MEMOIR

OF

THOMAS GRAHAM,

BY

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It would be difficult to find in the history of science a character more simple, more noble, or more symmetrical in all its parts than that of Thomas Graham, and he will always be remembered as one of the most eminent of those great students of nature, who have rendered our Saxon race illustrious. He was born of Scotch parents in Glasgow in the year 1805, and in that city, where he received his education, all his early life was passed. In 1837 he went to London as Professor of Chemistry in the newly established London University now called University College, and he occupied this chair until the year 1855, when he succeeded Sir John Herschel as Master of the Royal Mint, a post which he held to the close of his life. His death, on the 16th of September last, at the age of sixty, was caused by no active disease, but was simply the wearing out of a constitution enfeebled in youth by privations voluntarily and courageously encountered that he might devote his life to scientific study. As with all earnest students, that life was uneventful, if judged by ordinary standards; and the records of his discoveries form the only materials for his biography. Although one of the most successful investigators of Physical Science, the late Master of the Mint had not that felicity of language or that copiousness of illustration, which added so much to the popular reputation of his distinguished contemporary, Faraday; but his influence on the progress of science was not less marked or less important. Both of these eminent men were for a long period of years best known to the English public as teachers of Chemistry, but their investigations were chiefly limited to physical problems; yet, although both cultivated the border ground between Chemistry and Physics, they followed wholly different lines of research. While Faraday was so successfully developing the principles of electrical action, Graham with equal success was investigating the laws of molecular motion. Each followed with wonderful constancy, as well as skill, a single line of study from first to last, and to this concentration of power their great discoveries are largely due.

One of the earliest and most important of Graham's investigations, and the one which gave the direction to his subsequent course of study, was that on the diffusion of gases. It had already been recognized that impenetrability in its ordinary sense is not, as was formerly supposed, a universal quality of matter. Dalton had not only recognized that aëriform bodies exhibit a positive tendency to mix, or to penetrate through each other, even in opposition to the force of gravity, but had made this quality of gases the subject of experimental investigation. He inferred, as the result of his inquiry, "that different gases afford no resistance to each other; but that one gas spreads or expands into the space occupied by another gas, as it would rush into a vacuum; at least, that the resistance which the particles of one gas offer to those of another is of a very imperfect kind, to be compared to the resistance which stones in the channel of a stream oppose to the flow of running water." But although this theory of Dalton was essentially correct and involved the whole truth, yet it was supported by no sufficient evidence, and he failed to perceive the simple law which underlies this whole class of phenomena.

Graham, "on entering on this inquiry, found that gases diffuse into the atmosphere with different degrees of ease and rapidity." This was first observed by allowing each gas to diffuse from a bottle into the air through a narrow tube in opposition to the solicitation of gravity. Afterwards an observation of Doebereiner on the escape of hydrogen gas by a fissure or crack in a glass receiver caused him to vary the conditions of his experiments, and led to the invention of the well-known "Diffusion Tube." In this simple apparatus a thin septum of plaster of Paris is used to separate the diffusing gases, which, while it arrests in a great measure all direct currents between the two media, does not interfere with the molecular motion. Much later, Graham found in prepared graphite a material far better adapted to this purpose than the plaster, and he used septa of this mineral to confirm his early results, in answer to certain ill-considered criticisms in Bunsen's work on Gasometry. These septa he was in the habit of calling his "atomic filters." By means of the diffusion tube Graham was able to measure accurately the relative times of diffusion of different gases, and he found that *equal volumes of any two gases interpenetrate each other in times which are inversely proportional to the square roots of their respective densities*, and this fundamental law was the greatest discovery of our late Foreign Associate. It is now universally recognized as one of the few great cardinal principles which form the basis of Physical Science.

It can be shown, on the principles of pneumatics, that gases should rush into a vacuum with velocities corresponding to the numbers which have been found to express their diffusion times; and, in a series of experiments on what he calls the "*Effusion*" of gases, Graham confirmed by trial this deduction of theory. In these experiments a measured volume of the gas was allowed to find its way into the vacuous jar through a minute aperture in a thin metallic plate, and he carefully distinguished between this class of phenomena and the flowing of gases through capillary tubes into a vacuum, in which case, however short the tube, the effects of friction materially modify the result. This last class of phenomena Graham likewise investigated, and designated by the term "Transpiration."

While, however, it thus appears that the results of Graham's investigation were in strict accordance with Dalton's theory, it must also be evident that Graham was the first to observe the exact numerical relation which obtains in this class of phenomena, and that all-important circumstance entitles him to be regarded as the discoverer of the law of Diffusion. The law, however, as first enunciated, was purely empirical, and Graham himself says that something more must be assumed than that gases are vacua to each other, in order to explain all the phenomena observed; and according to his original view this representation of the process was only a convenient mode of expressing the final result. Such has proved to be the case.

Like other great men, Graham built better than he knew. In the progress of Physical Science during the last twenty-five years, two principles have become more and more conspicuous, until at last they have completely revolutionized the philosophy of Chemistry. In the first place it has appeared that a host of chemical as well as of physical facts are co-ordinated by the assumption that all substances in the state of gas have the same molecular volume, or, in other words, contain the same number of molecules in a given space; and in the second place, it has become evident that the phenomena of heat are simply the manifestations of molecular motion. According to this view, the temperature of a body is the *vis viva* of its molecules; and since all molecules at a given temperature have the same *vis viva*, it follows that the molecules must move with velocities which are inversely proportional to the square roots of the molecular weights. Moreover, since the molecular volumes are equal, and the molecular weights therefore proportional to the densities of the aëriform bodies in which the molecules are the active units, it also follows that the velocities of the molecules in any two gases are inversely proportional to the square roots of their respective densities. Thus the simple numerical relations first observed in the phenomena of diffusion are the direct result of molecular motion, and it is now seen that Graham's empirical law is included under the fundamental laws of motion. Thus Graham's investigation has become the basis of the new science of molecular mechanics, and his measurements of the rates of diffusion prove to be the measures of molecular velocities.

From the study of diffusion Graham passed by a natural transition to the investigation of a class of phenomena which, although closely allied to the first, as to the effects produced, differ wholly in their essential nature. Here also he followed in the footsteps of Dalton. This distinguished chemist had noticed that a bubble of air separated by a film of water from an atmosphere of carbonic anhydride gradually expanded until it burst. In like manner a moist bladder, half filled with air and tied, if suspended in an atmosphere of the same material, becomes in time greatly distended by the insinuation of this gas through its substance. This effect cannot be the result of simple diffusion, for it is to be remembered that the thinnest film of water, or of any liquid, is absolutely impermeable to a gas as such, and, moreover, only the carbonic anhydride passes through the film, very little or none of the air escaping outward. The result depends, first, upon the solution of the carbonic anhydride by the water on one surface of the film; secondly, on the evaporation into the air, from the other surface, of the gas thus absorbed. Similar experiments were made by Drs. Mitchell and Faust, and others, in which gases passed through a film of india-rubber, entering into a partial combination with the material on one surface, and escaping from it on the other.

Graham not only considerably extended our knowledge of this class of phenomena, but also gave us a satisfactory explanation of the mode in which these remarkable results are produced. He recognized in these cases the action of a feeble chemical force, insufficient to produce a definite compound, but still capable of determining a more or less perfect union, as in the case of simple solution. He also distinguished the influence of mass in causing the formation or decomposition of such weak chemical compounds. The conditions of the phenomena under consideration are simply these: —

First. A material for the septum capable of forming a feeble chemical union with the gas to be transferred.

Secondly. An excess of the gas on one side of the film and a deficiency on the other.

Thirdly. Such a temperature that the unstable compound may orm at the surface, where the aëriform constituent is present in large mass, while it decomposes at the opposite surface, where the quantity is less abundant.

One of the most remarkable results of Graham's study of this peculiar mode of transfer of aëriform matter through the very substance of solid bodies was an ingenious method of separating the oxygen from the atmosphere. The apparatus consisted simply of a bag of india-rubber kept distended by an interior framework, while it was exhausted by a Sprengel pump. Under these circumstances the selective affinity of the caoutchouc determines such a difference in the rate of transfer of the two constituents of the atmosphere that the amount of oxygen in the transpired air rises to forty per cent, and by repeating the process nearly pure oxygen may be obtained. It was at first hoped that this method might find a valuable application in the arts, but in this Graham was disappointed; for the same result has since been effected by purely chemical methods, which are both cheaper and more rapid.

These experiments on india-rubber naturally led to the study of similar effects produced with metallic septa, which, although to some extent previously observed in passing gases through heated metallic tubes, had been only imperfectly understood. Thus, when a stream of hydrogen or carbonic oxide is passed through a red-hot iron tube, a no inconsiderable portion of the gas escapes through the walls. The same is true to a still greater degree when hydrogen is passed through a red-hot tube of platinum, and Graham showed that through the walls of a tube of palladium hydrogen gas passes, under the same conditions, almost as rapidly as water through a sieve. Moreover, our distinguished Associate proved that this rapid transfer of gas through these dense metallic septa was due, as in the case of the india-rubber, to an actual chemical combination of its material with the metal, formed at the surface, where the gas is in excess, and as rapidly decomposed on the opposite face of the septum. He not only recognized as belonging to this class of phenomena the very great absorption of hydrogen by platinum plate and sponge in the familiar experiment of the Doebereiner lamp, but also showed that this gas is a definite constituent of meteoric iron, — a fact of great interest from its bearing on the meteoric theory.

We are thus led to Graham's last important discovery, which was the justification of the theory we have been considering, and the crowning of this long line of investigation. As may be anticipated from what has been said, the most marked example of that order of chemical compounds, to which the metallic transpiration of aëriform matter we have been considering is due, is the compound of palladium with hydrogen. Graham showed that when a plate of this metal is made the negative pole in the electrolysis of water, it absorbs nearly one thousand times its volume of hydrogen gas, — a quantity approximatively equivalent to one atom of hydrogen to each atom of palladium. He further showed that the metal thus becomes so profoundly altered as to indicate that the product of this union is a definite compound. Not only is the volume of the metal increased, but its tenacity and conducting power for electricity are diminished, and it acquires a slight susceptibility to magnetism, which the pure metal does not possess. The chemical qualities of this product are also remarkable. It precipitates mercury from a solution of its chloride, and in general acts as a strong reducing agent. Exposed to the action of chlorine, bromine, or iodine, the hydrogen leaves the palladium and enters into direct union with these elements. Moreover, although the compound is readily decomposed by heat, the gas cannot be expelled from the metal by simple mechanical means.

These facts recall the similar relations frequently observed between the qualities of an alloy and those of the constituent metals, and suggest the inference made by Graham, that palladium charged with hydrogen is a compound of the same class, — a conclusion which harmonizes with the theory long held by many chemists, that hydrogen gas is the vapor of a very volatile metal. This element, however, when combined with palladium, is in a peculiarly active state, which sustains somewhat the same relation to the familiar gas that ozone bears to ordinary oxygen. Hence Graham distinguished this condition of hydrogen by the term "Hydrogenium." Shortly before his death a medal was struck at the Royal Mint from the hydrogen palladium alloy in honor of its discovery; but although this discovery attracted public attention chiefly on account of the singular chemical relations of hydrogen, which it brought so prominently to notice, it will be remembered in the history of science rather as the beautiful termination of a life-long investigation, of which the medal was the appropriate seal.

Simultaneously with the experiments on *gases*, whose results we have endeavored to present in the preceding pages, Graham carried forward a parallel line of investigation of an allied class of phenomena, which may be regarded as the manifestations of molecular motion in *liquid* bodies. The phenomena of diffusion reappear in liquids, and Graham carefully observed the times in which equal weights of various salts dissolved in water diffused from an open-mouth bottle into a large volume of pure water, in which the bottle was immersed. He was not, however, able to correlate the results of these experiments by such a simple law as that which obtains with gases. It appeared, nevertheless, that the rate of diffusion differs very greatly for the different soluble salts, having some relation to the chemical composition of the salt which he was unable to discover. But he found it possible to divide the salts into groups of equi-diffusive substances, and he showed that the rates of diffusion of the several groups bear to one another simple numerical ratios.

More important results were obtained from the study of a class of phenomena corresponding to the transpiration of gases through india-rubber or metallic septa. These phenomena, as manifested in the transfer of liquids and of salts in solution through bladder, or a similar membrane, had previously been frequently studied under the names of exosmose and endosmose, but to Graham we owe the first satisfactory explanation. As in the case of gases, he referred these effects to the influence of chemical force, combination taking place on one surface of the membrane, and the compound breaking up on the other, the difference depending, as in the previous instance, on the influence of mass.

He also swept away the arbitrary distinctions made by previous experimenters, showed that this whole class of phenomena are essentially similar, and called this manifestation of power simply "osmose."

While studying osmotic action, Graham was led to one of his most important generalizations, — the recognition of the crystalline and amorphous states as fundamental distinctions in chemistry. Bodies in the first state he called crystalloids; those in the last state, colloids (resembling glue). That there is a difference in structure between crystalloids, like sugar or felspar, and colloids, like barley candy or glass, has of course always been evident to the most superficial observer; but Graham was the first to recognize in these external differences two fundamentally distinct conditions of matter not peculiar to certain substances, but underlying all chemical differences, and appearing to a greater or less degree in every substance. He showed that the power of diffusion through liquids depends very much on these fundamental differences of condition, — sugar, one of the least diffusible of the crystalloids, diffusing fourteen times more rapidly than caromel, the corresponding colloid. He also showed that, in accordance with the general chemical rule, while colloids readily combine with crystalloids, bodies in the same condition manifest little or no tendency to chemical union. Hence in osmose, where the membranes employed are invariably colloidal, the osmotic action is confined almost entirely to crystalloids, since they alone are capable of entering into that combination with the material of the septum on which the whole action depends.

On the above principles Graham based a simple method of separating crystalloids from colloids, which he calls "dialysis," and which was a most valuable addition to the means of chemical analysis. A shallow tray, prepared by stretching parchment paper (an insoluble colloid) over a gutta-percha hoop, is the only apparatus required. The solution to be "dialyzed" is poured into this tray, which is then floated on pure water, whose volume should be eight or ten times greater than that of the solution. Under these conditions the crystalloids will diffuse through the porous septum into the water, leaving the colloids on the tray, and in the course of a few days a more or less complete separation of the two classes of bodies will have taken place. In this way arsenious acid and similar crystalloids may be separated from the colloidal materials with which, in the case of poisoning, they are usually found mixed in the animal juices or tissues.

But besides having these practical applications, the method of dialysis in the hands of Graham yielded the most startling results, developing an almost entirely new class of bodies as the colloidal forms of our most familiar substances, and justifying the conclusion that the colloidal as well as the crystalline condition is an almost universal attribute of matter. Thus, he was able to obtain solutions in water of the colloidal states of aluminic, feoric, chromic, stannic, metastannic, titanic, molybdic, tungstic, and silicic hydrates, all of which gelatinize under definite conditions like a solution of glue. The wonderful nature of these facts can be thoroughly appreciated only by those familiar with the subject, but all may understand the surprise with which the chemist saw such hard, insoluble bodies as flint dissolved abundantly in water and converted into soft jellies. These facts are, without doubt, the most important contributions of Dr. Graham to pure chemistry.

In this sketch of the scientific career of our late Associate, we have followed the logical, rather than the chronological, order of events, hoping thus to render the relations of the different parts of his work more intelligible. It must be remembered, however, that the two lines of investigation we have distinguished were in fact interwoven, and that the beautiful harmony which his completed life presents was the result, not of a preconceived plan, but of a constant devotion to truth, and a childlike faith, which unhesitatingly pressed forward whenever nature pointed out the way.

Although the investigations of the phenomena connected with the molecular motion in gases and liquids were by far the most important of Dr. Graham's labors, he also contributed to chemistry many researches which cannot be included under this head. Of these, which we may regard as his detached efforts, the most important was his investigation of the hydrates and other salts of phosphorus. It is true that the interpretation he gave of the results has been materially modified by the modern chemical philosophy, yet the facts which he established form an important part of the basis on which that philosophy rests. Indeed, it seems as if he almost anticipated the later doctrines of types and polybasic acids, and in none of his work did he show more discriminating observation or acute reasoning. A subsequent investigation on the condition of water in several crystalline salts and in the hydrates of sulphuric acid is equally remarkable. Lastly, Graham also made interesting observations on the combination of alcohol with salts, on the process of etherification, on the slow oxidation of phosphorus, and on the spontaneous inflammability of phosphuretted hydrogen. It would not, however, be appropriate in this place to do more than enumerate the subjects of these less important studies; and we have therefore only aimed in this sketch to give a general view of the character of the field which this eminent student of nature chiefly cultivated, and to show how abundant was the harvest of truth which we owe to his faithful toil.

Graham was not a voluminous writer. His scientific papers were all very brief, but comprehensive, and his "Elements of Chemistry" was his only large work. This was an admirable exposition of chemical physics, as well as of pure chemistry, and gave a more philosophical account of the theory of the galvanic battery than had previously appeared. Our late Associate was fortunate in receiving during life a generous recognition of the value of his labors. His membership was sought by almost all the chief scientific societies of the world, and he enjoyed to a high degree the confidence and esteem of his associates. Indeed, he was singularly elevated above the petty jealousies and belittling quarrels, which so often mar the beauty of a student's life, while the great loveliness and kindliness of his nature closely endeared him to his friends. He was never married, keeping house with a sister at No. 4 Gordon Square, where he dispensed a liberal hospitality, which has been enjoyed by many of our scientific countrymen who have visited London during the last twenty years.

In concluding, we must not forget to mention that most genial trait of Graham's character, his sympathy with young men, which gave him great influence as a teacher in the College with which he was long associated. There are many now prominent in the scientific world who have found in his encouragement the strongest incentive to perseverance, and in his approval and friendship the best reward of success.