Indian Journal of History of Science, 50.3 (2015) 476-490 DOI: 10.16943/ijhs/2015/v50i4/48318

Historical Notes

Electrochemistry and Fuel Cells: The Contribution of William Robert Grove

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(Received 19 January 2015)

Abstract

William Robert Grove (1811-1896), a British lawer, judge, and researcher, discovered the voltaic cell that carries his name (more powerful than the Daniell one), the fuel cell, and carried fundamental research in the area of electrochemistry and allied phenomena. His general analysis of physical phenomena may be considered an expression of the first law of thermodynamics and the negation of perpetual motion.

Key words: Daniell cell, Electrochemistry, Energy conversion, First law of thermodynamics, Flame electricity, Gas fuel cell, Grove cell, Perpetual motion, Polarization.

1. Introduction

William Robert Grove[1] was born on July 11, 1811, in Swansea in South Wales, the only son of Anne Bevan and John Grove, a magistrate and deputy lieutenant of Glamorgan. After receiving private education he registered at Brasenose College (one of the constituent colleges of the University of Oxford), receiving a B.A. degree in 1832. He then moved to London to pursue a legal career at Lincoln's Inn and was called to the bar in 1835. In 1837 Grove married Emma Maria Powles and then traveled to Europe to improve his health. At some time in this period of his life he became interested in physical sciences and begun developing the battery, which would lead him to fame. In 1840 Grove was elected a fellow of the Royal Society; he became a member of the Council of the Society in 1846 and 1847, one of its secretaries in the period 1846-1847, and played an active role in the modernization of the Society. His achievements in the area of electrochemistry called the attention of John Peter Gassiot, one of the managers of the London Institution, and led to Grove being appointed to the first professorial chair of the Institution (1841-1846).

The financial needs for growing a long family forced him to return to the practice of law; in 1853 he became a Q.C. (Queen Council), in 1871 he was appointed a judge to the Court of Common Pleas, and in 1880 he was appointed to the Queen's Bench. In 1887, after retirement, he appointed a member of the Privy Council.

William Grove passed away on August 1, 1896, after a long illness and was buried at Kensal Green cemetery.

Grove received many honors for his legal and scientific work. He joined the Royal Institution in 1835 and in 1844 was one of its Vice-Presidents. He was one of the eleven founding members of the Swansea Literary and Philosophical Society (1835). He was elected President of the 1866 Nottingham meeting of British Association for the Advancement of Science; he was knighted in 1872 and in 1879 awarded an honorary degree by Cambridge University. He was also on a Royal Commission on patent law and on the Metropolitan Commission of Sewers.

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[1]For Life and Career, See Scott, 1970-1980; Morus, 2004

In December 1838, Grove sent a letter to the editors of the Philosophical Magazine Journal, describing a new voltaic cell much more efficient and cheap that the one invented by John Frederic Daniell in 1836 (Grove, 1838). The Daniell cell consisted of two cups separated by unglazed earthenware; one cup contained a cupric sulfate solution in contact with a copper plate, the other, sulfuric acid containing a zinc electrode; this arrangement produced an electromotive force (emf) of 1.1 volts. Grove cell was built of two vessels separated by a porous wall; one vessel contained a zinc electrode immersed in dilute sulfuric acid, the other a platinum electrode immersed in concentrated nitric acid (or a mixture of nitric and sulfuric acids), giving an emf of nearly two volts. Grove also communicated his findings to the Académie des Sciences in Paris, which Antoine Henri Becquerel (1852-1908; 1903 Nobel Prize for Physics) read in its session of April 15, 1839 (Grove, 1839a). The publications were followed by a large number of others describing new electrochemical findings, improvements of the original cell, molecular composition and decomposition (Grove, 1839e, 1843b, 1844a), the electrochemical decomposition and synthesis of water (Grove, 1839b, 1843ce, 1846a, 1847bc, 1853), discovery of polarization (Grove, 1839d), electrical conductivity by flames (Grove, 1854), today's fuel cell (Grove, 1842b, 1845a), Daguerreotype plates (Grove, 1843d), photography (Grove, 1844b), voltaic action on phosphorus, sulfur, and hydrocarbons (Grove, 1845c), of black bands (striae) in electrical breakdown (Grove, 1858, 1858-1862).

2. Scientific contribution

Grove wrote near seventy papers and books, mostly in the area of electrochemistry, and a few about astronomy, the conversion of energy, and the impossibility of perpetual motion. Here we describe some of the most significant ones.

2.1 Voltaic cells

In December 1838, Grove sent a letter to the editors of the Philosophical Magazine Journal, describing a new voltaic combination. In the opening statement he wrote that on hearing that porous porcelain could be employed to prevent the mutual precipitation in voltaic combinations, he thought about the possibility of replacing one the plates of metals usually employed by precipitation upon another, from a metallic solution (Grove, 1838). Based on this idea he built a trough divided into several non-communicated portions; each portion was covered alternatively by iron and unglazed porcelain. A cupric sulfate solution diluted with sulfuric acid was poured into the alternate cells. As a result, a very active voltaic series was obtained by the precipitation of copper on one surface face of the iron. Contacting one end of the series with a wire and the other with one hand resulted in the prompt decomposition of the water; this action was found to continue for about three without the need of adding acid or the sulfate. According to Grove, this new battery was very cheap because of the metals employed and the easy of their electrical connection (Grove, 1838).

Grove promptly communicated his findings to the Académie des Sciences in Paris, with an explanation of additional phenomena, which Antoine Henri Becquerel (1852-1908; 1903 Nobel Prize for Physics) read in its session of April 15, 1839 (Grove, 1839a). Grove referred to the powerful combination, which would be caused by the combination of four elements instead of three. He explained that he could now present an explanation of the well-known phenomenon of gold dissolution by aqua regia, but not by nitric acid or HCl alone. He cemented a bowl of tobacco pipe (porous) filled with nitric acid, into the bottom of a wine glass filled with aqueous HCl. He then submerged two strips of gold leaf into the HCl and noticed that the gold remained bright after one hour. With a one end of a gold wire he touched

the nitric acid, and with the other end, one of the gold leaf strips, the result was surprising: the strip instantly dissolved (Grove, 1839a).

According to Grove, as soon as the electric current was established, the hydrogen of HCl combined with the oxygen of nitric acid and the chlorine attacked the gold. A galvanometer indicated that in this sequence of events, gold represented the zinc electrode of an ordinary voltaic cell. This result suggested him to repeat the experience this time using amalgamated zinc instead of gold, platinum as the second electrode and making the contact with a platinum wire instead of one of gold: this new arrangement readily decomposed acidulated water. A similar powerful action was found when replacing KOH for HCl, or sulfuric acid diluted in four times its volume of water. Grove also colored the nitric acid with a small amount of litmus and noticed that HCl did not change its color. Grove concluded that the reaction of the two acids through the membrane, with the help of the electric current, resulted in their decomposition. Since platinum caused the maximum deviation of the galvanometer, he suggested that the most potent combination would take place when using the two acids and electrodes of platinum and zinc. The experimental results proved this assumption to be true. Similar results were obtained when using concentrated nitric acid instead of HCl, with the additional advantage of a lower cost (Grove, 1839a).

Grove remarked that submerging the positive electrode in diluted sulfuric acid and the negative one in concentrated nitric acid provided oxygen. If chlorine was needed, then aqueous HCl substituted sulfuric acid. A small battery, of circular shape (10.2 cm diameter and 3.2 cm high) consisting of seven wine glasses and seven pipe bowls, provided 16.4 cm^3 of mixed gases in two minutes. Grove also wrote, that with all other things kept equal, his battery was 16 times more powerful than John Frederic Daniell's (1790-1845) battery, and several times cheaper. The model he constructed cost £2 2s (Grove, 1839a).

Grove also reported his findings to the British Association for the Advancement of Science, during its ninth meeting held at Birmingham, in August 1839 (Grove, 1840a). There he remarked that during operation of his battery the successive loss of oxygen by the nitric acid led to its color changing from yellow, to green, and eventually to become colorless. Under the latter condition, hydrogen evolved now from the platinum, the battery became weaker, and its action became erratic. In the common zinc and copper battery of Daniell, "the resulting power was as the affinity of the anion of the electrolyte for zinc, plus the minus its affinity for copper. In the constant battery it is as the affinity of the anion for zinc plus that of oxygen for hydrogen, minus that of oxygen for copper." In Grove's battery "the resulting power was as the affinity of the anion for zinc, plus that of oxygen for hydrogen, minus that of oxygen for nitrogen; nitric acid being much more readily decomposed that cupric sulfate, the resistance is weakened and the power increased, and no hydrogen is evolved from the negative metal; there is no precipitation upon it, and consequently no counteraction" (Grove, 1840a). Grove republished this report in order to correct some errors that have been reported in several periodicals (Grove, 1839f).

In 1839 Grove presented two additional papers to the Académie des Sciences, showing (and explaining) why water could conduct electricity only when decomposed (Grove, 1839b). In another paper published the same year, Grove discussed the known experimental fact that common zinc of commerce, when immersed in water acidulated by sulfuric acid, phosphoric acid, or HCl, rapidly dissolved releasing a large quantity of hydrogen, while the same metal amalgamated was inactive unless touched by another metal submerged in the same solution. In the latter situation, the same amount of hydrogen was

released while the metal dissolved (Grove, 1839c). An accidental result led Grove to realize that mercury, which acted on acidulated water as the negative electrode of a voltaic cell, had the property of amalgamating platinum and iron (even steel), and that "strips of these metals, which had served as negative electrodes, were instantly and completely amalgamated by immersion in pure mercury." Grove eliminated the acid particles present in mercury, which had been used as negative electrode, and found it to give *an alkaline reaction*. He realized that the increased power of amalgamation originated from mercury amalgamating with an alkaline metal. Since Humphry Davy had already shown that mercury containing small amounts of an alkali metal was highly electro-positive, then the inaction of amalgamated zinc was simply due to a *polarization* effect. As a consequence of this phenomenon, the cations of the electrolyte instead of precipitating on the surface of the negative metal, "they combined with it, rendered it positive, and nullified the current" (Grove, 1839c). To prove his point, Grove carried a series of four experiments with copper and platinum electrodes, partially or completely amalgamated, submerged in water acidulated with sulfuric or phosphoric acids, and observed the intensity and duration of the release of gas. For example, he amalgamated half the surface of a strip of copper and immersed it in acidulated water, together with a strip of zinc. Bringing the strips into contact resulted in a rapid evolution of gas from the non-amalgamated part of the copper, while only a few bubbles of gas appeared in the amalgamated portion. The result of all the experiments indicated that due to polarization, the amalgamated metallic impurities present in zinc, which originally behaved as negative elements, had now become positive as the zinc particles; the whole behaved as pure zinc, and stopped the electrical phenomena (Grove, 1839c).

Additional experiments showed that mercury under the action of a voltaic current was able to absorb a small quantity of hydrogen and release it as soon as the electric connection was halted (Grove, 1839c).

Grove performed in front of the Royal Institution some experiments to illustrate the phenomenon of polarization, arranging his batteries in two forms, one to illustrate the intensity of the phenomenon, and the other the quantity of the same. The last one consisted of 40 pairs of four 25.8 cm^2 platinum plates, with double amalgamated zinc plates with porous cells and porcelain troughs arranged in series of eight 5 pairs of plates. The platinum electrode was submerged in nitric acid and the amalgamated zinc in diluted sulfuric acid. This arrangement was shown to produce 1.8 liters of gases per minute, per decomposition of water; the heat effect was strong enough of melt an iron wire 0.13 cm in diameter and 25 cm long, and to turn white hot a thick platinum foil, 30.5 cm long and 2.5 cm wide (Grove, 1839d).

In another paper, Grove showed that the porous membrane (diaphragm) "was of more practical importance in voltaic combinations than as a simple media for preventing cross precipitation. For the optimum operation of the cell, the generating metal should be selected as the one having the strongest affinity for the anion in contact with it, while the other solution should be most readily decomposable by the cation and did not cause a precipitate upon which its own anion would readily react" In a postscript to this publication he reported the result an experiment he had carried to illustrate the combination of oxygen and hydrogen gases into water by platinum. He ended the paper saying that he "hoped, by repeating this experiment in series, to effect decomposition of water by means of its composition" (Grove, 1839e).

The discovery of Grove's cell led to a hot discussion with Daniell who claimed that Grove had taken his ideas to develop his battery (e.g., Grove, 1842a, 1843f).

2.1 Voltage disruptive discharge

In 1840 Grove sent a letter to his friend Christian Friedrich Schönbein (1799-1868) informing him that with a high-intensity battery, composed of 36 pairs of platinum foil and zinc, 6.5 cm^2, he had been able to generate a one-cm long luminous arc between two carbon points. Grove believed that this effect was due to the medium traversed by the electrical spark, because the spark was brighter the more oxidizable and volatile was the metal that emitted it. Thus, zinc, mercury, and the alkaline metals gave a bright spark, and if the positive pole was connected to zinc and the negative to platinum, the spark was brighter than in the opposite arrangement. In addition, the spark generated between two platinum points in oxygen resulted in a contraction of the volume of the gas, proving that the platinum heated by the voltaic current was slightly liable to oxidation. This result did not take place when the discharge occurred through a hydrogen atmosphere (Grove, 1840b).

Grove went on to prove that that the quantity of matter transported or liberated in the voltaic arc corresponded to a current of definite intensity. To do so he repeated the experiment using a positive point of zinc and a negative point of platinum submerged in a graduated vase full of air containing an excess of oxygen. The results of forty experiments indicated that the quantity of oxygen absorbed by the deflagration of zinc was in the ratio 1:1.17 to the quantity disengaged during the same length of time in a voltmeter located within the circuit (Grove, 1840b).

In a short comment to this letter, Schönbein wrote that Grove's results seemed to prove that the current transmission from one pole to the other occurred by means of a chemical reaction, and that the chemical decomposition that took place in the battery and the current transmission were absolutely dependent one on the other (Grove, 1840b).

In a following paper, Grove added more details. He reported that the small battery employed required one pound of nitric acid and one pound of sulfuric acid, so that at the expense of one shilling he could operate it for 8 to 9 hours, without fresh charge. If the disruptive discharge was carried on in dry hydrogen, in nitrogen, or in vacuum, no difference was observed between the light and heat, whether the metals were liable or not to oxidation, or whether the oxidizable metal constituted the positive or negative electrode. The disruptive discharge was not affected by the volatility, the state of aggregation, or tenacity of the metal or conducting body. As examples, he mentioned that iron gave a brilliant arc in air or oxygen, a feeble one in hydrogen or vacuum, and mercury gave a tolerable brilliant spark in hydrogen, nitrogen, or vacuum, similar to the one it gave in air. There were several conditions for producing a brilliant spark in an oxidizing medium: oxidability, volatility, and looseness of aggregation. Grove listed thirteen metals in respect to the length and brilliancy of the arc they produced between two points of the same metal in atmospheric air: potassium, sodium, zinc, mercury, iron, tin, lead, antimony, bismuth, copper, silver, gold, and platinum. He also speculated that "the quantity of matter detached by the voltaic disruptive discharge was definite for a definite current, or bore a direct equivalent relation to the quantity electrolyzed in the liquid portions of the same circuit" (Grove, 1840c).

2.2 Electro-Nitrogurets[2]

In 1808 Thomas Johann Seebeck (1770-1831) described the amalgam formed by electrolyzing solutions of ammonia or its salts, with mercury at the cathode (Seebeck, 1808). This amalgam was thought by many to be the link between the metals and permanent gases. Grove decided to conduct additional experiments on this substance to try to connect it with the

[2]An old name of a nitrogen compound not containing oxygen. Ammonia, for example, was a nitroguret of hydrogen.

decomposition of ammonia flowing over heated metals, and to explain some anomalies in these effects (Grove, 1841). He froze the amalgam with the help of solid CO_2 and ether and noticed that the process was accompanied by a slightly contraction and no gas liberation. The solid was easily broken, and the fracture had little or no metallic luster. Upon thawing it gave out a mixture of ammonia and nitrogen. He then tried to obtain a solid ammonium compound by alloying the amalgam with Newton's fusible metal (an alloy containing 50 parts of bismuth, 31.25 of lead and 18.75 of tin). The resulting alloy was solid at room temperature and fused at 30^0C. Next, he used the ammonia amalgam as the cathode of a voltaic cell in a solution of ammonia chloride slightly heated. To his satisfaction he noted that it remained completed unchanged, releasing gases as any other solid electrode. This result suggested him that electrolysis of an ammonium salt in a cell having as an anode an oxidizable metal might result in the solution of the latter and its deposition at the cathode in conjunction with nascent nitrogen ad hydrogen, leading to the formation of a permanent compound (Grove, 1841).

The experiments made in this manner with lead, iron, tin, and platinum was unsuccessful, but those with zinc, cadmium, and copper, were quite successful. A floating spongy mass, which appeared to be formed of a cluster of foils collected at the cathode. This mass was washed with distilled water, dried over a sand bath, and then analyzed by heating in a tube retort. Three hundred and twenty-four mg of the zinc compound (density 4.6) gave 11.96 cm^3 of a gas mixture composed of nitrogen with one-fourth hydrogen. The same quantity of the cadmium compound (density 4.8) gave 3.39 cm^3 of only nitrogen, while the copper compound (density 5.9) gave 1.75 cm^3 of pure nitrogen. A mixed solution of gold chloride and ammonium chloride, electrolyzed with platinum electrodes, gave a black powder having specific gravity 10.3. Three hundred and twenty-four mg of the compound gave only 0.82 cm^3 of gas (Grove, 1841).

According to Grove, the strong analogy in character and the manner of formation between these compounds and that of the ammonia amalgam were strong evidence of being of similar constitution. He believed that the amalgam was a chemical combination of mercury, nitrogen, and hydrogen, and more probably, of mercury and nitrogen, swelled with hydrogen, and that the non-permanence of the substance was due to the mobility of the mercury. Inspection of the available on the subject indicated that Daniell had briefly noticed a deposit, somewhat analogous to those described above, which was found upon the negative plate of his constant battery, when this was charged on the zinc side with ammonium chloride (Grove, 1841).

2.3 Fuel cell

In a previous paper Grove wrote: "I hope…to effect the decomposition of water by means of its composition" (Grove, 1839f). In 1842 he converted this dream into reality using the available information that hydrogen and oxygen reacted in the presence of platinum sponge, and that the surface of a platinum electrode may be "platinized" with the help of nitric acid[3] (Smee, 1840, Grove 1842b). The experimental arrangement consisted of a series of 50 pairs of platinized platinum foil enclosed in tubes partially filled alternately with oxygen and hydrogen, and charged with sulfuric acid of specific gravity 1.2. Operation of the battery led to the following effects: (1) a shock was given, which could be felt by five persons joining hands, and which when taken by a single person was painful; (2) the needle of a galvanometer marked 60^0; with one person in the circuit it decreased to 40^0; (3) a brilliant park visible in broad daylight was given between charcoal points; (4) potassium iodide, HCl, and

[3] This treatment removes the film of air that prevents wetting of the surface.

water acidulated with sulfuric acid were strongly decomposed. The gases from the decomposed water could be collected and detonated; (5) at least twenty-six pairs were needed to decompose water, and four for decomposing potassium iodide; (6) exchanging the gases produced the same powerful effects and the direction of current was reversed; (7) no effect was observed when the tubes were charged with atmospheric air, with CO_2 and nitrogen, or with oxygen and nitrogen, respectively (Grove, 1842b).

Grove remarked that this battery was "peculiar in having the current generated by gases, and by the synthesis of an equal but opposite kind at both anode and cathode" and that "it was…more perfect than any other form…It established that gases in combining and acquiring a liquid form evolved sufficient force to decompose a similar liquid and cause it to acquire a gaseous form" (Grove, 1842). Again, Grove reported his findings to the Académie des Sciences (Grove, 1843a).

Grove's work on the battery earned him the 1847 Royal Medal from the Royal Society.

Fuel cells remained a curiosity for many years until Ludwig Mond (1839-1909) and C. Langer pushed the idea a long step forward by considering the possibility of building a dry battery in which the producer gas took the place of hydrogen. In their new cell the strips of platinum foil used by Grove, partly immersed in dilute sulfuric acid, were replaced by a number of elements formed of a porous diaphragm of a non-conducting material, such as plaster of Paris, earthenware, asbestos, and pasteboard, impregnated with dilute sulfuric acid. Thus, the cell became practically a dry battery. In their own words: "we have only succeeded by using an electrolyte in a quasi-solid form, viz., soaked up by a porous non-conducting material, in a similar way as has been done in the so-called dry piles and batteries" (Mond and Langer, 1888ab; Mond, 1889).

Mond calculated that if the same amount of hydrogen adsorbed in the battery was burned in a steam boiler, the steam generated converted into mechanical motion and then into electricity, the yield of electricity would in the most favorable case not exceed 8% of the energy in the gas (for the steam engines available then). He expressed his hope that one day this kind of battery would enable to perform chemical operations by electricity on the largest scale, and press this potent power into the service of the chemical industries (Mond, 1889).

2.4 Electro-chemical polarity of gases

The invention of the safety lamp (a flame arrester) by Humphry Davy (Davy, 1816) had substantially reduced the number of accidents in coalmines caused by the explosion of mixtures of inflammable gases and atmospheric air. The few accidents that still occurred were assumed to carelessness of the workmen in the use of this lamp. In 1845 Jean-Baptiste Boussingault (1802-1887) and Auguste-Arthur de la Rive (1801-1873) suggested improving the Davy lamp by employing voltaic disruptive discharge as the source of the light (Boussingault, 1845; De la Rive, 1845). In order to avoid some practical problems in the construction of the lamps suggested by Boussingault and de la Rive, Grove recommended using the voltaic ignition of a platinum wire (ignited by his nitric acid battery) instead of disruptive discharge. In his lamp, ignition was effected by a platinum wire coil, ignited as close as possible to its fusion point, in a closed vessel containing atmospheric air, hydrogen, CO_2, oxygen, or nitrogen (Grove, 1845b). Test of this idea showed that hydrogen produced no visible action of the eye, even in the dark (that is, hydrogen reduced the intensity of ignition of a platinum wire so as to make it apparently extinguished); CO_2 a cherry-red effect by daylight; and oxygen, nitrogen and atmospheric air, an incandescent effect by daylight (the observant

reader will note the relation of Grove's lamp to the modern light bulb).

In two additional papers, Grove extended the above experiments to gases such as ethylene, CO, compressed air, rarified air, and chlorine. He also enclosed a voltmeter in the circuit to measure the amount of gas released, and positioned a thermometer at a given distance to estimate the radiated heat. His results indicated that the *radiated* heat was in a direct ratio with the *visible* heat, and the amount of gas in some inverse ratio to the heat developed in the wire (Grove, 1847ab). Grove believed that although the phenomenon observed was apparently abnormal, it could possibly be explained by gas properties such the specific heat, electrical conductivity, and viscosity (Grove, 1849). To do so, he connected two glass tubes (one filled with oxygen and the other with hydrogen), closed at each end with corks penetrated with copper wires, with a coil of fine platinum wire. Each tube was immersed in identical separate vessels, filled with tree ounces of water, initially at 15.6^0C. Connecting the remaining copper ends with a nitric acid battery of eight cells could close the circuit. On doing so, Grove noticed that the wire in the tube containing oxygen become heated to red heat and the temperature of the water rose to 27.2^0C, while that in the hydrogen tube, did not show a visible effect and the temperature of the water increased to 21.1^0C. Similar results were obtained when the oxygen was replaced by nitrogen, CO_2, CO, or ethylene (Grove, 1849). In an additional set of experiments the gases were replaced by a variety of liquids: one tube contained water and the other turpentine, carbon sulfide, naphtha, alcohol sp. gravity 0.84, or ether. Again, the temperature of both liquids increased, in an amount depending on the their nature.

The results proved that the cooling effect of the gases on the ignited wires was not connected in any clear ratio to their specific gravities, specific heats, or electrical conductivity. Grove believed that the phenomenon was "mainly due to a molecular action at the surfaces of the ignited body and of the gas" (Grove, 1849).

In a following paper Grove wrote that his experiments had shown that hydrogen or atmospheric air intensively heated showed no sign of conducting "voltaic electricity" even when part of a circuit containing a highly powerful battery (Grove, 1852). He also pointed out that Gassiot had found that "the static effects of effects of tension produced by a voltaic battery were in some direct ratio with the chemical energies of the substances of which the battery was composed" (Gassiot, 1844). According to Grove, there was "no proof that the polarization of he dielectric was or could be of chemical nature, and that assuming a dielectric to be composed of two substances having antagonistic chemical relations (i.e. oxygen and hydrogen), the particles of the oxygen would be determined in one direction, and those of hydrogen in the other". Since the heat effects developed in the voltaic arc were strong enough to mask the proper electrical effect (and even destroy the terminals), Grove decided to conduct additional experiments using a Ruhmkorff coil. He described the results of sixteen experiments done under different conditions (Grove's paper gives a detailed figure and description of the circuit he built for his purposes). He indicated that the following one was the "most important and fundamental result": "On the plate of a good air pump was placed a silvered copper plate, such as is ordinarily used for Daguerreotypes, the polished surface being uppermost. A receiver with a rod passing through a collar of leathers was used, and to the lower extremity of this rod was affixed a steel needle which could thus be brought to any required distance from the silver surface. A vessel containing fused potash was placed in the receiver, and a bladder of hydrogen gas was attached to a stopcock, another orifice enabling the operator to pass atmospheric air into the receiver in such quantities as might be required. A vacuum being

made, hydrogen gas and air were allowed to enter the receiver in very small quantities so as to form an attenuated atmosphere of the mixed gases…Two small cells of the nitric acid battery were used to excite the coil machine and the discharge from the secondary coil was taken between the steel point and the silver plate; the distance between these was generally 0.25 cm…When the plate formed the *positive* terminal, a dark circular stain of oxide rapidly formed on the silver, presenting in succession yellow, orange, and blue tints, very similar to the successive tints given by iodizing in the ordinary manner a Daguerreotype plate. Upon the poles being reversed, and the plate made negative, this spot was entirely removed, and the plate became perfectly clean, leaving, however, a dark polished spot, occasioned by molecular disintegration, and therefore distinguished from the remainder of the plate". Grove repeated this experiment several times and found that the experiment always succeeded when using with hydrogen to air proportions from 1:1 to 1:2.5 (Grove, 1852).

Additional similar experiments were carried under vacuum, in a hydrogen atmosphere, of air enriched in nitrogen, of almost pure nitrogen, of a mixture of hydrogen and oxygen in the proportion to form water as well as other ratios, replacing the steel needle with copper, silver, or platinum wire, replacing the silver plates by plates of bismuth, lead, tin, zinc, copper, iron, an aluminum, etc. etc. (Grove, 1852).

Grove explained his results as follows: Since the discharges were successive and not continuous, the gaseous media became polarized before to each discharge. The polarization had a chemical and not a physical nature; the oxygen or *anion* was driven to the positive terminal (anode), and the hydrogen or *cation* to the negative one (cathode). Immediately before the discharge there would then be a molecule or superficial layer of oxygen, or of *electro-negative* molecules, in contact with the anode, and a similar layer of nitrogen or *electro-positive* molecules in contact with the cathode. In other words, the electrodes in gas would be polarized in the same manner as the electrodes in liquids are. The following discharge would ignite the superficial ends of metal or oxide, or chemical excited. The anode would, consequently oxidize and the cathode (if an oxide) be reduced (Grove, 1852).

In a postscript to the paper Grove remarked that in a well-exhausted receiver containing a small piece of phosphorus, "the discharge was throughout its course *striated* by transverse non-luminous bands, presenting a beautiful effect, and a yellow deposit...[of] allotropic phosphorus was deposited on the plate of the air pump…" (Grove, 1852).

Grove discussed the striae phenomena in a communication to the British Association for the Advancement of Science, published in 1858 (Grove, 1858). His first belief was that the black bands were probably connected with the interruptions of the contact breaker located in his experimental apparatus. He noticed that when the arm of the contact breaker was positioned over a slight spring, the bands became narrower. In this paper he described how he modified his initial setup so as to be able to produce a single breach of contact, without fusion of the metals at the contact point (which occasioned a double or triple disruption). In this situation two classes of sparks were noticed in the air, a thin blue one, heard as a single sharp sound, and a burred yellow one, with a sound not so clear and metallic. He was thus able to make at will discharges through gases under vacuum, presenting striæ or not. His results convinced him that the bands were due to the "mechanical interference or reciprocal impulsions of two or more discharges, or rather of the medium affected by them" (Grove, 1858. 1862).

2.5 Correlation of Physical Forces

The results of Grove's many experiments on different phenomena associated with electricity

and electrochemistry led him to develop a universal interpretation of the different aspects of energy and their inter conversion (Grove, 1846b). This work may be considered a prelude to the first law of thermodynamics; in it Grove denies the possibility of perpetual motion and shows that energy (forces) in its different faces, are expressions of the same physical concept (energy): Energy cannot be created or annihilated.

The following paragraphs are taken from this memoir to show his basic ideas and tenets.

> "Physical science treats of matter…and its affection, namely attraction, motion, heat, light, electricity, magnetism, and chemical affinity. When these react upon matter, they constitute Forces. The present tendency of theory tends to led to the opinion that all these affections are resolvable into one, namely Motion; however, should the theories on these subjects be ultimately generalized as to become laws, they cannot avoid the necessity for retaining different names for these different affection; or so they would be called, different Modes of Motion…Œrsted proved that electricity and magnetism are two forces, which act upon each other, not in straight line as all forces do, but in a rectangular direction…[This] discovery, by which electricity was made a source of magnetism, soon led philosophers to seek the converse effect, that is, to educe electricity from a permanent magnet. Had these experimentalist succeeded in their expectations of making a stationary magnet a source of electric currents, they would have realized the ancient notions of perpetual motion; they would have changed statics into dynamics, they would have produced power without expenditure. In other words, they would have become creators" (Grove, 1846b).
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> "Light, heat, electricity, magnetism, motion, and chemical affinity are all convertible electricity, electricity magnetism, and so of the rest. Cause and effect, therefore, in their abstract relation to these forces, are words solely of convenience; we are material affections; assuming either as the cause, one of the others will be the effect; thus heat may be said to produce electricity, electricity to produce heat; magnetism to produce totally unacquainted with the ultimate generating power of each and all of them, and probably shall ever remain so; we can only ascertain the normæ of their action; we must humbly refer their causation to one omnipresent influence, and content ourselves with studying their effects and developing by experiment their mutual relations" (Grove, 1846b).
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> "The theory that the so-called imponderables are affections of ordinary matter, that they are resolvable into motion, that they are to be regarded in their action on matter as forces, and not as specific entities, and that they are capable of mutual reaction, thence alternatively acting as cause and effect, has not at this time been publicly advanced" (Grove, 1846b).
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> "The relations of electricity and magnetism afford us a very instructive example of the belief in secondary causation. Prior to [Faraday's discovery of] magneto-electricity, electricity and magnetism were believed by the highest authorities to stand in the relation of cause and effect, i.e. electricity was regarded as the cause and magnetism as the effect; and where magnets existed without any apparent electrical currents to cause their magnetism, hypothetical currents were supposed for the purpose of carrying out the causative view, but magnetism may now be said with equal truth to be the cause of electricity, and electrical currents may be referred to hypothetical magnetic lines. If therefore electricity causes magnetism and magnetism causes electricity, why then electricity cause electricity, which becomes…a *reduction ad absurdum* of the doctrine" (Grove, 1846b).
>
> "The position which I seek…is that the various affections of matter which constitute the main objects of experimental physics, viz., heat, light,

> electricity, magnetism, chemical affinity, and motion, are all correlative or have a reciprocal dependence, that neither taken abstractedly, can be said to be the essential cause of the other, but that either may produce or be convertible into any of the others…it being an irresistible inference from observed phenomena that a force cannot originate otherwise than by devolution from some pre-existing force or forces. The term force…may be defined as that which produces or resists motion…I use the term force …as meaning that active principle inseparable from matter, which is supposed to induce its various changes" (Grove, 1846b).

> "Nothing repeats itself because nothing can be place again in the same condition: the past is irrevocable" (Grove, 1846b).

Grove went on to discuss the terms motion, heat, electricity, light, magnetism, chemical affinity, and other modes of force, such as catalysis, gravitation, inertia, and aggregation.

Before discussing heat, Grove explained that he would use the terms particles or molecules not in the sense of the atomist, "but for the purpose of distinguishing the action of indefinitely minute physical elements of matter from that of masses having a sensible magnitude. The effects of heat is simply an expansion de matter acted upon, and that the matter so expanded has the power by its own contraction of communicating expansion to all bodies in contiguity with it…Heat thus viewed is motion and this molecular motion we may readily change into the motion of masses, or motion in its most ordinary and palpable form" (Grove gives as an example the steam engine)…To produce continuous motion there must be an alternate action of heat and cold…There are some experiments which tend to prove that a repulsive action between separate masses is produced by heat…Water, fuse bismuth…expand as they approach very near to the freezing or solidifying point. The most probable explanation of these exceptions is that at the point of maximum density the molecules of these bodies assume a polar or crystalline condition; that by the particles being thus arranged in linear direction…interstitial spaces are left, containing matter of less density so that the specific density of the whole mass is diminished…Many of the phenomena of heat are involved in much mystery, particularly those connected specific heat…which appear to depend in some way hitherto inexplicable upon the molecular constitution of different bodies…When we examine substances of very different physical characters, we find that their specific heats have no relation to their density or rate of expansion by heat; [this] difference…must depend upon their intimate molecular constitution, in a matter accounted by no theory of heat hitherto proposed…When the structure of a substance is not homogeneous, we have a change in the conduction of different parts dependent upon structure…Crystals conduct heat differently in different directions with reference to the axis of symmetry, but definitely in definite directions…radiant heat is absorbed in different degrees, according as its direction is parallel or perpendicular to the axis of a crystal" (Grove, 1846b).

> "Heat having been shown to be a force capable of producing motion, and motion to be capable of producing the other modes of force, it necessarily follows that heat is capable of producing them. [It has been shown that heat will] immediately produce electricity (Grove quotes the experiments of Seebeck). Production of light by heat is a phenomenon familiar to everyone. "Heat and light appear to be modifications of the same force than distinct forces mutually dependent…in certain cases heat appears to become partially converted into light, by changing the matter affected by heat. Thus gas may be heated to a very high point without producing light, or producing it to a very slight degree, but the introduction of solid matter (platinum, for example), instantly produces light" (Grove, 1846b).

"Heat directly affects and modifies both the magnet and chemical compounds; the union of certain chemical substances is induced by heat; in other cases this union is facilitated by heat, and in many cases it is weakened or antagonized" (Grove, 1846b).

"The argument may be stated that by no mechanical appliance or difference of material acted on can a given source of heat be made to produce more heat that it originally possessed, and that if all is converted into mechanical power, an excess cannot be supposed, for that could be converted into a surplus of heat and be a creation of force, and a deficit cannot be supposed, for that would be annihilation of force" (Grove, 1846b).

"Of absolute rest Nature gives as no evidence; all matter, as far as we can ascertain, is ever in movement, not merely in masses…but also molecularly, or through its most intimate structure. Thus every alteration of temperature produces a molecular change throughout the whole substance being heated or cooled; slow chemical or electrical actions, actions of light or invisible radiant forces are always at play, so that as a fact we cannot predicate that any portion of matter is absolutely at rest. Supposing, however, that motion is not an indispensable function of matter, but that matter can be at rest, matter at rest would never of itself cease to be at rest, it would not move unless impelled to such motion by some other moving body, which has moved…A body once in motion will continue so for ever in the same direction and with the same velocity, unless impeded by some other body, or affected by some other force than that which originally impelled it…I submit that force cannot be annihilated but is merely subdivided or altered in direction or character…It may be asked, what become of force when motion is arrested or impeded by the countermotion of another body? This is generally believed to produce rest or entire destruction of motion and subsequent annihilation of force. So indeed it may, as regards the motion of masses, but a new force, or new character of force, now ensues, the exponent of which instead of visible motion, is heat. I…regard the heat, which results from friction on percussion, as a continuation of the force which was previously associated with the moving body…ceasing to exist as…motion, continues to exist as heat…Friction is impeded motion. The greater the impediment…the greater is the resulting heat" (Grove, 1846b).

"Commencing with electricity as an initiating force, we get motion directly produced by it in various forms, for instance, in the attraction and repulsion of bodies…It would follow, from the reasoning in this essay, that when electricity perform any mechanical work, which does not return to the machine, electrical power is lost…Electricity directly produces heat, as shown in the ignited wire, the electric spark, and the voltaic arc…In the phenomenon of electrical ignition…the relation of force and resistance, and the correlative character of the two forces, electricity and heat, are strikingly demonstrated…In the phenomenon of the voltaic arc…electricity directly produces light of the greatest known intensity. It directly produces magnetism, as shown by Oersted who distinctly proved the connection between electricity and magnetism. These two forces act upon each other, not in straight lines, as all other known forces do, but in a rectangular direction…Electricity produce chemical affinity and by its agency we are enabled to obtain effects of analysis or synthesis…" (Grove, 1846b).

"Light is, perhaps, that mode of force the reciprocal relations of which with the others have been the least traced out…Certain chemical compounds (i.e. from silver)…have the property of suffering decomposition when exposed to light…Light would seem directly to produce heat in the phenomena of what is termed absorption of light; in these we find that heat is developed in the some

> proportion to the disappearance of light…Wherever light is absorbed, then heat takes its place…affording an instance of the conversion of light into heat, and the fact that the force of light is not absorbed or annihilated, but merely changed in character…" (Grove, 1846b).

> "Magnetism…will produce electricity but with this peculiarity – that in itself is static, and therefore, to produce a dynamic force, motion must be superadded to it; it is in fact, directive, not motive, altering the direction of the forces, but not, in strictness, initiating them" (Grove, 1846b).

> "Chemical affinity is the force by which dissimilar bodies tend to unite and form compounds differing in general in character from their constituents…By chemical affinity we can directly produce electricity…Volta related the forces of chemistry and electricity…I have shown that the flame of the common blowpipe gives rise to a very marked electrical current, capable not only of affecting the galvanometer, but of producing chemical decomposition…Heat is an immediate product of chemical affinity. I know of no exception to the general proposition that all bodies in chemical combining produce heat…Light is directly produced by chemical action, as in the flash of gunpowder, the burning of phosphorus…Chemical action produces magnetism whenever it is thrown in a definite direction, as in the phenomenon of electrolysis…The gas voltaic cell [is a simple] instance of the direct conversion o magnetism by chemical synthesis…a magnet adjacent to this line of action is deflected and places itself at right angles to it" (Grove, 1846b).

Grove mentioned catalysis as another mode of force and described it as the chemical action induced by the mere presence of a foreign body. "The force so developed by catalysis may be converted into a voltaic form thus: in a single pair of the gas battery…one portion of a strip of platinum is immersed in a tube of oxygen, the other in one of hydrogen, both the gases and the extremities of the platinum wire being connected by water or other electrolyte; a voltaic combination is thus formed and electricity, heat, light, magnetism, and motion, produced at the will of the experimenter" (Grove, 1846b).

In his concluding remarks, Grove wrote:

> "I have gone through the affection of matter for which distinct names have been given…that other forces may be detected, differing as much from them as they differ from each other, is highly probable, and that when discovered…they will be found to be related *inter se*, and to these forces, as these are to each other…The greatest problem which remains to be solved, in regard to the correlation of physical forces, is the establishment of their equivalents of power, or their measurable relation to a given standard." Grove went on to discuss the term "perpetual motion" and remarked that it was strange that its impossibility was not self-evident. He also refers to the impossibility of converting one kind of energy completely into another: "The inevitable dissipation or throwing off a potion of the initial force presents a great experimental difficulty in the way of establishing the equivalents of the various natural forces" (Grove, 1846b).

Grove substantiated most of the above statements with a large variety of experimental examples taken from different physical areas.

Grove closed his memoir saying that

> "in all phenomena the more closely they are investigated, the more we are convinced that, humanly speaking, neither matter nor force can be created or annihilated, and that an essential cause is unattainable. – Causation is the will, Creation, the act, of God" (Grove, 1846b).

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