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AN EARLY PHYSICAL CHEMIST—M. W. LOMONOSSOFF.[1]

BY ALEXANDER SMITH.

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At the present day, it seldom happens that due credit is not given to each chemist for any new facts which he may add to the sum of chemical knowledge and, conversely, it is usually an easy matter to attach to any given fact the name of the investigator who first discovered it. For reasons which, in part, at least, are obvious, these conditions are not always so easy to fulfil in the case of the fathers of the science. It is certain, at all events, that frequently recognition has here been long delayed and, even where the most fundamental facts are concerned, the determination of the parentage has had repeatedly to be revised.

At the very start, there is the difficulty in settling what constitutes *discovery*. Scheele's preparation of oxygen undoubtedly took place a year or two before Priestley's, but his publication of the results was delayed until three years after Priestley's, and priority in discovery is generally held to require priority in publication.

Again, Paracelsus obtained what is now known as hydrogen by the action of iron filings upon vinegar, but Cavendish defined the substance by its properties, and so the discovery dates from 1766. Liebig prepared bromine, but set the sample aside, believing it to be a chloride of iodine, and Balard, who prepared the substance later and recognized it to be a new halogen, became the discoverer. Similarly, a hundred years before Priestley's time, Borch (1678) prepared what is now known as oxygen in large quantities by heating saltpeter, but he failed to ascertain any of its properties; and again, forty-five years before Priestley's experiment, Hales collected the gas from the same source over water (the first record

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[1] Presidential Address delivered before the American Chemical Society at Washington, December 28, 1911.

of any attempt to collect a gas in this way) and obtained, by measurement, 97% of the theoretical amount. But Priestley, on Aug. 1, 1774, liberated it from mercuric oxide. A lighted candle happened to be standing before him at the moment. By pure chance, as he himself says, and without any particular reason which he could afterwards recall, he immersed the candle in the gas and found that the combustion was unusually brilliant. He thus ascertained one distinct property of the substance and became the discoverer of oxygen. True, he thought at first that it was a compound of nitrous acid, earth and phlogiston, and only in the light of the views of Lavoisier and others, and after long delay, did he accept in 1786 the conclusion that it was an elementary substance. It may be noted that, although Scheele was a better experimenter, his idea of the nature of oxygen was not much clearer. He thought that fire-air (oxygen) united with phlogiston to give heat, and that the last was a compound of the first two. Evidently, in those days, isolating the substance, and defining one or two of its properties, together conferred discoverer's rights, no matter how grotesquely the nature of the substance was misunderstood.

I say, "in those days," for Curie made several compounds of radium, establishing their relations to one another, and is justly held to be the "discoverer of radium," although no isolation of the element was attempted. Now that the science has developed, isolation can be dispensed with, and, in point of fact, was omitted in most of the exploratory work among the rare metals. If this principle could have been applicable in earlier days, several of the decisions of chemical history might have been reversed. A hundred years before Priestley's time, Mayow (1669) had shown by conclusive experiments that atmospheric air was made up of two components, of which the active one formed 25% of the whole. In measuring the amount, he employed the same reaction subsequently used by Priestley, namely, removal of the oxygen by the introduction of nitric oxide and absorption of the product in water. But, whereas Priestley was thereby estimating the "goodness" of the air, and had no idea that he was dealing with a mixture, Mayow was perfectly clear as to the interpretation of the results. The latter demonstrated that the same component was removed in combustion, by rusting metals, by the alcohol in vinegar-making, and by the blood in respiration. He traced the animal heat of the body to a process analogous to that which heated the mass when marcasite rusted in the air. He identified this active component of the air as a constituent of saltpeter, and particularly of the acid part of this substance, and (like Lavoisier more than a century later) held that it was contained in all acids. Finally, he considered it to be an element, in the modern sense of the word. Unfortunately circumstances conspired to relegate to obscurity all his wonderful work and magnificently clear reasoning. Mayow was a young physician, and the divergent view-point of Boyle, as an older man and an eminent philosopher, received more attention. Again, the logical conclusiveness of Mayow's proof of the existence of oxygen as a distinct substance was entirely over the heads of his contemporaries, and his way of thinking quite out of harmony with theirs. In this point of view, he came a century and a half too soon. Such a proof, if offered at the present day, would be accepted as conclusive. The final isolation of the element would now be considered a matter of mere routine that could be assigned to a beginner in research, as the basis of his dissertation for the degree of doctor of philosophy. Finally, the clouds of the phogistic theory soon began to darken the sky of the science, and before long the spread of this remarkable notion, diligently fostered by Stahl who had been born nine years before the appearance of Mayow's work, enveloped chemistry and the whole chemical world in an impenetrable fog. Since the believers in phlogiston started always with one absurd idea as the major premise, namely, that in combustion and oxidation some kind of matter *left* the burning or rusting material, the more rigorous the logic of the subsequent steps in the reasoning, the more certain was the attainment of uniformly false conclusions. The inveterate phlogistian, and everybody down to the time of Lavoisier, not excluding Priestley and Scheele, was forthwith an inveterate phlogistian, saw in simple, almost modern modes of thought like those of Mayow, only the sheerest nonsense. If we all stood habitually upon our heads, naturally any one caught persisting in a tendency to view the universe in the normal way would be instantly adjudged insane. For these various reasons, Mayow's work was first neglected and then forgotten.

The story of Mayow suggests some additional conditions which determin the recognition of a discoverer, and the acceptance of his discovery. How often in the history of science has a dominating but conservative personality diverted attention from younger or less prominent men, or at the least, by hostile criticism, delayed the acceptance of their ideas? The discoverer who occupies a conspicuous social position is, often, more readily detected. Then again, for the dealing of strict justice, the consequences may be almost as unfortunate when the discoverer is a century ahead of his time, like Mayow, as when he is three years late, like Scheele. And finally, an intellectual plague like the phlogistic theory may be epidemic. An infection runs until a milder generation of the infecting organism is gradually evolved, or until the presence of the organism results in physiological changes which automatically give rise to substances that destroy it. Lavoisier was fortunate in arriving upon the scene when the disease was ready to loosen its hold. It was not that his fundamental experiments, upon the subject of air and oxygen, were new—the same conclusions could have been reached by putting together the work of his predecessors and contemporaries. It was largely because of his personality, and because he arrived at the psychological moment.

I have prefaced my address in this way, in order to furnish a setting for its subject. He lived from 1711 to 1765. He thus was educated, did his life-work, and died in the most virulent period of the phlogistic epidemic. Heat, light and weight were then forms of matter, yet, when he notices them at all, he combats these views, and makes experiments to disprove them. In a day when the jargon of the phlogistian was the only language of polite intercourse among chemists, he speaks and writes the language of modern chemistry—of the most modern chemistry, for he was a physical chemist. Needless to say, he lived at a time far removed from the psychological moment for a man holding such a viewpoint. Naturally, credit for his discoveries, and they were many, has all been distributed among others. It is quite likely that some of you have never happened to hear his name—the name of Michael Wassiliewitsch Lomonossoff.

Even in Russia, although his work in literary and linguistic lines, his success as a man of affairs, and his investigations as a geographer and a meteorologist had won for him enduring fame, the fact that he was primarily a chemist had been completely forgotten. It was Menschutkin[1] who, a few years ago, rediscovered him as a chemist, reprinted in Russian his scattered memoirs, and collected all that could be found of his manuscripts, letters, and laboratory note-books.

Although trained—chiefly in Germany—by, and along with men who ardently supported the current views, he seems with astonishing ease to have thrown off the prejudices of his contemporaries, and to have achieved a perfectly independent view-point of his own. At that time, the emission of light-matter explained the phenomena of light. Largely through the enormous influence of Newton's selection of the emission theory in preference to the wave theory (first developed by Huygens in 1690), this remained the accepted explanation until after a hard struggle against the influence of Laplace (1817) and others, who were unconvinced, with the explanation of the phenomenon of polarization, by Fresnel, the ether-wave theory finally triumphed. But Lomonossoff discusses (1753–56) the possible motions of ether—progressive, rotatory, and wave-like—identifies the last as the basis of light, and goes in great detail into the nature of ether and the properties of light-waves and the mode of their propagation.

In Lomonossoff's day, heat was also a form of matter. The classical experiment of Rumford was made (1798) thirty years after his death.

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[1] M. W. Lomonossoff, as Physical Chemist, St. Petersburg, 1904. See also an article by Menschutkin, *Annalen der Naturphilosophie*, 4, 203.

But so strong was the prejudice that, even then, the proof (by quantitative experiments) that heat could be generated without limit from friction, under conditions such that the addition of any substance or form of matter was impossible, did not carry conviction. Lavoisier believed (with some hesitation it is true) in an imponderable *matière de chaleur*. It was not until after the work of Mayer (1842), who was at first persecuted for his views, and especially after the demonstration by Joule (1855–60) that heat and work were mutually and quantitatively interconvertible, that the theory that heat was matter finally disappeared. Yet Lomonossoff, more than a century earlier (1744-47), in a paper on "The Causes of Heat and Cold," discusses in detail the experimental evidence that motion is a source of heat, and that molecular motions are caused by heating. Radiant heat, of which then little was known, was transmitted by motions of the ether, which he believed to be of the rotatory variety. In all his papers, heat is always a mode of molecular motion. The paper named was the subject of vigorous discussion, particularly in Germany, and after the views contained in it had been sufficiently abused they were consigned to oblivion.

The kinetic molecular theory of gases used to be attributed to Krönig (1856) and Clausius (1857). But Lord Rayleigh discovered in the archives of the Royal Society a very complete form of it, contributed by Waterston in 1845. The state of public opinion among physicists, even then, a century after Lomonossoff's work, may be judged from the fact that the committee of the Society considered the content of the paper to be nonsensical, and refused to permit its public presentation. Lomonossoff's paper, read before the Academy of St. Petersburg in 1744, nearly suffered the same fate, for it was withheld from publication for three years. Starting with the view of Daniel Bernoulli (1738), to the effect that the pressure of gases was due to the impacts of their particles, Lomonossoff proceeded to develop ideas very much like those now held. According to him, for example, a rise in temperature caused increased motion of the particles, and resulted therefore in increased pressure. His theory differs from ours mainly in the fact that rotatory motions played a large part, and that the molecules had rough surfaces. Incidentally he points out that there is no limit to the possible amount of motion, and therefore no maximum of temperature, but that there is a minimum of motion, when the latter becomes zero, and there must therefore be a minimum of temperature. In a later paper (1750) he proves by his hypothesis that the pressure *should* be, as it was then known to be, inversely proportional to the volume. And he goes further, for, with surprising insight, he shows that, with increasing pressure, this relation will no longer hold, since the volumes of the particles themselves are not diminished. The reputed discoverer of this consequence of the theory is Dupré (who was thus anticipated by

115 years), and in 1873 van der Waals finally put the same fact into definit form.

In all this, it must not be supposed that Lomonossoff was simply a reasoner, much less a speculator. The discussion is loaded with a wealth of experimental facts, many of them ascertained by himself. It is especially noteworthy, also, that his experiments, almost without exception, were quantitative. When we remember that the balance is a stubborn instrument, and that its evidence always went contrary to the conclusions of those who pinned their faith to heat-matter and phlogiston, we perceive how completely his habits of work and attitude of mind were out of harmony with those of his contemporaries, and how startlingly independent were his modern ways of experimenting and reasoning.

Before turning to the part of his work that was more especially of a chemical and physico-chemical nature, a few words about his career may be of interest. He was born of peasant parents—Russian peasant parents of the early eighteenth century—about the year 1711, and in a village forty-five miles from Archangel. Opportunities for education there were none. Finally, at the age of 19, he reversed the procedure of the typical boy and ran away to go to school. At 24 he left the school in Moscow to attend the lectures of the professors in the Academy of Sciences in St. Petersburg. At 25 he was sent on a traveling scholarship to Marburg, where he studied chemistry under Wolff. After three years he went to Freiberg, and two years later he returned to St. Petersburg. In both places, when he moved, the Academy had to pay the debts that he had incurred. Upon his return home, he became adjunct professor at a salary of $900, but the Academy, being poor in money, paid its professors largely by gifts of copies of its publications, a sort of product for which there is an almost infinitesimally small market. A year later we find him in the University, lecturing in Latin on chemistry, geography and the Russian language. Lecturing in Latin upon the Russian language to Russian students! Such simple, blind devotion to a tradition surprises us, even when it occurs in a University. His active experimental work as a chemist began in 1844, when he was 33 years of age, and in 1745 he was appointed to the professorship of chemistry.

After three years of planning, a chemical laboratory was built, and on the 12th of October, 1748, it was opened. The building, a modest one, measured 45 × 36 feet, and was divided into a large room for work and two small rooms for lectures and storage. It cost $4000, and about $1800 additional was spent on furnaces and other equipment. Thus, in providing a place for laboratory instruction, as well as for research in chemistry, Lomonossoff was fifty years ahead of Hope in Glasgow and seventy-five years ahead of Liebig.

Lomonossoff's period of greatest chemical activity was compressed into the nine years that followed the opening of the laboratory, for in 1757 he resigned his chair. During the remaining eight years of his life the numerous activities of a public man, and a diversion of his interests into other scientific lines, interfered with chemical work.

Up to the end of the eighteenth century, there was utter confusion of thought in regard to the composition of materials. In considering the make-up of a specimen, and the changes occurring during an experiment, heat-matter, light-matter and weight-matter, as well as phlogiston, were taken into account. As we have seen, even Scheele interpreted the phenomena he observed upon the theory that heat was an oxide of phlogiston. The composition was often stated in terms of salt, sulphur and mercury, whether there was evidence of their presence or not. The "elements" of Aristotle, and cognate ideas, were used in describing and in thinking about chemical phenomena. In consequence, Priestley thought he had a method of measuring the "goodness" of air—as a quality—when in point of fact he was measuring the amount of oxygen—as a component. With the basal conceptions thus in a state of utter chaos, it is no wonder that the simplest chemical situations were wholly misunderstood, and that the simplest experimental results, being described in terms of non-existent entities, and thought of in terms of non-existent relations, failed of their object. It was Lavoisier who received the credit for setting our ideas permanently in order, by his emphasis upon the significance of the evidence of the balance, and by his setting forth clearly the idea of chemical compounds and their component elementary substances, and by giving a classified list of the latter.

The chemical reformation might have come half a century sooner, however, if Lomonossoff's papers had been more widely known. As we have seen, to him heat and light were not forms of matter and phlogiston had no existence. His forms of matter were the same as ours, and his ideas of chemical composition, what it included and what it excluded, the same as ours. In his "Elements of Mathematical Chemistry"[1] (1741) and in a later paper, "On the Imperceptible Physical Particles, which Compose Natural Materials and in which is to be Found a Sufficient Basis for the Specific Properties" (1742–3), he gives a singularly clear and minute discussion of the whole subject. He distinguishes between the attributes (weight, volume, etc.) of a body or specimen, and the specific properties which characterize a substance. In modern fashion, he defines the "imperceptible particles" or "corpuscles" (molecules), which are portions of a substance, and the "physical monads" or "elements" (atoms) which are not decomposed in chemical change. He draws clearly and in detail the distinction between simple and com-

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[1] This and parts of others of his papers are published, in German translation, in Ostwald's *Klassiker*, 178.

pound substances, the latter of which contain the "principia" (elementary forms of matter) in chemical combination. The explanations are in experimental, and not obscure, theoretical terms.

In the paper on "Heat and Cold" (1744–7) he refers to Boyle's experiment, in which lead was sealed up in a retort and heated, when the lead and calx, upon removal, were found to have increased in weight. According to Boyle, this result showed that the heat, which alone could enter through the glass, had weight. Lomonossoff, of course, will not accept this conclusion and points out that the increase in weight of metals when heated in air must be due to union with material from the air, just as their increase in weight when placed in the flame of burning sulfur is due to union with "acid" from the sulfur. Later, in 1756, he repeats Boyle's experiment, and finds that, until the retort is opened and air rushes in, no increase in weight is observable. He thus performed one of Lavoisier's most fundamental and convincing experiments eighteen years in advance, and interpreted it correctly. It is apparent that Lomonossoff's sound views were based upon many quantitative experiments on combustion, although the laboratory note-books containing the details have not yet been found.

But if Lomonossoff anticipated Lavoisier in his work upon the chemical relations of the forms of matter, he went far beyond Lavoisier in his views in regard to the uses of mathematics and physics in chemistry, and in this direction anticipated many of the points of view of the later nineteenth century. Lomonossoff's unfinished treatise, "The Elements of Mathematical Chemistry" (1741), of which only a fragment survives, deals with a conception which, in all his writings, he never ceased to urge, namely, the value of mathematical methods in chemistry. Ten years later, in an "Address on the Uses of Chemistry" (1751), he speaks as follows:

"If chemistry unites to solid form the separated and scattered particles in a solution, and brings forth various formations, it must be that she relies upon the strictest and most highly developed Geometry........If she changes solids into liquids and liquids into solids, and divides and unites them to give various substances, it must be that she seeks counsel of the most exact and ingenious Mechanics. If chemistry, by union of different substances, gives rise to different colors, she needs the help of the most profound optics........If the knowledge-seeking, tireless investigator [in response to this] will only survey her through geometry, measure her forces by mechanics, and consider her through the science of optics, he will probably reach his desired goal." In this we seem to see at least an adumbration of chemical crystallography, and of chemical dynamics and statics. He continues: "Why have investigators had no success? I answer that for this a very skilful chemist is needed, who is at the same time a mathematician." Has not the recent development of the science been along the precise lines which he thus lays down?

Lomonossoff's applications of geometry in *De Nitro* (1749), a comprehensive study of saltpeter, will illustrate his own attempts to use mathematical methods. He discusses at length the crystalline form of the substance and proceeds to develop theory of crystalline structure. In saltpeter, the prismatic form can be accounted for by an arrangement of round particles, in such a way that lines drawn through their centers always form equilateral triangles. In other substances, the arrangement is different, so that, for example, in common salt, the lines through the particles may form squares. As usual, he paid the penalty of being far ahead of his time. Yet he had anticipated by a century the essential conceptions of Bravais (1850), whose mathematical study of all possible space nets, and their relation to existing crystalline forms, coming at a more favorable time, led almost immediately to the completion of development along this line by Sohncke (1867).

In the same address, he continues: "[The chemist] is surely unapt, who has made a mass of experiments, but in the effort to secure quickly accessible products, hastens to the attainment of this as his sole goal; he overlooks those phenomena and changes occurring in his operations which might lead to the explanation of nature's secrets." If this viewpoint, with its contempt for purely preparative chemistry, had been as prominent in the creed of all the chemists of the century and a half since Lomonossoff's time, as it was in his own, instead of being until recently the ideal of only a few scattered chemists, what a different science ours would have been! How many papers, signed by notable names, might have offered something of substantial scientific value, in place of a mass of new entries for the indexes of Beilstein and Dammer! In the preface to his treatise on saltpeter, he develops the same idea: "Since as yet no general physical bases for explaining the formation and composition of chemical substances exist, and since few physical experiments have been applied in chemistry so as to lead to the desired results, it may seem difficult, but we believe it to be possible, scientifically, to describe the greater part of chemistry in terms of the interrelations of its own principles and their connections with those of physics. We do not doubt that, after the union of chemical with physical truths, we shall be able more successfully to understand the inner nature of substances." Be it understood, these generalities are only summaries of the plans of study which, in his experimental work and in his papers, he attempts in thoroughgoing fashion to put into practice. Uttered as they were in the heart of the period of phlogiston, of heat-matter, and of confused experimentation and reasoning, they have an uncanny sound, and almost terrify us with their supernatural prescience. How long have we had to await the psychological moment for the general application of these ideas! Had only the times been ripe; had only the atmosphere been healthy for the propagation of such ideas as his, instead of being virulently poisonous to them, our science might easily, by now, have been a hundred years ahead of its present position, and we might to-day have been listening to papers which, as it is, will not be read for a century. If Dante's *Divina Commedia* were to be revised by a chemist and brought up to date, the chief change he would make would be the provision of some horrible and revolting torment, calculated to give Stahl his just deserts.

The occasion is not a suitable one for going in detail into the mass of (for that time) novel and suggestive quantitative physico-chemical experiments which occupied Lomonossoff from 1752 to 1756. The extent of his plans—only partially fulfilled—may be judged from his *Dromus ad veram chyniam physicam* (Course in True Physical Chemistry, 1752), of which a considerable part was written, and much survives. In the introduction he mentions, among other aims of physical chemistry, this: "One must determine the specific properties of every substance as exactly as possible, in order that, after the composition has been ascertained by chemical operations, one may judge whether, and to what extent each property is altered by changing a given constituent." No statement of one of the purposes of physical chemistry could be clearer.

In the experimental part of the book, salt solutions receive much attention, and many modern problems may be recognized, such as measurement of exact solubilities at various temperatures, volume changes in solution, heats of solution, boiling points of solutions, relative cohesion in water and in solutions, capillary phenomena, action of electricity upon solutions, and relative deliquescent tendencies of salts. There is, of course, a good deal about crystallography. In the absence of the laboratory note-books, only parts of some of the tabulated results have been found. One set of experiments, chiefly with common salt, led to the conclusion that the freezing points of solutions are lower in proportion to the amount of the dissolved body. Even the most insignificant experiments were carried out quantitatively.

In Lomonossoff's laboratory, a good deal of special apparatus was devised. Measurements of the coefficient of expansion of air had been made, and a value (recalculated to 1° C.) of 0.003 (in place of 0.00367) was found. This led to the construction of an air thermometer for measuring low temperatures. Incidentally, he reformed the Delisle scale of temperatures, which ran downwards from 0° at the boiling point of water to 150° at the freezing point, by simply inverting it (0° L. = 0° C., 150° L. = 100° C.). A thermostat for ice and water was employed in some experiments, and instruments for the study of oceanography, devised by him, came afterwards into general use. One of the most extensive pieces of work done in his laboratory was a study of colored glasses and mosaics, the results of which led to the establishment of a factory, still in successful operation, near St. Petersburg.

The achievements of Lomonossoff outside of chemistry were as remarkable as those within that science. He wrote a treatise on Metallurgy, made investigations in Meteorology and especially atmospheric electricity, in Geology, and in Mineralogy, and he superintended the equipment of expeditions for geographical exploration. He observed the transit of Venus of 1761, and drew from his observations the conclusion that the planet had an atmosphere "similar to, or perhaps greater than that of the earth," a discovery generally attributed to Schröter and Herschel (1791).

No undertaking that required courage and originality was outside the comprehensive sphere of his interests. He was the first to attempt to apply modern forms to the writing of poetry in the Russian language, and was the author of odes, poems, and even of tragedies to be performed in the Court Theater. He prepared a Russian grammar and a treatise on rhetoric. He devised a vocabulary for expressing scientific conceptions, and his terms are those now in use in Russia. As the most prominent Russian man of science of his time, public affairs claimed much of his strength. Taking him all in all, the rediscovery of Lomonossoff has added at once a chemist of the first magnitude and a personality of marvelous force and range to the limited gallery of the World's very greatest men.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY. NO. 79.]

THE POTENTIAL OF THE POTASSIUM ELECTRODE.

BY GILBERT N. LEWIS AND FREDERICK G. KEYES.

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The method employed by Lewis and Kraus[1] for the determination of the potential of the sodium electrode is applicable in a number of similar cases. We shall describe in this paper a similar determination of the potential of the potassium electrode, together with some preliminary experiments carried out for the purpose of seeing how far the same method is available in the case of lithium, rubidium, caesium and the metals of the alkaline earths.

We first determined the potential of a dilute potassium amalgam in an aqueous solution of potassium hydroxide, against a normal calomel electrode, and thus were able to calculate the potential of this potassium amalgam against a normal solution of potassium ion in water. It remained to determine the difference in potential between this amalgam of potassium and pure metallic potassium. This difference of potential

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[1] THIS JOURNAL, 32, 1459 (1910).