''it is not a question of a few manufactories, but of industries all over the country, which in relation to man are causing pollution of the air in degrees sufficient to make them common-law nuisances.'' Nevertheless, they stroke balance with the fact that ''noxious vapors were inevitable of the nation was to prosper, hence. . .Regulation was only practical if it did not involve ruinous expenditure.''Many of their recommendations were embodied in the amended Alkali Acts of 1891 and 1892. The amended Acts extended the schedule of works in which the escape of acid fumes could be regulated, provided for an apportionment of damages amongst the various contributors thereto; and provided that all acid drainage must be kept apart from the alkaline drainage of the waste heaps, thus preventing a serious nuisance from the escape of hydrogen sulfide (Roscoe, 1906).

As stated Roscoe: ''The escape of noxious vapors cannot in all cases be prevented without seriously interfering with trade. For instance, in glass works an enormous quantity of salt cake (sodium sulfate) is employed, the sulfuric oxide being given off in the process of fritting the materials. None has yet proposed a method by which these acid fumes could be collected or absorbed without greatly damaging the industry by reason of the costliness of such a process. There is, however, no doubt that the recommendations were of great value in extending the operation of the Acts and in rendering their provisions more effective''(Roscoe, 1906).

Another legislative measure promoted by Roscoe, was a bill for the better sanitation of dwelling houses, schools, colleges, hospitals, workshops, hotels, lodging houses, and other buildings. The object was to establish a complete system of sanitary registration, especially with regard to the sanitary arrangements and drains of each house, and it was proposed that after January 1, 1890, no building should be used unless it had received a sanitary certificate (Roscoe, 1858, 1906; Thorpe, 1916b).

Conflict of interest

The authors declare no conflict of interest.

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