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Wisniak, Jaime
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Georges Urbain

Jaime Wisniak

Department of Chemical Engineering, Ben-Gurion University of the Negev, Beer-Sheva, Israel 84105
wisniak@exchange.bgu.ac.il

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Key words: analytical chemistry, atomic theory, chemical thermodynamics, hafnium, lutetium, metal chemistry, mineral complexes, rare earths, spectral analysis, spectroscopy.

RESUMEN. George Urbain (1872-1938), químico francés que investigó especialmente el aislamiento, la separación, y las propiedades de las tierras raras. Como resultado de este trabajo desarrolló una serie de métodos muy eficientes para separar las tierras, determinar su espectro, sus propiedades magnéticas, y sus masas atómicas; aisló el europio y el gadolinio y determinó su masa atómica correcta, y descubrió los elementos lutecio y celtio (hafnio). Además, estudió en forma detallada el fenómeno de eflorescencia de las sales hidratadas.

ABSTRACT. George Urbain (1872-1938), a French chemist who did most of his research on the isolation, separation, and properties of the rare earths. As a result of this work he developed a series of very efficient methods for separating them, determine their spectrum, magnetic properties, and atomic masses; he isolated europium and gadolinium and determined their correct atomic mass, and discovered the elements lutetium and celtium (hafnium). In addition, he carried on a detailed study of the phenomenon of efflorescence of saline hydrates.

Life and career[1,3]

Georges Urbain (Figure 1) was born in Paris, on April 12, 1872, the son of Victor Urbain, an engineer of technologies and manufactures and teacher at the École Primaire Supérieure Lavoisier, preparing students for the entrance examination to the École Municipale de Physique et Chimie Industrielles of the city of Paris, then directed by Paul Schützenberger (1829-1897). After completing his basic education at the Lycée Charlemagne and École Lavoisier, Georges entered the École de Physique et Chimie Industrielle, from where he graduated as a chemist in 1894 at the top of his class. At the same time he passed his licence ès physique et chimie at the Sorbonne. He then began a fast academic and scientific career serving in different teaching positions at various academic institutions: Préparateur at the École de Physique et Chimie Industrielle (1894-1895) and at the organic chemistry laboratory of Charles Friedel (1832-1899) in the Faculté des Science P.C.N. (Physique) (1895-1898), and teacher of physics and chemistry at the École Alsacienne (1897-1899). Under Friedel he began his life-long research work on rare earths, which culminated in his doctorate in 1899, with a thesis named *Recherches sur la Séparation des Terres Rares*.[4] After working for five years as head of the laboratories of the Compagnie Générale d'Electricité (1899-1904) investigating, among other things, the manufacture of sticks of rare earth oxides for arc lamps, he returned to the academy as sub-director-chef of electrochemical experiments at the École de Physique et Chimie (1905-1906) and teaching a complementary class on analytical chemistry at the Sorbonne (1906). In 1907 Urbain replaced Henri Moissan (1852-1907; 1906 Nobel Prize for Chemistry) at the Commission Internationale des Poids Atomiques, and in 1908, at the age of 30, he was promoted to professor of mineral chemistry at the Sorbonne. During the First World War he served in different positions in the Ministry of War: Director of the chemistry laboratory of the technical section Artillery, technical advisor of the Parc d'Artillerie de la Place de Vincennes (1915), member of the Inspection des Etudes et Expériences Chimiques (1916), and president of the Comité Scientifique des Poudres of the Commission des Substances Explosives. After the war he taught for some time mineral and analytical chemistry at the École Centrale

des Arts et Manufactures; in 1928 he succeeded André Job (1870-1928) at the chair of general chemistry at the Sorbonne while simultaneously serving as Director of the Chemistry Service at the Institute of Biologie (1928), just founded by Edmond James de Rothschild (1845-1934). Urbain was also appointed head of the Chemistry Section of the Palais de la Découverte, director of the Chemical Treatment laboratory of Thiais (a southern suburb of Paris), and president of the 2nd section of the École Pratique des Hautes Etudes.[2,3]

Urbain passed away on November 5, 1938.

Urbain worked most of his life on the question of the rare earths; he developed very efficient methods and reagents for separating them, for example, using their ethyl acetates, acetylacetonates, double nitrates with bismuth, etc., combined with fractional crystallization. He also determined their spectra, atomic mass, and magnetic properties. He prepared the acetylacetonate of thorium and confirmed that the element was quadrivalent. He showed that between samarium and holmium existed four rare earths: europium, gadolinium, terbium, and dysprosium, that the victorium, ionium, and incognitum of William Crookes (1832-1919) were not new elements but a mixture of gadolinium and yttrium, and he also isolated terbium, dysprosium, holmium, erbium and thulium. Urbain also isolated europium and gadolinium and determined their correct atomic mass. Afterwards he showed that the ytterbium of Jean Charles Galissard de Marignac (1817–1894) was actually a mixture, from which he separated a new element, which he named lutetium. In 1922 he discovered a new element, which he named celtium (today, hafnium).[2,3]

Honors and awards

Urbain received many awards and honors for his contributions to science and technology: Laureate of the Société d'Encouragement pour le Développement de Industrie Nationale (1902), twice laureate of the Institute [Prix Hughes and Berthelot Medal (1905, 1907)], laureate of the Société Chimique (Prize Nicolas Leblanc for 1906); La Caze chemistry Prize (1912); member of the chemistry section of the Académie des Sciences (1921), corresponding member of the Sociedad Real de Ciencias de Madrid (1909) and of the Académie Royale des Sciences of Bruxelles (1919), honorary member of the Chemical Society of London (1920); president of the Société Chimique de Paris, of the Société de Chimie Physique (1909), of the Société de Minéralogie, and of the Société Philomathique; chevalier of the Légion d'Honneur (1918), and promoted to commandeur in 1933; director of the chemical physics and analytical chemistry of the Institute d'Hydrologie, director of the Institute of Chemistry of the École Nationale Supérieure de Chimique de Paris (1928); and member of the Comité Consultatif de l'Enseignement Supérieur and of the Conseil Supérieur de la Recherche Scientifique.

SCIENTIFIC CONTRIBUTION

Urbain wrote about 120 papers and books[5-12] about his research activities on the isolation, separation, and properties of the rare earths, efflorescence of hydrates, spectroscopy, inorganic and organic chemistry, etc. As customary for all candidates to the Académie des Sciences, Urbain published a booklet describing his researches and achievements.[6]

Rare earths

Urbain's doctoral thesis about the separation of the rare earths was published at length (90 pages) in 1900.[13] The first section was an historical review of the knowledge about rare earths and a description of the different publications regarding their properties and possible composition. According to Urbain, the name rare earths were given to a large group of elements that in their natural state always appear associated. They were characterized by the insolubility of their oxalates in neutral or slightly acid liquors. From a classification viewpoint, they were located between the alkali earth metals and alumina. They were the elements most difficult to separate. Only the first terms of the series, thorium and cerium, had been obtained pure without much difficulty. The extremely small difference in their properties had not allowed the development of a rational method of separation; only the difference in their solubility had permitted their isolation in minute amounts. Even so, many fractions assumed to be pure element had later proven to be a complex mixture of rare earths. As an example, Urbain quoted that until 1878 the substance known as *didyme* was believed to be a homogenous substance, having all the properties of an element. Further work had first claimed that didyme was a mixture of samarium and another element named *decipium*, and then, that decipium was a mixture of terbium and gadolinium. Further publications claimed that didyme exempt of samarium, contained neodymium and praseodymium; that the substance identified as praseodymium actually contained three different elements, etc. etc. The increasing number of elements being found led to a subdivision of the group of rare earths into two sub-groups: the ceric earths (elements numbered 57 to 69) and the yttric earths (elements numbered 70 and 71, ytterbium and lutetium).[13]

The next section described the diverse methods available for the partial fractionation of the earths, based mainly on the relative solubility of their double sulfates with potassium in a saturated solution of potassium sulfate; and on the relative solubility of their acetylacetonates and ethylsulfates. This section was followed by another describing the treatment of the minerals containing the earths, e.g. monazite sands (a reddish or yellowish-brown mineral, formed by a phosphate of thorium cerium, and lanthanum), eschynite (a mineral containing chiefly niobium, titanium, thorium, and cerium), cerite (a brownish or cherry red mineral, containing hydrous cerium silicate and allied metals),

gadolinite or ytterbite (a silicate mineral containing gadolinium, holmium, and rhenium), and thorite (a yellow or black mineral containing thorium silicate); the fractionation process itself, and the spectrophotometric methods (line, phosphorescence, and absorption) used for following its progress. Urbain indicated that he had also followed the march of the fractionation process by determining the atomic mas of the products. According to him, the best method for determining the atomic mass *M* was by transforming a given mass of anhydrous sulfate into its oxide; thus calling *P* the weight of the sulfate and *p* the weight of the oxide then

$$\frac{P}{p}=\frac{M_2(SO_4)_3}{M_2O_3}=\frac{288+2M}{48+2M} \qquad M=\frac{288p-48P}{2(P-p)} \qquad \textbf{(1)}$$

The following sections gave a detailed description of the methods followed for the purification of thorium, the separation of lanthanum, praseodymium, neodymium, and terbines, and the fractionation of the yttric acetylacetonates and ethylsulfates from monazite sands and eschynite.[13]

In 1903, Urbain and Henri Lacombe reported the preparation and properties of several double nitrates of bismuth and magnesium, zinc, nickel, manganese, and cobalt, having the general formula $3M_x(NO_3)_2{\cdot}2Bi(NO_3)_3{\cdot}24H_2O$, where M represented the corresponding metal. Urbain and Lacombe believed their results indicated that the relation of bismuth to the rare earths was the same as that of zinc to magnesium. Their new nitrates belonged to the same type as the double nitrates of the rare earths did with the corresponding nitrates of the magnesium series; they had the same shape and were completely isomorphous with the latter.[14] In a following paper they discussed the possible use of this phenomenon as the base of a method for separating the rare earths.[15] Fractional crystallization of a binary solution of two non-isomorphous compounds allowed separating in a pure state the less soluble or the most abundant of the two components; from a certain composition on, the two salts crystallized together as an eutectic and further separation could be not achieved no matter how many times the process was repeated. This was not the situation with isomorphous salts. By a series of well-conducted fractional crystallizations it was possible to separate the pure components in the order of their solubility. In a solution of this nature, a very soluble component diminished the solubility of another little soluble. This meant the less soluble component would be practically insoluble in a saturated solution of the most soluble one. The solubility of a pure substance was strongly affected by the presence in their solution of a homolog of the series. These characteristics seemed particularly appropriate for separating a mixture of rare earths because their relative solubility varied little from one member of the series to another. The best results could be obtained by partial crystallization of very soluble salts; for two given members, the difference in solubility of their double salts was substantially larger than the solubility difference of their simple salts.[15]

Urbain and Lacombe found the solubility of their new double nitrates of bismuth in acid water to be intermediate to that of the double nitrates of bismuth and samarium and europium, suggesting bismuth could be used as separating agent between the latter. If the whole mixture was completely fractionated, the foreign salt intentionally added would locate itself in a intermediate place determined by its solubility among the salts of the original mixture At a certain step of the fractionation process, one of the fractions would be composed of pure foreign salt. If the original mixture was binary, separation of the previous fraction (head product) from the following one (tail product) meant a clean scission between the two components. According to Urbain and Lacombe, the foreign salt functioned as a separating agent. This assumption proved to be true: addition of a large quantity of the double nitrate of magnesium and bismuth to a mixture of the double nitrates of magnesium and rare earths, followed by systematic fractional crystallization, yielded after *several months of daily crystallizations*, a fraction containing the pure double nitrate of magnesium and bismuth. Elimination of the bismuth present in the other fraction (using appropriate reagents, such as hydrogen sulfide) resulted in a clear separation between samarium and europium. The head product was bismuth accompanied by samarium while the tail one was bismuth accompanied by europium. This method also allowed separating gadolinium from samarium.[15,16] Eventually Urbain and Lacombe used the same procedure for separating gadolinium from europium[17] and gadolinium from terbium.[18,19] Years later Urbain, Pierre Weiss (1865-1940) and Félix Trombe (1906-1985) proved gadolinium was ferromagnetic.[20]

In 1892 Paul-Émile Lecoq de Boisbaudran (1838–1912) reported that the electrical spectrum of certain samarium salts showed the presence of a new element (which he named Z_e) characterized by the three lines of wavelengths 466.2, 466.7, and 459.3. He also observed that several similar products presented a fluorescent band located between the wavelengths 622 and 611, signaling the presence of a second new element, which he named samarium.[21] A few years later, Eugène Anatole Demarçay (1852-1903) isolated from the rare earths a new component (which he first designed by S and then by *europium*) having all the properties of Z_e and Z_x. Urbain and Lacombe used their procedure to separate europium from gadolinium and determine that the atomic mass of the former was 151.79, with a maximum error of 0.06 (the actual value is 151.964 ± 0.001).[17] In a following paper they reported they had used the same method to separate samarium from neodymium, to prepare pure samarium oxide (samarine), and to determine

the atomic mass of samarium as 150.34 (assuming oxygen as 16) (the actual value is 151.36 ± 0.02).[22] Afterwards they reported the preparation of pure gadolinium oxide (Gd_2O_3, gadoline) from a raw material containing this oxide and several impurities originating from treatments of europium and element Z_e. From this material they calculated the atomic mass of gadolinium as 157.23 (the actual value is 157.25 ± 0.07).[23]

In 1878, Jean Charles Galissard de Marignac (1817–1894) reported that his analysis of gadolinite had indicated the presence of four earths: yttria, erbine, terbine, and X. The latter had a yellow color very similar to that of erbine, but a lower atomic mass.[24] At the request of Marignac, Jacques Louis Soret (1827-1890) determined the ultra violet absorption spectrum of a mixture of rare earths containing a large percentage of substance X, and reported all the wave lengths of the three lines he believed belonged to X (the line in the red at 640, the line in the yellow green at 536, and the line in the blue at 453-449).[25] The next year Per Theodor Clève (1840-1905) reported that earth X corresponded to a new element, which he named *holmium*.[26] In 1886 Lecoq de Boisbaudran reported that after carrying on a very large number of partial fractionations he had found the holmium of Clève to actually be a mixture of two earths, which he named holmium and dysprosium, each presenting two bands, holmium at 640.4 and 536.3 and dysprosium at 753 and 451.5.[27,28]

In 1906, Urbain reported he had been able to prepare dysprosium oxide highly pure and that this material was white, did not oxidize further in a stream of oxygen, and that its salts were yellow green. The composition of the oxide indicated that the atomic mass of dysprosium was 162.49 (the actual value is 162.5 ± 0.001). The properties of the compounds of dysprosium, including solubility, basicity of the oxide, etc. indicated it should be located between terbium and the new holmium. Its ultra violet spectrum was composed of intense and diffuse bands overlapping those of terbium and holmium and masking them completely in their mixtures.[29] Other publications in the same area included determination of the atomic mass and spark spectrum of terbium[30] and determination of the atomic mass of dysprosium.[31]

In 1907 Urbain reported he had separated a new element by splitting the earth ytterbium. He remarked that when separating the elements of the yttric group he had observed that yttrine always produced the most soluble salts. For this reason he decided to investigate these salts further by subjecting a solution of the nitrates in a solution with nitric acid of density 1.3. to a long fractional crystallization process. He noticed that the atomic mas of the product increased progressively from one crystallization to another. Thus, the atomic mass grew from 169.9 for the 17th stage to 173.8 for the 31st one. These crystallizations were accompanied by a determination of their spark spectrum. Eventually, it became clear that certain of the lines corresponded to a new element, which he named *lutetium* (derived from an ancient name for Paris), Urbain concluded that Marignac's ytterbium was actually a mixture of two elements, *neo-ytterbium* (today, ytterbium), and lutetium; he indicated that the atomic masses of neo-ytterbium and lutetium should be around 170 and 174, respectively.[32,33] In 1914, J. Blumenfeld and Urbain isolated neoytterbium and determined his atomic mass as 173.54 (today 173.04 ± 0.03).[34]

Shortly thereafter, Urbain reported the discovery of a new element, which he named *celtium* [today hafnium, as suggested by Dirk Coster (1889-1950) and George Charles von Hevesy (1885-1966, 1943 Nobel Prize in Chemistry],[35,36] which accompanied the lutetium and scandium of the rare earths of gadolinium.[37]According to Urbain, the atomic numbers of (neo)ytterbium, lutetium, and celtium were, 70, 71, and 72, respectively.[38]

Phosphorescence

Another significant research area of Urbain was related to phosphorescence. In a general paper published in 1907, he first reviewed this phenomenon and that of thermo luminescence. The first term described the luminescence emission, which persisted after the light excitation had ceased, and the second referred to the emission of light under the influence of a slight increase in temperature.[39] It was accepted that in phosphorescence light seemed to behave like a volatile substance, which was released by heat. It was possible to heat a fluorite and have it release all its light. If heated after cooling the fluorite was unable to emit again, unless left to the influence of solar light for a sufficiently long time. If instead of heating the insolated fluorite it was examined in the dark, only ordinary phosphorescence would be observed, which resulted from the spontaneous decomposition of an unstable combination of the fluorite and light. According to Urbain, phosphorescence and thermo luminescence were identical phenomena, which occurred at different temperatures: heat exerted only a decomposing effect, while light acted in the opposite direction. If a body ordinarily phosphorescent were excited by light at very low temperature, it would behave immediately as a thermo luminescent substance; phosphorescence would appear only at a sufficiently high temperature.[39]

Admitting phosphorescence was the result of a combination of the light excitation with the material substance, it had to be that it made a selection between the rays it received. It was a known fact that a phosphorescent body always emitted the same radiations, which gave place to a spectrum of fixed positions, of characteristic wavelengths. This implied certain rays played a true role, while the others were hardly useful. Eliminating the latter, it was possible to obtain the corresponding excitation spectra by dispersing the selected rays with a prism. George Stokes (1819-1903) proved that the radiation of a phosphorescence was provoked by a radiation of shorter wavelength, so that phosphorescent bodies should be considered as "light transformers"; phosphorescent bodies not only accumulated the

incident radiation, they also modified its nature. Phosphorescence could also be generated by cathode vacuum tubes and radiating bodies (e.g. radium β rays); the radium α rays were about 20 times slower than those from cathode tubes. Another important observation was that all phosphorescent substances lost this property as they become more and more pure. Not only that, different impurities resulted in different spectra. In other words, the spectra of cathodic phosphorescence were not attributable to the main component but to the impurities (*phosphorogenes*) it contained. The principal role was played by the electrons of these impurities, the main components acted simply as a diluent of the active substance. According to Urbain, in liquid solutions, the diluents were the ionizers and the phosphorogenes were the positive ions. It seemed legitimate to admit that up to a certain point a solid solution would behave similarly. In these, the ions of the phosphorogene manifested their presence in different diluents by spectra, which although different, were significantly analogous. Although the ions in a solid solution were not free, it was possible to admit that under the influence of a radiation they acquired a certain freedom in relation to the ions of opposite sign, which neutralized their charge. In a binary system, composed of one phosphorogene and one diluent, it was frequently observed that the color of the phosphorescence changed in a continuous manner with the proportion of the two components. For example, europium, in a concentrated solution in gadolinium, emitted red phosphorescence, which changed to a white orange when highly diluted. Similarly, the phosphorescence of manganese in calcium carbonate changed from orange to blue as the solution became more diluted. When the solution contained two diluents (ternary solution), the spectra appeared as a superposition of that of the two binary systems, although it could well be that one was completely masked by the other. When the solution contained two phosphorogenes and one diluent the situation became more complex; depending on the relative concentration it was possible to observe the spectrum of one or the other phosphorogene, or a mixture of both. The complexity of the spectra grew substantially when the mixture contained several diluents and several phosphorogenes.[39]

Two years later Urbain published a lengthy treatise (160 pages) about the cathodic phosphorescence of the rare earths; remarking that this mode of excitation was the one producing the most beautiful luminous effects.[40]

The introduction of this publication repeated some of the basic concepts described in the previous one, e.g. phosphorescence and thermo luminescence, phosphorogene and diluent, Stokes law, etc. etc. It was admitted that cathodic rays were composed of electrons moving on a straight line normal to the cathode, at a velocity somewhat below that of light. The electrons had a feeble mass but were extremely penetrant. Their effect manifested itself by an emission of luminous radiations of specific wavelengths. The phosphorescence created by cathodic rays was extremely sensitive: the presence of one millionth of a phosphorogene in an appropriate diluent was enough to make a substance phosphorescent. The fact a pure body was not phosphorescent did not imply that the lack of phosphorescence meant that the body was pure. It was known that impure oxides, the same as salts, had a conductivity of the same order as the electrolytic ones, and hence, they played a role similar to of water in aqueous solutions: ionizers. At a proper temperature, their impurities become ionized and acquired enough mobility to transport electric charges.[40]

In the following two sections, Urbain described the work done by Crookes, Lecoq de Boisbaudran, Friedrich Wilhelm Muthmann (1861-1913) and his students, etc. For example, Crookes had widely studied the phenomenon of cathodic phosphorescence and found that the corresponding spectra of the rare earths were composed of narrow bands.[41] For most natural substances phosphorescence yielded large and diffuse bands, but in a few cases the spectrum was discontinuous. Crookes was particularly interested in a lemon yellow band, sometimes nebulous sometimes narrow, which appeared at a wavelength of 474. He believed the brightness of this band increased with the concentration of the element producing it. He also remarked this band appeared particularly in the products obtained when the sample examined had been treated with sulfuric acid. Eventually, Crookes concluded this particular yellow lemon band characterized the rare earth element yttrium. The spectrum of "pure" yttrium observed by Crookes showed other bands colored red, green, blue, and violet, accompanied the yellow lemon one. Sometime latter Lecoq de Boisbaudran showed Crookes had reached the wrong conclusion; the phosphorescence of the sample was caused by the impurities it contained and not by yttrium itself.[42] Further work by Crookes about other bands, led him to identify them belonging to samarium, gadolinium, etc., and three new elements, which he named *victorium*, *ionium*, and *incognitum*.[43]

Section four described the methods used for separating the yttric earths employed in the research program. According to Urbain, the fastest and most efficient for a first classification of yttric earths was crystallization of the ethylsulfates, which he had described in a previous publication.[44] The first stages separated the ceric earths (lanthanum, cerium, praseodymium, neodymium, and samarium), the next one separated europium, gadolinium, and terbium, and the remaining fractions contained particularly yttrium. Further fractionation of the latter produced holmium and erbium, while the tails were rich in ytterbium. The head fractions, free of yttrium, were further separated using Demarçay's method, based on transforming the ethylsulfates into double nitrates of the magnesium series.[40,45]

The next pages gave a detailed description of the separation of samarium from europium, europium from gadolinium, gadolinium from terbium, dysprosium from holmium, holmium from yttrium, yttrium from erbium, and erbium from thulium and ytterbium. Afterwards, Urbain described in detail the construction and operation of the

equipment he had used for observing visible and UV phosphorescence. Of particular interest was the arrangement he had used for the simultaneous determination of the spectra of several samples, for the purpose of comparison.[40]

Urbain wrote that none of the oxides of the four yttric earths he had purified exhibited live phosphorescence; under the action of cathodic rays in the dark. Europium oxide presented a hardly perceptibly dark red phosphorescence while the one of gadolinium oxide was slightly white. The oxides of terbium and dysprosium showed no effect. He also wrote that the correct procedure for observing and comparing the different spectra required preparing, as pure as possible, the two substances which would operate as diluent and as phosphorogene. For this purpose he utilized a mixture of calcium oxide and manganese oxide. The pertinent nitrates were purified by fractional crystallization in nitric acid, followed by precipitation with ammonia and ammonia carbonate. The precipitated carbonates were filtered, washed and dried, and then transformed in oxides by calcination. Eighteen mixtures were prepared with composition varying from one pure oxide to the other. The optimal phosphorescence was obtained with a mixture containing 0.55% manganese oxide and 99.45% calcium oxide. Afterwards, Urbain repeated the same series of experiments, using a mixture of rare earth diluted in calcium oxide to determine the composition exhibiting the optimal effect; for all of them, the best effect was obtained for highly diluted mixtures of the rare earth in calcium oxide (e.g. 0.01% samarium oxide; 0.005% terbium oxide, etc.). The results confirmed Lecoq de Boisbaudran's claim that the pure components did not exhibit sensible phosphorescence, that the phenomenon was a particular property of the diluted substance, and that the coloration of the phosphorescence of a binary system varied with the degree of dilution of the phosphorogene.[40]

The next stage was determination of the phosphorescence spectra of the impure rare earths in calcium oxide as diluent. Urbain reported the particular wavelengths of the spectra observed for praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium and erbium in a mixture with calcium oxide. One important result was that the victorium, ionium, and incognitum of Crookes were not new elements but a mixture of several of the known elements.

Sections 10 and 11 described in detail the phosphorescence spectra of a large number of binary and ternary mixtures of rare earths and their anhydrous sulfates, and of fluorites.[40]

Efflorescence of saline hydrates

In 1912 Charles Boulanger and Urbain began researching the efflorescence of hydrated salts.[46,47] This relatively fast phenomenon depended on a number of circumstances, which complicated the necessary manipulations to measure the weight of the sample as a function of time and temperature. For this reason Urbain developed a new laboratory balance capable for following the fast decomposition of substances with release of gas, under vacuum and at several temperatures. His balance allowed managing the weights from the outside and without the need of trial and error. It provided a very satisfactory answer to the question (a) by replacing the weights by a solenoid and a magnetized needle suspended vertically from one extreme of the beam of the balance, (b) by locating the pan, suspended at the other end of the beam, at the center of an electrical resistance furnace heated to a temperature regulated at will and measured by a sensitive thermocouple, (c) by providing a water-tight cage capable of operating under vacuum, and (d) by introducing within the cage of the balance the necessary reagents to absorb the gases as they were being generated. The balance was constantly brought to zero by adjusting the intensity of the current passing through the solenoid, so that the needle remained in the same position relative to the solenoid and the attraction was proportional to the current intensity (that is, the balance operated by electromagnetic compensation). Use of an appropriate shunt at the terminals of a galvanometer located within the circuit of the solenoid, allowed the instant and direct reading (on a scale) of the weight of the substance being tested. In order for this mode of electromagnetic compensation to operate appropriately it was necessary to keep the magnetism of the needle constant. This was achieved by operating the solenoid at a low magnetic field and low current to avoid heating the needle. According to Urbain the weight variation of his balance were of the order of several milligrams and the sensitivity was about 0.01 mg.[48]

Boulanger and Urbain's model for efflorescence assumed an isotropic crystal of surface S, efflorescing at constant temperature in a dry unlimited atmosphere.[46] Under these circumstances, the efflorescence propagated from the periphery to the center. At any one time it was possible to distinguish two zones clearly delimitated: The external efflorescent zone, and the internal unaffected zone, having area s. The latter could be considered saturated of water vapor at the dissociation pressure P of the hydrate. Near this surface, but in the efflorescent zone, the vapor pressure was lower ($\pi < P$); and became even lower as the external surface (ϖ) was approached. The diffusion of the vapor through the effloresced was relatively slow but extremely fast in the atmosphere surrounding the original crystal. Hence, it changed very rapidly from the value ϖ to zero. At the beginning of the process the value of ϖ was equal to P, and as the process advanced, the value ϖ decreased continuously. According to Boulanger and Urbain, the efflorescence process had the same characteristics as the process of concentrating a solution by spontaneous solution in a dry and limited atmosphere. Assuming this assumption to be true then $dm = KS\varpi dt$, were dm was the amount of water evaporating in the time period dt. The same equation could be applied to the surface s, so that $d\mu = Ks(P - \pi)dt$ were $d\mu$ was that mass evaporating during dt. The values of π and ϖ depended on the thickness ρ of the efflorescent

layer. Applying Fick's law of diffusion $dn = bS(d\varpi/d\rho)dt$ and carrying on some algebraic steps, Boulanger and Urbain, arrived at the final formula

$$\frac{KSP}{q^{\frac{b}{b}}(b+1)} = a \qquad (1)$$

Calling $\frac{b}{b}+1 = A$ the above equation became

$$\ln(m_q - m_t) = \ln a + A\ln(q - t) \qquad (2)$$

where q was the total time for efflorescence and m_q the corresponding loss of mass (as determined experimentally). Hence the final equation had only two parameters *a* and *A*.

According to Boulanger and Urbain, their equation (2) appeared to describe very well the efflorescence of saline hydrates. Their experimental results indicated that *A* seemed to be independent of the temperature and the rate of the process, and that the value *A* = 1.6 fitted the equation for most hydrates.[46]

In a following paper Boulanger and Urbain considered the effect of the thickness of the crystal, for two similar crystals of different weight, and showed that equation (2) changed to

$$\ln a' = \ln a + \left(1 - \frac{A}{3}\right)\ln\frac{p'}{p} \qquad (3)$$

where *p'* and *p* represented the weight of each crystal.[47]

A third publication discussed the effect of temperature. Here Boulanger and Urbain confirmed their previous result that parameter *A* was independent of the temperature and derived the following expressions describing the influence of the temperature on parameters θ (time of efflorescence) and *a*, based on the following expression for the rate of efflorescence:

$$v = KSP\left(1 - \frac{t}{q}\right)^{A-1} \qquad (4)$$

$$\ln q_T = \ln q_{T_0} + \frac{0.4343q}{2T}\left[\frac{T}{T_0} - 1\right] \qquad (5)$$

$$\ln a_T = \ln a_{T_0} + \frac{0.4343qA}{2T}\left[\frac{T}{T_0} - 1\right] \qquad (6)$$

were *q* represented the heat of dissociation. These equations indicated that if the efflorescence parameters were known at one temperature, say T_0, they could be used to describe the process at another temperature *T*.[4]

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