

Thomas Graham. I. Contributions to thermodynamics, chemistry, and the occlusion of gases

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ABSTRACT

Thomas Graham (1805-1869) is known as the founder of colloidal chemistry and for his fundamental research on the nature of phosphoric acid and phosphates, diffusion of gases, liquids, and solutions, adsorption of gases by metals, dialysis, osmosis, mass transfer through membranes, and the constitution of matter.

KEYWORDS: absorption of gases, gas liquefaction, occlusion of gases, phosphoric acid, polybasicity

Resumen

A Thomas Graham (1805-1869) se le conoce como el fundador de la química coloidal y por sus investigaciones fundamentales en las áreas de la naturaleza del ácido fosfórico y los fosfatos, difusión de gases, líquidos y soluciones, adsorción de gases por los metales, diálisis, osmosis, fenómenos de transferencia a través de membranas, y constitución de la materia.

Palabras clave: absorción de gases, licuefacción, oclusión, ácido fosfórico, polibasicidad

Life and career (Kerker, 1987; Odling, 1871; Russell, 2005; Smith, 1870, 1876, 1884; Stanley, 1987; Williamson, 1870)

Thomas Graham was born in Glasgow on December 21, 1805, the second out of the seven children of Margaret Paterson and James Graham, a Glasgow prosperous merchant and manufacturer of light woven fabrics. From 1811 to 1814 he attended William Angus's English preparatory school and then transferred to the Glasgow Grammar School. In 1819, at the age of 14, he entered Glasgow University where he learned Latin, Greek, Logic, Belles-lettres and Composition, Moral Philosophy, and from 1823 to 1824 he attended for the first time Thomas Thomson's (1773-1852) Chemistry class and William Meikleham's (1771-1846) Natural Philosophy class, winning one of the class prizes for the latter subject. Thomson's classes so impressed Graham that he became convinced that his future lied in the field of chemistry. While at Glasgow he also enrolled as a Divinity student in the sessions 1824-1825 and 1825-1826, to superficially satis-

fy his father's wishes that he should follow a long family tradition and became a Minister in the Church of Scotland. In September 1825 Graham read his first chemical paper on the absorption of gases by liquids (Graham, 1826) to the Glasgow University Chemical Society and in 1826 he was awarded the degree of MA. At this time, the profound difference of opinion with his father insistence that Thomas should follow a religious career, led to a rupture of relations and the suspension of the paternal economical support. This crisis forced Thomas to return to Glasgow, where he believed he could better find means for supporting himself (Russell, 2005). In Glasgow he gave private lessons of mathematics and chemistry for one year, while continuing his medical studies so that he might qualify himself to become a university teacher of chemistry, which required being either a physician or a member of the Faculty of Physicians and Surgeons of Glasgow (Stanley, 1987).

In 1829, he was appointed lecturer in the Mechanic's Institute, succeeding Thomas Clark (1801-1867) who had been appointed to the chemistry chair at Marischal College (Aberdeen's second university). In the same year Graham submitted to the university's medical faculty an essay on gaseous diffusion (Graham, 1829). Johann Wolfgang Döbereiner (1780-1849) had observed this phenomenon earlier, while studying the escape of gases through cracks in a metal wall (Döbereiner, 1823), but Graham's study was the first systematic approach to the subject. The significance of this work was such that it gained him an appointment as professor of chemistry at Anderson's College (later the Royal College of Science and Technology), succeeding Alexander Ure (1810-1866), who had moved to London to practice medicine and teach at the North London Medical School. This promotion was sufficient for his father to relent and for reconciliation between them. At Anderson, Graham taught theoretical and applied chemistry to medical students as required by the Royal College of Surgeons of Edinburgh and as recommended by the Medical Boards (Russell, 2005).

Graham remained in Glasgow until 1837 where he completed his work on diffusion of gases, on arsenates and

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phosphates, and on water of hydration. The significance of his findings led to his election as fellow of the Royal Society in 1834 and his appointment as professor of chemistry at University College, London, replacing Edward Turner (1796-1837) who had recently passed away in 1837 (Kerker, 1987). Graham resigned his professorship in 1854 to replace John Herschel (1792-1891) as master of the mint. His intensive load work deteriorated his health and led to his early death on 16 September 1869 (Smith, 1870; Russell, 2005).

Graham received the Royal Medal of the Royal Society twice (1837 and 1863), for his papers on the constitution of salts and on the motion of gases; the Copley Medal of the Royal Society (1862), and the Prix Jecker of the French Académie des Sciences (1862), for his papers on the diffusion of liquids and on osmotic force (Graham, 1854, 1861a). He delivered the Bakerian Lecture twice (1849 and 1854); the first one was about the diffusion of liquids and described many experiments in which salt diffused from a concentrated solution into a layer of pure distilled water carefully introduced above it (Graham, 1850). The 1854 Bakerian lecture was about the osmotic force (Russell, 2005).

He was elected a corresponding member of the Institute de France in 1847 and an honorary member of the Academies of Sciences of Berlin, Munich, Turin, and the National Institute of Washington, among others. In 1853 Oxford University conferred him an honorary degree of doctor of civil law. In 1841 he participated in the founding of the Chemical Society and became its first president. Graham served on the Chemical Committee of the British Association for the Advancement in 1834 and 1835 and recommended the adoption of Jöns Jacob Berzelius's (1779-1848) symbols for chemical nomenclature (Stanley, 1987).

In 1830 Graham submitted the required Probationary Essay, entitled "On the tendency of air and the different gases to mutual penetration", to become a member of the Faculty of Physicians and Surgeons of Glasgow. He observed that in a given time, the more diffusive gas in a mixture escaped in a greater proportion than it did when it was on its own, a result that led him to suggest that the diffusion process must involve ultimate particles and not sensible masses of a gas. In 1833 he reported to the Royal Society of Edinburgh his finding that the rate of diffusion of a gas is inversely proportional to the square root of its density (Graham's law) (Graham, 1833b; Russell, 2005). He differentiated between *effusion* (through a porous wall) and *transpiration* (through a capillary tube), each mode having its own specific rate laws. It was already known that the velocity with which different liquids issued from a hole on the side or bottom of vessel was inversely proportional to the square root of their respective specific gravities and Jean Léonard Marie Poiseuille (1799-1869) had reported that this law was not applicable to liquids flowing under pressure through capillary tubes. In the latter situation the velocity was proportional to the pressure and the fourth power of the diameter and inversely proportional to the length of the capillary

(Poiseuille, 1840, 1841). Graham showed that if a liquid was diluted with water, its transpirability did not vary proportionally to the degree of dilution; dilution up to a certain point corresponding to the formation of a definite hydrate, usually increased the transpiration time to a maximum, after which it diminished with further dilution. He also found that the transpiration times of homologous liquids increased regularly with the complexity of the molecules. He then extended his work to solutions, showing that the rate of diffusion of a solute was roughly proportional to its concentration (Graham, 1850, 1861a; Russell, 2005). These studies were followed by others on the effusion of gases through porous plates, their transpiration through capillary tubes and sheets of rubber, and their adsorption, particularly hydrogen, on metal surfaces (Graham, 1864, 1866, 1867, 1868, 1869ab). Graham showed how gases like hydrogen and oxygen might be separated in this way, a process used today to separate uranium isotopes. He discovered what he called the *occlusion* of hydrogen by palladium and speculated if hydrogen might not be some kind of metal (Graham, 1869ab; Russell, 2005). For his discoveries on the subject of gaseous diffusion he was awarded the 1834 Keith Prize of the Royal Society of Edinburgh.

Other significant researches involved the discovery of the hydrates and alcoholates of several salts (Graham, 1828b, 1834a, 1835, 1836), the existence of various polybasic acids and salts and of the anhydrous acids and salts, as well as the phenomenon of polybasicity (Graham, 1833a, 1837), the spontaneous inflammability of phosphine (Graham, 1828c, 1834b), and the theory that the absorption of gases by liquids corresponds to a liquefaction of the gas (Graham, 1826). Graham argued that when a gas was absorbed by a liquid, it liquefied and some of its latent heat was released as measurable or sensible heat. The liquefied gas was retained in the liquid state by the attractive force of chemical affinity acting between different liquid molecules (Stanley, 1987). He used his theory to account for some assorted phenomena such as the limitation of the atmosphere, which occurred when the air was cooled by expanding upwards until it ultimately solidified producing luminous or phosphorescent clouds or even the Aurora Borealis (Graham, 1827a); the fixing of nitrogen, which involved the liquefaction of nitrogen and oxygen in water followed by their combination in the presence of calcium bicarbonate to make nitric acid (Graham, 1828a). He studied the metal amines, and he became the first to regard them as substituted ammonium compounds like $\text{NH}_3\text{-CuCl}_2\text{-NH}_3$ (Russell, 2005).

At about the same time (1848), he made some crucial experiments on colloids and osmosis, a phenomenon discovered by Abbot Jean-Antoine Nollet (1700-1770) a century before (Graham, 1854; Nollet, 1752).

Graham published his many chemistry findings in his textbook *Elements of Chemistry* (Graham, 1842), which became widely used in England and translated into other European languages.

Scientific contribution

Graham published about 70 papers in the areas of chemistry, thermodynamics, diffusion of gases and liquids, dialysis, osmosis, colloidal phenomena, and the constitution of matter.

Thermodynamics

Graham studied in detail the experimental evidence regarding the absorption of gases by liquids (Graham, 1826). It was known that two liquids may mix in any proportion, as alcohol and water, or in limited proportions, as ether and water. Some mixtures even exhibited chemical union, for example, water decreased the volatility of alcohol (the concept of hydrogen bonding was yet to be developed). The physical states of gas, liquid and solid were not permanent and could be assumed by any body. According to Graham, gases could be considered volatilized liquids and as such to have the common properties of liquids; their plain injection into an absorbing liquids would occasion their liquefaction, and consequently, bring into play the affinities of liquids and the corresponding diminution in volatility. Hence, it could be assumed then that gases liquefied by pressure or other means, would also mix with liquids in some proportion. Graham illustrated his ideas with the following example: Sulfuric acid, which boils at about 327°C at atmospheric pressure, if heated to 316°C is able to liquefy steam at the same temperature and bring the boiling point of the diluted sulfuric acid also to 316°C. This situation corresponded to the absorption of a gaseous body by liquid at the same temperature, yet in order to liquefy the gaseous body, it would be necessary to cool it down by nearly 216°C, or to 100°C. Obviously, the same composition of sulfuric acid and water could be obtained more directly by *simply mixing together* the ingredients in the liquid state. Consequently, the absorption of a gas by a liquid was dependent upon the affinity, which occasioned the miscibility of liquids, and gases owed their absorption to their capability of being liquefied and to the apparent affinity of liquids (apparent in their miscibility) (Graham, 1826).

Experience indicated that the same liquid absorbed different quantities of different quantities of gases, and different liquids, absorbed unequal quantities of the same gas because of the difference in affinities. Diminution of pressure or increase of temperature decreased the quantity of a gaseous body retained by a liquid because the absorbed gas was itself in a liquid state; and the volatility of all liquids, whether by alone or mixed with other liquid, was dependent upon pressure and temperature. Graham pointed out that William Henry's (1774-1836) conclusion that the solubility of a gas was directly proportional to the pressure, contradicted experience. He would have reached a different conclusion had he experimented with the more absorbable gases. Henry's law was probably true only for slightly soluble gases (Graham, 1826).

The partial displacement of a gas absorbed by a liquid by another gas was a phenomenon similar to the addition of a

third liquid to a mixture of two. For example, addition of water to an alcoholic solution of a volatile oil in solution resulted in the separation of a large fraction of the oil, while the alcohol united with the water. The simultaneous absorption of several gases by a liquid belonged to this class of appearances. The final conclusion was that when gases appeared to be absorbed by liquids they were actually reduced into the liquid inelastic form, which otherwise (by cold or pressure) they might be compelled to assume. Thus the phenomena of absorption of gases belonged into the same class as those of the miscibility of liquids (Graham, 1826).

Graham extended his ideas to prove that the atmosphere had to have a finite height (Graham, 1827a). According to William Hyde Wollaston (1766-1828), the finite extent of the atmosphere could be explained on mechanical principles. Its lightweight might afford at a certain degree of rarefaction, a balancing resistance to further expansion. Michael Faraday (1791-1867) had shown that in certain instances such a balance exists between the expansive power of gaseous matter and its clogging gravity. According to Graham admitting that the cause assigned would be fully adequate to produce the effect, the question still remained, but was it really the cause, which produced the effect? "The atmosphere could possess some well-known property, which necessarily made it limited, and the proposal of any supposition cause could be therefore unnecessary." The law of expansion of gases by heat and their contraction by cold involved a curious consequence, which had attracted the attention of several researchers. Bodies could exist in that state below a certain temperature. For example, considering a volume of air at 0°C, it was known that this volume increased by 1/266.7 for every centigrade degree the air was heated above 0°C, and vice versa if it was cooled. Hence *cooling* it by 266.7°C, would be to reduce its volume infinitely, it would really be annihilated. To avoid this absurdity it was necessary to assume that cooling would reduce all gases into the liquid or solid state, as long as the temperature fall did not exceed 266.7°C below the freezing point of water. The proposition, therefore, that the Earth's atmosphere cannot exist in the gaseous state at the temperature below 266.7°C was susceptible of demonstration *ad absurdum* (Graham, 1827a).

Graham (Graham, 1827b) also used his theory that gases dissolved in a liquid were also in the liquid state to criticize Longchamp's (Longchamp, 1836) theory explaining the natural production of niter in various soils and superficially upon certain rocks. According to Longchamp, nitric acid was formed exclusively from the elements of the atmosphere, without the participation of any vegetable or animal matter. Water absorbed air and exercised such an action on oxygen and nitrogen that they combined more intimately than they existed in the atmosphere. The molecular action of the gases dissolved became more intense and forced a combination that led to nitric acid. Materials present in the soil, such a chalk, lime, and tufa (a rough, thick, rock-like calcium carbonate deposit that forms by chemical precipitation

from bodies of water with a high dissolved calcium content), would absorb water and air and lead to the formation of the acid (Longchamp, 1836). According to Graham (Graham, 1827b), the greater portion of oxygen was due simply of its being more soluble in water than nitrogen. Since both absorbed nitrogen and oxygen were really in the liquid state, they possessed a higher power of combination that would act upon calcium carbonate and lead to the production of calcium nitrate. Hence the process of nitrification was one that took place constantly in nature and required only and only the action of calcium carbonate and the elements of the atmosphere. The beneficial action in the nitrification process of the decomposition of vegetable and animal matter was due to the production of carbon dioxide, because the latter made calcium carbonate more soluble in water, and thereby allowed it to act more effectually upon the dissolved oxygen and nitrogen.

In another work Graham studied the heat effect of reactions that take place in aqueous solutions (Graham, 1841-1843, 1843-1845). The heat manifested itself as the change in temperature of the solution, which could be readily measured. Nevertheless, the increase in temperature was often greatly affected by additional phenomena circumstances, such as the liquefaction of the product of the combination, arising from its solution in the solvent employed, or the hydration of the compound formed, which usually occurred with a salt formed by the reaction of an acid with a base. Hence it was a rare case that the heat effect could actually be taken as the total expression of the heat disengaged from the combination itself. Graham performed a few preliminary experiments to ascertain whether different bases of the same class evolved the same amount of heat when combining with the same acid. His results indicated that the increase in temperature produced by dissolving equivalent amounts of copper and zinc oxides, and magnesium in highly diluted sulfuric acid were different. All the sulfates formed were hydrated salts and a large portion of the heat effect was found to be due to the hydration. When the salts were dissolved their liquefaction of salts was attended by heat absorption, that is, by a fall of temperature. He performed a large number of experiments to determine the heat of hydration of sulfuric acid, at different concentrations; hydration of the sulfates of manganese, copper, zinc, and magnesium, the sulfates, bisulfates, and chromates of potassium, ammonia, the double sulfates of magnesium and potassium, iron and ammonia, zinc and potassium, copper and ammonia, zinc and ammonia, iron and potassium, etc. Graham also studied the neutralization by potassium hydroxide of acids such as hydrogen chloride, nitric acid, acetic acid, oxalic acid, arsenic acid, and phosphoric acids (Graham, 1841-1843, 1843-1845).

Chemistry

Phosphorus and derivatives

In his studies about the slow oxidation of phosphorus (Graham, 1828c) Graham found that in the presence of pure oxygen at atmospheric pressure and temperatures below 64°C, the usual white smoke was not seen around phosphorus in daylight and was not luminous in the dark, that is, no absorption of oxygen took place. When the air was diluted with gases such as H₂, N₂, CO and CO₂, a slow combustion took place and the phosphorus became luminous. Combustion was prevented by dilution with minute amounts of gases such as ethylene, ethyl ether, turpentine oil vapors, etc. Graham also studied the formation of and properties of phosphine. Two compounds of hydrogen and phosphorus were known, which were believed to be of different composition and properties, one being spontaneously inflammable in air and the other not so. Heinrich Rose (1795-1864) proved that both compounds had exactly the same composition and that they were mutually convertible without addition or subtraction of matter (Rose, 1826). For this reason, Rose assumed the two compounds to be isomers. Graham was puzzled by these results and looked into the possibility that a foreign substance was present in one of the two isomers that resulted in they having different properties. His first results indicated that phosphine prepared by heating a mixture of phosphorus, lime, and water, yielded the inflammable species, while phosphine prepared by heating hydrated phosphorus acid was not. Two interesting findings were that passing electrical sparks through the latter phosphorus was deposited but the gas continued to be non-inflammable. Addition of small amounts of gases such as H₂, CO₂, N₂, C₂H₄, H₂S, HCl, and NH₃, made the inflammable variety to become non-inflammable. Presence of small amounts of a substance, which appeared to be nitrous acid or a nitrogen oxide, rendered the non-inflammable species inflammable. Graham conclusion was that the two known varieties of phosphine were not isomers and that their apparent difference in inflammability was simply due to the presence of a very small amount of a nitrogen oxide.

In 1827 Graham observed that magnesium phosphate effloresced very rapidly; a fact, which he believed, proved that the salt had a weak affinity for water. A weak affinity meant that the hydrated salt would be decomposed by heat, a hypothesis he demonstrated experimentally: Heating the hydrate led to its precipitation in anhydrous form. He extended his claim to other hydrates, and in 1835 he found that the tendency of sodium phosphate to combine with an additional amount of soda was connected with the existence of closely combined water. This induced him to separate the water present in salts into crystalline and basic water, the first being easily removed; the second requiring more than the boiling point of water to remove it (Graham, 1835).

Graham's major contribution to inorganic chemistry is his paper "Researches on the Arseniates, Phosphates, and

Modifications of Phosphoric Acid," in which he elucidated the differences between the three phosphoric acids (Graham, 1833b). Before Graham's work, the relationship between the various phosphates and phosphoric acids was very confusing. As stated by Alexander Williamson (1824-1904) (Williamson, 1870), it was known that solutions of phosphoric acid vary in their properties, and chemists were satisfied with giving a name to the changes without investigating their nature. Since these solutions contained phosphoric acid and water, they were assumed to have a similar composition and thus called isomeric. Considering sodium phosphate as the general phosphate type led to some important discrepancies; some argued that in this salt the ratio of the base to the oxygen of the acid was as 1:2, while others claimed it was as 1:2.5 (or 2:5). Phosphates in which the oxygen ratio was the same as in sodium phosphate were considered to be neutral. Graham observed that these phosphates were actually different when compared on the basis of *proportion of water* combined with the acid. As stated by Odling (Odling, 1871) Graham established the existence of sub-phosphates, analogous to the yellow insoluble silver phosphate, and that in sub-phosphates, ordinary phosphates, and diphosphates, the non-acid oxygen was divided in different proportions between the metallic base and water. Compounds of one and the same anhydrous acid with one and the same anhydrous base, in different proportions, had long been known, but Graham was the first to establish the concept of *polybasic* compounds, that is, a class of hydrated acids having more than one proportion of water replaceable by a basic metallic oxide so that several series of salts could be formed. Graham concluded that the individual properties of the phosphoric acids could not be expressed if they were regarded as anhydrides; they must contain chemically combined water essential to their composition. He named the three modifications of phosphoric acid as phosphoric acid, $\overset{\cdot\cdot}{\text{H}}\overset{\cdot\cdot}{\text{P}}$, that is, $3\text{HO}\cdot\text{PO}_5$ (nowadays, $3\text{H}_2\text{O}\cdot\text{P}_2\text{O}_5$ or H_3PO_4); pyrophosphoric acid, $\text{H}_2\overset{\cdot\cdot}{\text{P}}$, i.e., $2\text{HO}\cdot\text{PO}_5$ (nowadays, $2\text{H}_2\text{O}\cdot\text{P}_2\text{O}_5$ or $\text{H}_4\text{P}_2\text{O}_7$); and metaphosphoric acid, $\overset{\cdot\cdot}{\text{H}}\overset{\cdot\cdot}{\text{P}}$, i.e., $\text{HO}\cdot\text{PO}_5$ (nowadays, $\text{H}_2\text{O}\cdot\text{P}_2\text{O}_5$ or HPO_3 (Graham, 1833a).

According to Odling (Odling, 1871), in this paper Graham established the existence of two new, and, at that time, unanticipated classes of bodies, namely the class of polyacids and salts, and the class of the so-called anhydro-acids and salts.

Jöns Jacob Berzelius (1779-1848) declared that this paper was one of the more important pieces of research published that year. He insisted, however, that differences between the three acids should be explained by isomerism rather than by different degrees of hydration (Stanley, 1987).

According to Graham (Graham, 1837) it was a fact of extraordinary interest that heat did not convert the acid of sodium sub-phosphate into pyrophosphoric acid, as it did with the acid of common sodium phosphate. On the one hand, a solution of sodium pyrophosphate, to which sufficient caustic soda or sodium carbonate had been added,

could not be evaporated to dryness without becoming sub-phosphate. On the other hand, it was possible to boil sodium pyrophosphate with caustic soda for hours without sensible alteration, provided the solution was not evaporated to dryness. The remaining liquor crystallized afterwards in its original form, exhibiting no disposition whatever to form a sub-pyrophosphate. Graham explained these findings by assuming that phosphoric acid, in contradistinction to pyrophosphoric, was characterized by a disposition to unite with three atoms of base; that common sodium phosphate, for instance, was a phosphate of sodium and of water represented by $\overset{\cdot\cdot}{\text{Na}}\overset{\cdot\cdot}{\text{H}}\overset{\cdot\cdot}{\text{P}}$. In this basic water it was possible to replace an atom of any of the usual bases may be substituted; sodium, for example, with the symbol $\overset{\cdot\cdot}{\text{Na}}\overset{\cdot\cdot}{\text{P}}$, an atom of silver, as the yellow sub-phosphate of silver, etc. Hence, although a phosphate of neutral composition, such as the common sodium phosphate, could be made anhydrous without becoming pyrophosphate, the sub-phosphates, having an excess of fixed base, could be made anhydrous. Sodium phosphate contained three atoms base (two sodium atoms and one water atom); when added to the earth or metallic salts, it gave precipitates, which uniformly contained three atoms base, namely three atoms of the foreign oxide, as in the case of the sub-phosphate of silver, or one atom water and two atoms of the other oxide, as in the barite phosphates. According to Graham, these precipitations were the strongest proof of the basic function of that atom of water, which was essential to sodium phosphate. Now, since sodium pyrophosphate, contained only two sodium atoms as base, it precipitated, accordingly, dibasic salts (Graham, 1837).

According to Graham, the two atoms of water retained were essential to the constitution of sodium diphosphate, hence its composition should be expressed by the formula $\overset{\cdot\cdot}{\text{Na}}\overset{\cdot\cdot}{\text{H}}\overset{\cdot\cdot}{\text{P}}$. This formula showed that the salt contained three atoms base (one sodium atom and two water atoms) united to a double atom of phosphoric acid. The salt could lose any portion of this water without assuming a new series of properties. There were, accordingly, three oxygen atoms in the base (two in the water and one in the base) and five in the acid. Graham prepared several varieties of sodium diphosphate, for example, one which he named bipyrophosphate, containing atom of basic water, and having the formula $\overset{\cdot\cdot}{\text{Na}}\overset{\cdot\cdot}{\text{H}}\overset{\cdot\cdot}{\text{P}}$ (Graham, 1837).

In Graham's words: "Now, it is a matter of certainty that if we take one combining proportion of any modification of phosphoric acid and fuse it with soda or its carbonate, we shall form a metaphosphate, a pyrophosphate, or a phosphate, according as we employ one, two or three proportions of base. It would appear, therefore, that the acid is impressed with a disposition to form different bases of salts by the proportion of base to which it has united, and that it retains this disposition even when liberated from the original compound. Graham believed that the modifications of phosphoric acid in a free state are still in combination with their usual proportion of base, and that that base is water.

liquid. The final mixture was divided into two portions; one was mixed with half its volume of water, the other with half its volume of alcohol and both sealed in glass tubes and heated again to 143°C. According to the ordinary view of water setting free ether from sulfovinic acid, it was to be expected that much ether would be liberated in the mixture with added water. Experience showed the contrary to be true: very little ether was formed. In the other sample, on the contrary, there was considerable formation of ether. This experience showed that sulfovinic acid by itself was almost incapable of yielding ether, even when treated with water, but it was able to etherize the alcohol added to it, in the second mixture able to etherify the added alcohol, like done by sodium bisulfate or any other salt of sulfuric acid (Graham, 1851).

From these results Graham concluded that the most direct and normal procedure for preparing ether seemed to be exposing a mixture of sulfuric acid and 4 to 8 volumes of alcohol, at 160°C for a short time. Owing to the volatility of the alcohol, this process had to be conducted under pressure, as in a sealed tube. Sulfuric acid seems to exert on alcohol an action similar to the one it exerted when mixed with in small proportion with essential oils. Oil of turpentine, mixed with 1/20 of its volume of sulfuric acid, was transformed completely into a mixture of two other hydrocarbons, terebene and colophene, one of which has a much higher boiling point temperature and greater vapor density than that of the oil of turpentine (Graham, 1851).

According to Graham, this view of the etherification theory should be considered as an expression of the contact theory advocated by Eilard Mitscherlich (1794-1863). Formation of sulfovinic acid did not seem to be a necessary step in the formation of ether because the etherification procedure proceeded most advantageously with sodium bisulfate or with sulfuric acid mixed with a large proportion of alcohol and water, which would greatly impede the production of sulfovinic acid. It appeared indeed that the combination of alcohol with sulfuric acid in the form of sulfovinic acid greatly decreased the chance of the former being afterward etherized because when in the previous experiences the proportion of sulfuric acid was increased (which would produce much sulfovinic acid), the formation of ether rapidly diminished. The prior conversion of alcohol into sulfovinic acid appeared, therefore, to be actually detrimental and to stand in the way of its subsequent transformation into ether (Graham, 1851).

Occlusion of gases by metals

Henry Sainte-Claire Deville (1818-1881) and Louis Joseph Troost (1825-1911) had reported that ignited platinum and ignited iron was permeable to hydrogen and ignited iron was permeable to carbon monoxide. They remarked that hydrogen was capable of crossing the metallic wall of a tube because of the "endosmotic energy of the metal molecules. The tube walls acted like a perfect pump, capable of trans-

ferring the hydrogen to the external surface..." (Deville and Troost, 1863ab). Graham (Graham, 1868, 1869ab) duplicated their results with platinum, but modified their method by letting hydrogen pass into a space kept under vacuum by a Sprengel pump, instead of an atmosphere of another gas. Graham heated platinum shaped in different forms to redness and then allowed it to cool in a continuous stream of hydrogen. He found that no hydrogen was extracted at ordinary temperatures, even at temperatures up to 220°C. At dull red heat and upward the hydrogen was given off at the rate of 100 cm³/min·m², amounting in volume (measured cold) to up to 5.5 times the volume of platinum. Wrought platinum took up 5.53 volumes of hydrogen, which on cooling were retained or occluded in the mass. Fused platinum took only 0.17 volumes and hammered platinum 2.28-3.79. With a heated platinum plate 1.1 mm thick hydrogen was transmitted at the rate of 489.2 cm³/min·m². Experiments made under the same conditions with oxygen, nitrogen, methane, and carbon monoxide, indicated that their permeability was about 0.01 cm³ in half-an-hour. Another important result was that with an ignited platinum tube surrounded by a mixture of coal gas (45% methane, 40% hydrogen, and 15% of other gases) only pure hydrogen passed through the heated metal. This property of selective transmission was qualitatively similar to that shown by natural rubber; which transmitted nitrogen of the air in a much smaller ratio (but noticeable) than the oxygen. The septum of ignited platinum transmitted the other constituents of coal gas in an infinitely smaller ratio than the hydrogen. The same procedure was carried on with many metals; the most interesting results were obtained with silver, iron, and palladium. Although silver retained little hydrogen, it was able of absorbing and retaining as much as seven times its volume of oxygen. Iron was found particularly characterized by its absorption of carbon monoxide; in many experiments it was found to be 7 to 12.5 times the volume of the metal. According to Graham, this property of iron should have an important bearing on the theory of production of steel by cementation. Except for palladium, it was found that the gases could be pumped out from the reheated, but could not be removed from the cold metal (Odling, 1871).

The results with palladium where the most impressive ones; the metal was found to transmit hydrogen with extreme facility, even at temperature very far below redness. Thus a piece of palladium foil maintained at a temperature of 90 to 97°C for three hours and then allowed to cool down while surrounded by an atmosphere of hydrogen, gave off, after being heated under vacuum, 643 times its volume of the gas, measured cold; and even at ordinary temperatures it absorbed 376 times its volume of gas. The results indicated that the amount of hydrogen absorbed by palladium varied considerably with the physical state of the metal, whether fused, hammered, spongy, or deposited by electrolysis. The lowness of the temperature at which palladium was able to absorb hydrogen suggested other means of bringing

about the result. Thus it was found that palladium was chargeable with hydrogen in three different ways, namely, by being heated or cooled in an atmosphere of the gas, by being placed in contact with zinc dissolving in an acid, and lastly, by being made the negative electrode of a battery. The reversal of the position of the palladium plate in the decomposing cell of the battery afforded a ready way of completely extracting its hydrogen (Odling, 1871). When a plate of zinc was placed in dilute sulfuric acid, hydrogen disengaged freely from the surface of the metal, but no hydrogen was occluded and retained at the same time. This negative result was expected from the crystalline structure of zinc. But a thin plate of palladium immersed in sulfuric acid and brought into metallic contact with the zinc, soon became heavily charged with the hydrogen, which was then transferred to its surface. The experimental data indicated that in one hour, a thick plate of palladium at 12°C, took 173 times its volume in hydrogen. The absorption of the gas was even more obvious when palladium was used as the negative electrode in acidulated water in a Bunsen battery of six cells. The evolution of oxygen at the positive electrode was very copious; the effervescence at the negative electrode was suspended for the first 20 seconds in consequence of the hydrogen being occluded by the palladium. The first absorption amounted to 200.4 volumes and was greater in amount than the volume of hydrogen occluded by the same plate heated and cooled in an atmosphere of the gas, which did not exceed 90 volumes (Graham, 1868).

According to Graham, it had often been maintained on chemical grounds that hydrogen gas is the vapor of a highly volatile metal. If this was true then it had to be concluded that palladium with its occluded hydrogen was simply an alloy of this volatile metal, in which the volatility of hydrogen was restrained by its union with the other. Hence the alloy owed its metallic aspect equally to both constituents; the strength of this supposition could be tested by examining the properties of the compound substance which, could appropriately be named *hydrogenium*. The density of palladium charged with eight or nine hundred times its volume of hydrogen was clearly lowered. The linear dimensions of the charged palladium were altered considerably. Supposing the alloy to be constituted by the two metals without any change in volume, the alloy would be composed of 95.32% volume palladium and 4.68% hydrogenium, which would give the density of the latter 1.708 (similar to magnesium, 1.743). Similar results were obtained in other experiments with wires. A wire of palladium charged with hydrogen, if rubbed with powder of magnesia (to make the flame luminous) burned like a waxed thread when ignited in the flame of a lamp (Graham, 1868).

The occlusion of upward of 900 times its volume of hydrogen lowered the tenacity and electric conductivity of palladium appreciably, but still the hydrogenized palladium possessed a most characteristically metallic tenacity and conductivity. Measurement of the change in tenacity indi-

cated 100 for palladium wire alone and 81.29 when with hydrogen. Measurement of the electrical conductivity gave pure copper 100, palladium 8.10; alloy of 80% copper + 10% nickel 6.63, and palladium + hydrogen 5.99. Graham also found that the magnetic properties of the alloy were stronger than those of palladium itself (Graham, 1869ab).

The chemical properties of hydrogenium also distinguished it from ordinary hydrogen. The palladium alloy precipitated mercury and calomel from a solution of mercury chloride without any disengagement of hydrogen; that is, hydrogenium was able to decompose mercury chloride while hydrogen alone did not (Graham, 1869ab).

An interesting fact was that although hydrogen entered the entire mass of the palladium, the gas exhibited no disposition to leave the metal and escape into a vacuum at the temperature of the absorption. It appeared that when hydrogen was absorbed by palladium the volatility of the gas seemed to be entirely suppressed, and hydrogen may be largely present in metals without exhibiting any sensible tension at low temperatures. Occluded hydrogen was certainly no longer a gas and the same conclusion was arrived at when the metal was iron (Graham, 1869ab).

Graham found that the occluded hydrogen was readily extracted from palladium by reversing the position of the latter in the decomposing cell of the battery so as to cause oxygen to be evolved on the surface of the metal. The hydrogen was drawn out rapidly and completely. When palladium charged with hydrogen was left exposed to the atmosphere, the metal was apt to become suddenly hot, and to lose its gas completely by spontaneous oxidation (Graham, 1869ab).

Platinum may be charged with hydrogen by voltaic action as well as palladium but to a lesser amount, 2.19 volumes.

Graham was inclined to conclude that the passage of hydrogen through a plate of metal was always preceded by the condensation or occlusion of the gas, although the velocity of penetration was not proportional to the volume of gas occluded, otherwise palladium would be much more permeable at a low than at a high temperature. A plate palladium was sensibly exhausted of hydrogen gas at 267°C, but continued to be permeable, and in fact increased greatly in permeability at still higher temperature and without becoming permeable to other gases at the same time. In a striking experiment, a mixture of equal volumes of hydrogen and carbonic acid was carried through a small palladium tube, of internal diameter 3 mm and thickness of the wall 0.3 mm. The outer surface of this tube, heated to red heat, released gas into a vacuum with the enormous velocity of 1017.54 cm³/min·m². This gas reacted with baryta water and was shown to be pure hydrogen (Graham, 1869ab).

The familiar igniting power of platinum sponge upon a jet of hydrogen in the air seemed to depend solely upon the influence of the metal upon its occluded hydrogen. According to Graham a possible explanation of the phenomenon was to consider that hydrogen, formed by association of two

atoms, a hydride of hydrogen, then it is the attraction of platinum for the negative or *chlorylous* atom of the hydrogen molecule, which attaches the latter to the metal. The tendency, imperfectly satisfied, was due to the formation of a platinum hydride. The hydrogen molecule was accordingly polarized with its positive side turned outwards, and having its affinity for oxygen greatly increased. The fact that the two atoms of a molecule of hydrogen were considered to be inseparable was not inconsistent with the replacement of such atoms of hydrogen as were withdrawn, on combining with oxygen, by other hydrogen atoms from the adjoining molecules. It was only necessary to assume that a pair of contiguous hydrogen molecules acted together upon a single molecule of external oxygen. They would form water, and still leave a pair of atoms or a single molecule of hydrogen attached to the platinum (Graham, 1869ab).

According to Graham, the idea of a definite chemical combination was opposed by the fact that metallic palladium suffered no visible change by its association with hydrogen. The hydrides of certain metals such as copper and iron were known to be brown pulverulent substances with no metallic characters. Hence his belief that the passage of hydrogen through a plate of metals was always preceded by a condensation or occlusion of the gas (Graham, 1869ab).

According to Graham (Graham, 1867), it was possible to study the history of metals, which are found in nature in the state of soft colloids, such as native iron, platinum, and gold, by analyzing the gases they occlude. These gases were necessarily taken from the atmosphere in which the metallic mass had been in a state of ignition. William Huggins (1824-1920) and William Allen Miller (1817-1870), as well as Father Pietro Angelo Secchi (1818-1878), had concluded that hydrogen is one of the gases found on the spectrum of the fixed stars, and especially mentioned it as found with the unusual increased light of T coronæ in November 1866. The meteoric iron of Lenarto appeared to be well adapted for testing this idea because it contained more than 90% weight iron. Graham heated a sample of the meteorite to red-hot and found it to yield 2.85 times its volume of gas, of which the preponderant component (87.5%) was not CO but hydrogen. CO amounted to only 4.5% and nitrogen constituted the remaining 9.8%. From these results it became clear that the iron of Lenarto had come from an atmosphere in which iron and hydrogen prevailed. The meteorite was to be looked upon as holding within it hydrogen of the stars. Graham findings had already shown that it was very difficult to impregnate malleable iron with more than an equal volume of hydrogen, under atmospheric pressure. Since the meteoric iron gave up to three times that amount, it meant that the meteorite had, at some time or another, ignited in an atmosphere having hydrogen as its principal constituent, and judging by the high volume content, the hydrogen atmosphere had to be in a highly condensed state (Graham, 1867; Odling, 1871).

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